12176 *J. Am. Chem. Soc.* **1995,** *117,* 12176−12180

Structure of $\{[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}P(C_6H_5))]_2\}\{[(THF)_3Li]_2(\mu\text{-}Cl)\}$ and Its Implications for the Nature of Dilithium Dinitrogen Complex

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Received June 22, 1994. Revised Manuscript Received July 28, 1995[®]

Abstract: X-ray structure of the complex salt $\{[Cp_2Zr(\mu\text{-}PPh)]_2\}\{[(THF)_3Li]_2(\mu\text{-}Cl)\}$, **1**, as well as its EPR spectrum and magnetic susceptibility have been investigated. The results indicate that the anionic part of the complex is the mixed valence [Zr(III)Zr(IV)] monoanion. From the comparison of the complex **1** and dinitrogen complex $\{[Cp_2Zr(\mu\text{-}PPh)]_2\}\{[(THF)_3Li]_2(\mu\text{-}N_2)\}$, **2**, published elsewhere it follows that the anions of both the complexes are identical and therefore the cation of **2** has also a unit charge. it is concluded that the cation $\{[(THF)_3Li]_2(\mu\text{-}N_2)\}^+$ can be regarded as a complex of N_2 with the pair $(Li\cdots Li)^+$ or that of N_2^- stabilized by two Li^+ cations. Theoretical grounds for the existence of such complex ion are discussed.

Introduction

In 30 years since Allen and Senoff[1] discovery of the first transition metal dinitrogen complex, many N_2 complexes of various structures have been synthesized in a number of laboratories (see reviews[2−4]) and their role as intermediates in the reduction of dinitrogen has been demonstrated.

By contrast, the reactivity of dinitrogen with non-transition metals, particularly its reduction by lithium metal, was known much earlier, yet no intermediate dinitrogen complexes were observed until recently. The first example of a dinitrogen complex of a non-transition metal was reported[5] to be the salt $[Li_2N_2\cdot 6THF][(Cp_2ZrPPh)_2]$, **2** (Figure 1), which was obtained from the treatment of Cp_2ZrCl_2 with the product of reaction of *n*-BuLi and $PhPH_2$ in THF under a dinitrogen atmosphere. According to the X-ray crystal structure data, the N_2 moiety is incorporated into the $[(THF)_6Li_2N_2]$ cation of the salt, whereas the $[(Cp_2ZrPPh)_2]$ anion contains phosphinidene bridges formed by *μ*-PPh groups. The authors[5] conclude that dinitrogen is bound to two lithium cations (each solvated by three THF molecules) and that the salt **2** consists of a dication and a dianion. Both lithium atoms are symmetrically bound side-on to the dinitrogen in the complex

the NN bond distance being very close to that of free dinitrogen.

No doubt the discovery of the dilithium dinitrogen complex is a new step in understanding of dinitrogen activation, the more so as there are only very few examples of side-on NN configuration with transition metals. However it is difficult to reconcile the formulation of the Li_2N_2 species as the dication $[(THF)_6Li_2N_2]^{2+}$ with extremely weak basic properties of N_2 molecule, and addition of two lithium cations in the presence of an excess of the strong base, tetrahydrofuran, seems very surprising. The authors[5] suggest that "fortuitous use of the Zr-phosphinidene dianion results in the solid state effects which favor the Li_2-N_2 dication instead of fully solvated counterions", yet it would be expected that Coulombic repulsion of the two lithium cations should greatly destabilize the ion. Formulation of $[(Cp_2ZrPPh)_2]$ as dianion containing dimeric Zr(III) moiety is also difficult to accept. The anion is found to be paramagnetic and reveals the EPR spectrum. However according to experimental and theoretical evidence[6] dimers of Zr(III) have to be diamagnetic because of a strong through-space metal−metal coupling.

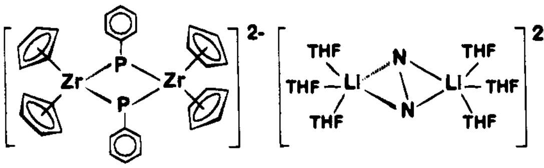

Figure 1. Schematic representation of molecular structure $\{[Cp_2Zr(\mu\text{-}PPh)]_2\}\{[(THF)_3Li]_2(\mu\text{-}N_2)\}$, **2**, according to Stephan et al.

