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$[Cp_2Zr(\mu\text{-}PPh)]_2[((THF)_3Li)_2(\mu\text{-}N_2)]$: A Remarkable Salt of a Zirconocene Phosphinidene Dianion and Lithium Dication Containing Side-Bound Dinitrogen

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The classic work of Allen and Senoff[1] in 1965, in which the first complex of N_2 (i.e., $[Ru(NH_3)_5N_2]^{2+}$) was described, was the inception of an area of research in inorganic chemistry that remains active almost 30 years later.[2] Over the years the most familiar binding mode established for N_2 is one in which the diatomic nitrogen binds in an "end-on" fashion to a single metal center or bridges two metal atoms. The "side-on" bonding mode was originally claimed for $[((PhLi)_3Ni)_2{\cdot}N_2{\cdot}(OEt_2)]_2$[3] and subsequently in $[Ph(Na(OEt_2))_2(Ph_2Ni)_2N_2NaLi_6(OEt_2)_4{\cdot}OEt_2]_2$.[4] However, in these clusters, the Ni_2N_2 cores form a pseudotetrahedral arrangement with four additional interactions with Li ions. More recently, planar side-on and end-on binding modes of N_2 between two lanthanide or early transition-metal atoms have been characterized by the research groups of Evans,[5] Fryzuk,[6] and Gambarotta.[7] It is interesting to note that prior to 1965 the only known reaction of N_2 was that with Li metal, affording Li_3N, yet to date the only report in which N_2 interacts with Li is that described in the Ni clusters mentioned above. In this report, we describe the first $Li{-}N_2$ dication where N_2 binds in a side-on fashion between two Li atoms. This unprecedented dication was serendipitously prepared during the course of our studies of the chemistry of binuclear Zr phosphinidene dianions.

To a solution of $PPhH_2$ in THF at −78 °C were added 2 equiv of *n*-BuLi. After the solution was warmed to room temperature, 1 equiv of Cp_2ZrCl_2 was added. The addition was accompanied by an immediate color change from yellow to red-brown. Stirring overnight was followed by filtration and cooling to −35 °C. This afforded the crystallization of an *extremely* air-sensitive black crystalline solid (**1**) which exhibited a triplet solution EPR signal.[8] The *g* value and the hyperfine coupling constants are consistent with the presence of Zr(III) centers to which two P atoms are bonded, while the observation of a half-field transition in the EPR spectrum of a solid-state sample supports a dimeric Zr(III) formulation. X-ray quality crystals were obtained on standing of the THF/hexane solution of **1** at −35 °C. A crystallographic study of **1** revealed it to be a salt containing a Zr(III)–phosphinidene, the dimeric dianion $[Cp_2Zr(\mu\text{-}PPh)]_2^{2-}$, and the dication $[((THF)_3Li)_2(\mu\text{-}N_2)]^{2+}$,[9]

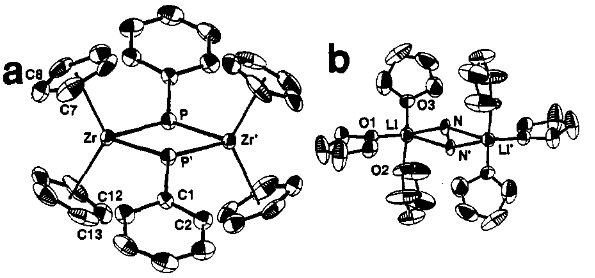
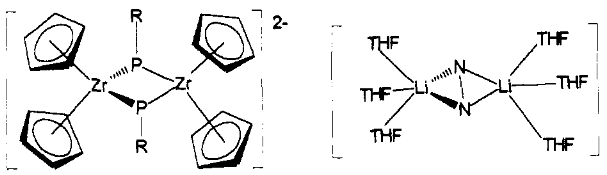


Figure 1. (a) ORTEP drawing of the dianion of **1**. Zr–P 2.574(3) Å, Zr–P′ 2.570(2) Å, P–Zr–P′ 88.90(8)°, Zr–P–Zr′ 91.10(8)°. (b) ORTEP drawing of the dication of **1**. 30% thermal ellipsoids are shown. All hydrogen atoms are omitted for clarity. Li–N 2.27(2) Å, Li–N′ 2.25(2) Å, Li–O1 1.94(2) Å, Li–O2 1.96(2) Å, Li–O3 1.91(2) Å, N–N′ 1.06(1) Å.



The dianion, which sits on a crystallographically imposed center of symmetry, contains two Cp_2Zr moieties which are bridged by two phenylphosphinidene groups (Figure 1a). The pseudopyramidal geometry about P results in a *transoid* disposition of the phenyl substituents with respect to the planar Zr_2P_2 core. This is in contrast to the planar geometry about the P atom in the phosphinidene-bridged species $(Cp_2ZrCl)_2(\mu\text{-}P(C_6H_2Me_3)$.[10] The nonplanar nature of the $Zr_2P_2C_2$ core of **1** suggests an analogy to cyclobutadiene.[11] The Zr–P distances average 2.572(3) Å, considerably shorter than the corresponding Zr–P seen in the neutral Zr(III) phosphide dimers $[Cp_2Zr(\mu\text{-}PHCy)]_2$ (2.645(4) Å)[10a] and $[Cp_2Zr(\mu\text{-}PHPh)]_2$ (2.663(4) Å).[10b] Similarly, the presence of the phosphinidene ligands in **1** results in minor perturbations of the Zr–P–Zr′ and P–Zr–P′ angles.

While the characterization of the dianion is a rare example of a Zr–phosphinidene species,[10] the truly unique feature of this molecule is the dication. The crystallographic study of **1** shows that the dication is formulated as $[((THF)_3Li)_2(\mu\text{-}N_2)]^{2+}$ (Figure 1b). A crystallographically imposed center of symmetry relates the two pseudotetrahedral $Li(THF)_3$ fragments, which are bridged by a side-on N_2 moiety. The Li–O distances are typical, while the Li–N distances of 2.25(2) and 2.27(2) Å are comparable to those seen in the $Li{-}Ni{-}N_2$ clusters.[3,4] The N–N distance is 1.06(1) Å and is indistinguishable from that in free N_2, suggesting only a weak Lewis acid–base attraction between Li and N_2.

Ab initio molecular orbital calculations were performed on the model dication $[((H_2O)_3Li)_2(\mu\text{-}N_2)]^{2+}$.[12] Not unexpectedly, the bonding interactions between Li and N_2 is attributable to the overlap of the Li(2s) and N(2s) orbitals. A secondary, much

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[8] Spectral Data: EPR (THF, 25 °C) $g = 2.018$, $\langle a_P \rangle = 17.7$ G, $\langle a_{Zr} \rangle = 7.0$ G; ^1H NMR (C_6D_6, 25 °C) δ 7.57, 7.39, 7.35, 7.31 (Ph), 6.02 (Cp), 3.55, 1.45 (THF). The isolated yield after recrystallization of **1** varied between 22 and 25%.

[9] Crystal Data: $C_{28}H_{39}LiNO_3PZr$, black blocks, triclinic, space group $P1$, $a = 11.810(5)$ Å, $b = 12.891(4)$ Å, $c = 10.110(4)$ Å, $\alpha = 106.67(3)°$, $\beta = 93.98(4)°$, $\gamma = 83.19(4)$, $V = 1463(1)$ Å^3, $d_c = 1.29$ g cm^{-3}, $Z = 2$, $\mu = 4.482$ cm^{-1}. Mo Kα radiation $\lambda = 0.710\,