We suggested that in fact both the cation and anion had unit charge and that the dilithium−dinitrogen interaction can be represented formally as $[Li^+N^-{}_2Li^+]$. The complex may be considered the first step in lithium atom activation of dinitrogen with participation of Li^+. According to this suggestion, the monoanion $[(Cp_2ZrPPh)_2]^-$ would be paramagnetic and contain the pair of Zr(III)Zr(IV), actually mixed valence zirconium atoms. In this paper we give the results which seem to support this conclusion.

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[®] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

(1) Allen, A. D.; Senoff, C. V. *J. Chem. Soc., Chem. Commun.* **1965**, 621.

(2) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

(3) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197.

(4) Shilov, A. E. *Pure Appl. Chem.* **1992**, *64*, 1409.

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(6) Benard, M.; Rohmer, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 4785.

(7) The authors[5] mention that their attempts to prepare a complex under argon atmosphere did not yield crystalline product.

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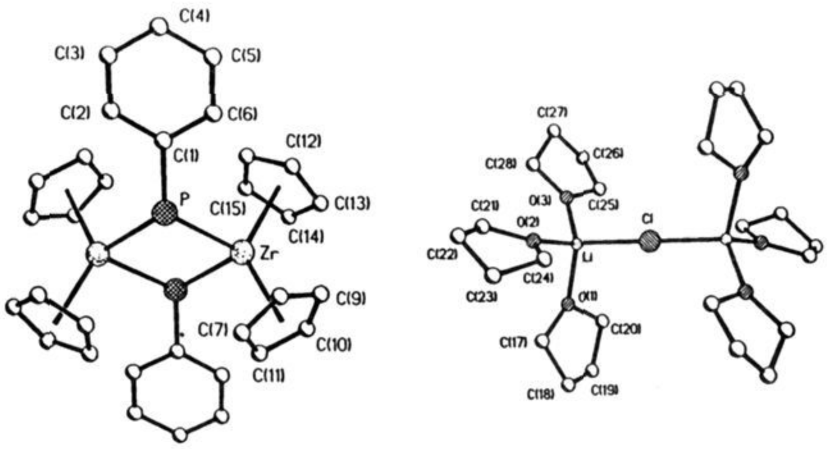

Figure 2. General view of the centrosymmetric cation (right) and anion (left) in the molecular structure **1**. Important bond distances and bond angles: Zr–P 2.591 (5), Zr–P′ 2.568(5), Zr···Zr′ 3.654(6), Zr-center Cp-rings 2.24 and 2.25 E; Li–Cl 2.25 (2), Li–O (1) 1.96 (2), Li–O (2) 1.92 (2), Li–O (3) 1.94 (2); P–Zr–P′ 89.8 (1)°, Zr–P–Zr′ 90.2-(1)°, Cp–Zr–Cp 128.9°, Li–Cl–Li′ 180.0°, Cl–Li–O 107.1–111.6 (8)°, O–Li–O 107.0–113.3 (8)°.

Table 1. Selected Bond Lengths and Bond Angles in **1** and **2**

bond and angle	complex N_2 (**2**)	complex (**1**)
Zr–P	2.574(3) Å	2.591(5) Å
Zr–P′	2.570(2) Å	2.568(5) Å
Zr–Zr′	3.64 Å	3.65 Å
P–Zr–P′	88.90(8)°	89.8(1)°
Zr–P–Zr′	91.10(8)°	90.2(1)°
Li–Li′	4.41	4.5
Li–O(1)	1.94(1)	1.94(3)
Li–O(2)	1.96(2)	1.96(2)
Li–O(3)	1.91(2)	1.92(2)
	Li–N 2.25 Å	Li–Cl 2.25 Å

Results and Discussion

Repeating the experiments of the paper[5] we have confirmed the coordination of dinitrogen in conditions described by the gas analysis of the decomposition products although for a somewhat higher ratio of *n*-BuLi to $PhPH_2$. So far we could not prepare single crystals of the complex **2**. However, we succeeded in preparation of crystalline product and X-ray analysis of single crystal of the complex formed *under argon* instead of dinitrogen.[7]

The crystal and molecular structure of the title complex **1** (Figure 2) is very similar to that for **2** (Figure 1). Compounds **1** and **2** are isostructural and form isomorphous crystals. Thus, the cell parameters for **2** measured at room temperature are similar to those for **1** and the unit cell volume for the crystals of **2** is equal to 1463(1) Å^3, in comparison to 1374(4) Å^3 for **1**.

The crystal structure **1** contains a centrosymmetrical cation $[(THF)_3Li-Cl-Li(THF)_3]^+$ with a linear bridging Cl-atom and a Li–Cl distance of 2.25(2) Å. Coordination of Li-atom is usual slightly distorted from tetrahedral coordination (bond angles in the interval 107.0–113.8(8)° with the Li–O bond distances 1.92–1.96(2) Å), which are quite typical. Comparison of the structure of **1** with that of **2** indicates that the anions are virtually identical. In both cases the anion is the dimer $[(Cp_2ZrPPh)_2]$, with equivalent distances and angles. Thus, the Zr–P bonds in **1** are equal to 2.568(5) and 2.591(5) Å (in **2**–2.574(3) and 2.570(2) Å). The central Zr_2P_2 planar ring is almost rectangular for both structures and the pseudo pyramidal geometry of the P-atom results in a transoid disposition of the Ph-substituents with respect to the planar Zr_2P_2 core (Table 1).

Undoubtedly the cation in **1** has a unit charge with two lithium cations bridging by Cl^-. Taking into account the 1:1 cation and anion stoichiometry in both complexes **1** and **2** we can conclude that both complexes consist of monocations and monoanions and therefore indeed the cation of **2** has the formal structure $[LiN_2Li]^+$. This is strongly confirmed by the very close lattice parameters: the change from unit charges in the complex **1** to double charged ions in the complex **2** if the formulation on[5] had been correct would have presumably greatly changed the lattice.

Recently Stephan et al reported[8] on the protonation of a complex with a given formula $[Cp_2Zr(\mu\text{-}PPh)]_2[Li(THF)_3]_2$,[9] **3**, by TMEDA·HCl. The resulting product is formulated as $[(Cp_2Zr)_2(\mu\text{-}PHPh)(\mu\text{-}PPh)][(THF)_2Li(TMEDA)]$, **4**. Hence **4** is the salt of *monocation* and *monoanion*. The authors[8] formulate the anion again as a triplet state (this time protonated) formed by two Zr(III), although there is no evidence for proton addition either from X-ray structure or from NMR spectrum (protons of cyclopentadienyl, phenyl, TMEDA, and THF are, however, observed despite the paramagnetism of Zr(III)). EPR spectrum of **4** is similar to that of **1** and **2**.[10] Hence in all three cases (complexes **1**, **2**, and **4**) the same monoanions of mixed-valence Zr(III) Zr(IV) are most likely to be the case, the more so as the reported X-ray structure of the anion of **4** is virtually identical with those of **1** and **2**. If **3** is in fact identical with **2**, the formation of the lithium cation from $[Li(THF)_3]_2N_2^+$ may be explained by its reaction with H^+·TMEDA to form N_2, $^1/_2H_2$, and $[(THF)_2Li(TMEDA)]^+$.

The EPR spectra of complexes **1** and **2** consists of three main lines with intensity ratio 1:2:1, $g = 2.0189$, $a_p = 21.6$ G. This corresponds to the main zirconium isotopes with nuclear spin $S = 0$ (89% of the total Zr) interacting with two phosphorous nuclei ($S = 1/2$). There are also 11 weak lines (about 50 times weaker than the main ones) with the same *g*-factor and $a_{Zr} = 7.0$ G, which correspond to the splitting at two equivalent ^{91}Zr nuclei ($S = 5/2$, natural abundance 11%). In frozen solutions of both the complexes we have not observed the middlefield EPR adsorption reported in ref 5 which would have corresponded to the triplet state of the anion if it were the triplet and had a double charge. We simulated the EPR spectrum of the complex **1** using the magnetic properties and the content of the elements involved in the complex and obtained full agreement of the simulated and experimental spectra confirming the complex structure and the fact that the EPR spectrum belongs to the same species whose structure was established (Figure 3).

The cation $[Li_2N_2]^+$ in **2** must be paramagnetic and should produce an EPR signal. No signal has been so far detected, however. Possibly at low concentration of **2** for EPR measurements the cation was decomposed or oxidized and replaced by some diamagnetic cation, e.g., $[Li(THF)_4]^+$.

Magnetic susceptibility of the complex crystals **1** was measured and magnetic moment μ_{eff} at 80 and 293 K was found to be 0.87 and 0.83 μB, respectively. The values of μ_{eff}, and its weak (if any) dependence on temperature confirm the presence of one unpaired electron in the complex **1** according to its proposed formula $[LiClLi]^+[Cp_2ZrPPh)_2]^-$.

Thus our results together with those obtained by Stephan et al. confirm the suggestion that the cation $[LiN_2Li]^+$ has +1

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(8) Ho, J.; Hou, Zh.; Drake, R. J.; Stephan, D. W. *Organometallics* **1993**, *12*, 3145–3157.

(9) The complex **3** is produced in N_2 atmosphere, but no N_2 is included in the formula of the cation (although the number of THF per Li is given by the authors[5,8] to be the same is in **1** and the synthetic procedure is reported to be identical).

(10) Some indication to the weak hyperfine splitting of the EPR signal to a doublet of equal signals which is attributed[5] to the interaction with proton bound to P atom could be in fact due to some paramagnetic impurity producing a signal in close vicinity to the main signal. According to the interpretation[8] the proton bound to phosphorous must be equally shared between two P atoms which is difficult to accept, taking into account a rather large distance between the two.

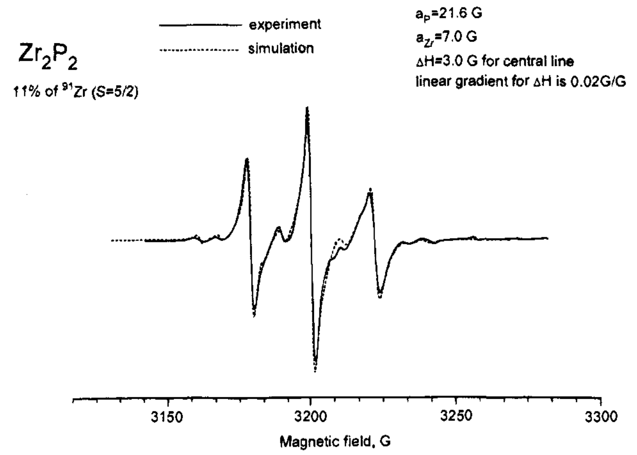


Figure 3. EPR spectra (experiment and simulation) of complex $\{[Cp_2Zr(\mu\text{-}PPh)]_2\}\{[(THF)_3Li]_2(\mu\text{-}Cl)\}$, **1**.

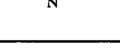
charge. Therefore it is of interest to consider theoretical grounds of the existence of such unusual cation.

A simple Coulombic model corresponds to essential gain of energy on electron transfer from Li,Li$^+$ to N_2 even taking into account negative electron affinity of dinitrogen (−1.9 eV).[11] According to this model for experimental Li−N and N−N distances the gain of energy for monocation

and $[Li\text{-}N{\equiv}N\text{-}Li]^+$ formation from Li, Li$^+$, and N_2 is 50 and 31 kcal/mol, respectively.[12]

The very small difference between the interatomic NN distance in the complex **2** and that in free dinitrogen indicates that, despite electron transfer from lithium to N_2, dinitrogen is very weakly activated. The NN bond distance in N_2^- anion is known to be 1.17 Å.[13] Clearly there is back donation of electron density to lithium cations, probably at least partly from $2\sigma_u^*$ antibonding orbital which results in very weak total effect. It should be noted that although the electron affinity of N_2 is negative, the N_2^- ion can be stabilized by K$^+$ ions in the crystal lattice of KI when it is formed by the high energy irradiation of the crystals containing N_3^-.[13] In $(LiN_2Li)^+$ the cation has to be stabilized by the bonding of N_2^- with Li$^+$ ions.

We have studied stable state in the system Li$^+$ + Li + N_2 in more details using nonempirical quantum chemical methods. The results are presented in Tables 2 and 3. For symmetrical σ- and π-complexes the unpaired electron is localized mainly on N_2 molecule. The initial positive charge on Li$^+$ are naturally decreased due to the polarization of N_2^-. In 6-31+G(d) basis the energies of these complexes are close to each other, particularly if we take into account correlation energy on UMP4 level and zero point energy correction, and their formation energy (ca. 35.5 kcal/mol) corresponds well to the estimate according to the Coulombic model. However π complex



is more compact. Therefore solvation energy will presumably contribute more to the stabilization of the π complex in solution.

Probably these complexes could be thermodynamically unstable with respect to the solvated Li$^+$, Li atom, and N_2 molecule because of low basicity of N_2 and its negative electron affinity.

The presence of extra electron in monocation is of crucial importance for its kinetic stability. The removal of the electron without change of the geometry requires 9.57 eV in UMP4/6-31+G(d)//UHF/6-31+G(d) approach, and this corresponds to high repulsion energy between two Li$^+$ of dication. This energy is higher than ionization potential of Li (5.4 eV). This result helps to understand the kinetic stability of the salt of monocation $[Li_2N_2]^+$ with monoanion Zr^{III}Zr^{IV} and also explains the difficulties in reproducible preparation of this salt. Some impurities acting as catalysts may destabilize the salt and induce its decomposition to 2Li$^+$, N_2, and diamagnetic Zr^{III}Zr^{III} dimer.

From the equilibrium distances r_{NN} and the frequencies ω_{NN} obtained at different approaches the state of N_2 in both types of the ions $[Li_2N_2]^+$ (σ and π) is indeed close to N_2^-. The absence of a small lengthening of the NN distance which is expected according to the theory may be the consequence of large amplitude rocking of N_2 molecule around the Li−Li axis in $[(THF)_3LiN_2Li(THF)_3]^+$.

The electron transfer from donor $1\pi_g^*$ orbital of N_2^- can occur only to 2p orbital of Li$^+$. This transfer leaves the unfilled 2s orbital of Li$^+$ free for accept electrons from the donor THF molecules. But the value of this transfer is much less than electron density transfer from double occupied orbitals of N_2^- to free 2s orbital of Li$^+$ (compare the values of spin and charge transfer from N_2^- to Li$^+$ in Table 2).

According to ref 5 and our preliminary observations, complex **2** is more stable under dinitrogen atmosphere. Therefore the decomposition of the cation to yield N_2 may be reversible, and thus the solvated cations $(Li\cdots Li)^+$ may be an independently existing species. If the existence of these cations is confirmed, their formation mechanism and unusual coordinating properties will deserve closer examination. Formation of neutral dimer containing two four-valent Zr atoms might be suggested as the first step of Cp_2ZrCl_2 interaction with $PhPLi_2$ followed by electron transfer from excess *n*-BuLi. Taking into account polymeric structure of alkyllithiums, a complex ion $[BuLi]_m^+$ must be formed initially. The following interaction of two butyl groups in the ion (intramolecular disproportionation[14]) would lead to C_4H_8 and C_4H_{10} together with the $(Li\cdots Li)^+$ pair and remaining $[BuLi]_{m-2}$. Another source of the $(Li\cdots Li)^+$ ion may be Li_2PPh, which also could form this cation in the process of electron transfer to the acceptor with subsequent recombination of two PPh. According to the theoretical estimate the formation of the cation

observed in complex **2** is preceded by the linear precomplex $(LiLi)^+(N{\equiv}N)$.

Conclusions

From the structure of the complex salt $\{[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}P(C_6H_5))]_2\}^-\{[(THF)_3Li]_2(\mu\text{-}Cl)\}^+$, its EPR spectrum, and magnetic succeptibility data it follows that both the cation and anion have unit charges.

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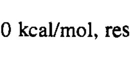
[11] Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Doorecht, New York, 1970.

[12] The same Coulombic model corresponds to the great loss of energy for dication

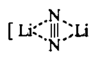


and $[Li\text{-}N{\equiv}N\text{-}Li]^{2+}$ 76 and 60 kcal/mol, respectively, confirming its high instability.

[13] Brailsford, J. R.; Morton, J. R.; Vannotti, L. E. *J. Chem. Phys.* **1969**, *50*, 1051.

[14] Dyachkovskii, F. S.; Shilov, A. E. *Zhurn. Obsch. Khim. (russ.)* **1963**, *33*, 406.

Table 2. Total Energies in Hartree

System	UMP2/6-31G	QCISD/6-31G	UHF/6-31+G(d)	UMP4/6-31+G(d)//UHF/6-31+G(d)	UHF/6-31+G(d) ZPE corr.
$N_2 + Li + Li^+$	-123.77782	-123.76382	-123.61412	-123.94034	0.00627
$N_2 + Li_2^+$	-123.82258	-123.80859	-123.65980	-123.98602	0.00687
$N_2^- + Li^+ + Li^+$	-123.45785	-123.45718	-123.32445	-123.66208	0.00475
 $[\mathrm{Li}\overset{N}{\underset{N}{\vert\vert\vert}}\mathrm{Li}]^+ D_{2h}$	$-123.81755^{a)}$	-123.81660	-123.66116	-123.99770	0.00863
$[LiNNLi]^+ D_{\infty}h$	-123.83314	-123.83570	-123.66350	-123.99840	0.00958
$[LiLiNN]^+ C_{\infty}v$			-123.67342	-124.00151	0.00868

[a] Hartree–Fock solution is unstable.

Table 3. Geometry, Frequencies and Electronic Structure[a]

System	UMP2/6-31G	QCISD/6-31G	UHF/6-31+G(d)
$N_2 + Li + Li^+$			
r_{NN}	1.154	1.129	1.078
ω_{NN}	1959	2269	2753
$N_2 + Li_2^+$			
r_{LiLi}	3.187	3.187	3.166
ω_{LiLi}	261	261	260
$N_2^- + Li^+ + Li^+$			
r_{NN}	1.259	1.235	1.166
ω_{NN}	1511	1729	2086
 $[\mathrm{Li}\overset{N}{\underset{N}{\vert\vert\vert}}\mathrm{Li}]^+ D_{2h}$			
r_{NN}	$1.249^{b)}$	1.225	1.164
r_{LiN}	2.112	2.032	2.026
ω_{NN}	-	1710	2142
q_{Li}	0.784	0.779	0.626
s_N	0.462	0.464	0.455
$[LiNNLi]^+ D_{\infty}h$			
r_{NN}	1.213	1.197	1.148
r_{LiN}	1.871	1.875	1.854
ω_{NN}	1808	1967	2292
q_{Li}	0.801	0.797	0.574
s_N	0.457	0.449	0.477
$[LiLiNN]^+ C_{\infty}v$			
r_{N1N2}			1.077
r_{Li1Li2}			3.161
r_{Li2N1}			2.138
ω_{NN}			2768
ω_{LiLi}			366
q_{Li1}			0.583
q_{Li2}			0.203
s_{Li1}			0.401
s_{Li2}			0.598

[a] Interatomic distances, *r*, in Å, frequencies, *ω*, in cm^{-1}, atomic charges, *q*, and spin densities, *s*, in shares of electron. [b] Hartree–Fock solution is unstable.

The complex $\{[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}P(C_6H_5))]_2^-\{[(THF)_3Li]_2(\mu\text{-}N_2)\}^+$ synthesized under N_2 by Stephan et al.[5] has the identical anion, and therefore its cation may be considered as N_2^- stabilized by two Li^+ ions. Theoretical grounds are given for the existence of this complex cation formed from N_2 and the pair $[Li_2]^+$.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free argon employing either Schlenk techniques or a vacuum atmospheres inert-atmosphere glovebox. Solvents were distilled from $LiAlH_4$ under argon and degassed by the freeze–thaw method. Cp_2ZrCl_2 was purchased from the Aldrich Chemical Co. $PhPH_2$ was synthesized by reduction of $PhPCl_2$ with $LiAlH_4$.[15]

Synthesis of $\mathbf{\{[Cp_2Zr(\mu\text{-}PPh)]_2\}\{[(THF)_3Li]_2(\mu\text{-}Cl)\}}$**, 1.** To a solution of phenylphosphine (0.33 mL, 3 mmol) in THF at −80 °C 2.5 equiv of *n*-BuLi (3.75 mL, 2 M, 7.5 mmol) was added. A suspension of yellow solid in yellow-orange solution rapidly formed and after warming it up to room temperature, 1 equiv of Cp_2ZrCl_2 (0.877 g, 3 mmol) was added. The addition was accompanied by a fast color change from yellow to red-brown. The mixture was stirred 10 h, and after filtering the mixture was allowed to stand overnight at −18 °C during which time black extremely air sensitive crystals of **1** were deposited (0.94 g): yield 55%. Recrystallization of **1** from THF/pentane gave black blocks suitable for X-ray analysis. Anal. Calcd: C, 58.95; H, 6.84; Cl, 3.11. Found: C, 58.55; H, 6.32; Cl, 3.05. EPR (THF, 25 °C): $g = 2.0189$, $\langle a_P \rangle = 21.6$ G, $\langle a_{^{91}Zr} \rangle = 7.0$ G.

EPR spectra were recorded on a SE/X-2544 (Radiopan) EPR spectrometer at microwave power 0.2 mW and magnetic field modulation 0.32 mT.

Simulation of the EPR Spectrum. We simulated the EPR spectrum of the complex **1** using the following data: the nucleus spin *S* for ^{91}Zr (natural abundance 11%) is equal to 5/2, the spin for other isotopes of Zr is zero; the spin for *P* is 1/2. We suggested that two nuclei of Zr and two nuclei of P are equivalent. According to natural abundance of ^{91}Zr, 80% of Zr_2P_2 species (species **1a**) contain both Zr nuclei with $S = 0$, 19% of the species (species **1b**) contain one Zr with $S = 0$ and one with $S = 5/2$, and 1% of the species (species **1c**) contain two nuclei with $S = 5/2$. The simulated EPR spectrum is the sum of ESR spectra of species **1a**, **1b**, and **1c**; the major contributions to the ESR spectrum give species **1a** and **1b**. We used the following hyperfine constants for the simulation: $a_P = 21.6$ G and $a_{^{91}Zr} = 7.0$ G. These constants were determined from the experimental EPR spectrum (Figure 3). It was assumed that the width of EPR lines increase linearly with magnetic field on 0.02G/G, the width of the central line being equal to 3.0 G. A computer program was written which carries out splittings of the EPR lines due to hyperfine interactions with each nucleus of species; hyperfine splittings for equivalent nuclei were taken equal each other. The EPR spectra of species **1a**, **1b**, and **1c** were summed with weights 0.8:0.19:0.01; the weighting was carried out on the basis of second integrals of first derivatives.

Magnetic susceptibility *χ* of **1** was measured at Faraday balance at 80 and 293 K in the magnetic field of 0.1 − 1*T* strength. The μ_{eff} was calculated according to the formula $\mu_{eff} = 2.84\sqrt{}(\chi T)$.

X-ray Data Collection and Reduction. The crystals were manipulated and mounted in quartz capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. A Sintex P21 diffractometer (Mo Kα-filtred radiation, *θ*/*2θ* scan, $2\theta < 50°$) was used for data collection at the temperature 190 K. The total number of the measured reflections was 2935, and 1963 independent observable ones with $I > 2\sigma(I)$ were used in structure solution and refinement with the SHELXTL PLUS software package running on IBM PC/AT. The positions of the hydrogen atoms were calculated, and their contributions were included but not refined. The results of the refinement were as follows: 310 variables, $R = 0.053$, $R_w = 0.054$, GOF = 1.20.

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Crystal data: $C_{56}H_{78}Li_2O_6P_2ClZr_2$, $M = 1140.9$, triclinic, space group $P1$, at 190 K: $a = 10.011\ (10)$ Å, $b = 11.722(17)$ Å, $c = 12.739(11)$ Å, $\alpha = 82.79(9)^\circ$, $\beta = 69.70(7)^\circ$, $\gamma = 79.07(10)^\circ$, $V = 1373.7(4.4)$ Å^3, $d_c = 1.379$ g cm^{-1}, $Z = 1$; $\mu = 5.34$ cm^{-1}. Selected bond lengths and bond angles in **1** are presented in Table 1.

Molecular Orbital Calculation. Molecular structure calculation were performed on IBM PC/AT 486 with an aid of Gaussian 92 program for Windows.[16] Frozen core used throughout calculations including correlation effects.

Acknowledgment. The research described in this publication was made possible in part by Grant No. RET000 and RET300 from the International Science Foundation and Grant No. 93-04-7252 from Russian Foundation of Fundamental Research. We are grateful to Dr. I. N. Ivleva for her kind help in performing of the magnetic susceptibility measurements.

Supporting Information Available: Tables of crystallographic data, atomic coordinates and thermal parameters, and bond distances and angles (9 pages); listing of observed and calculated structure factors for structure **1** (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA941978X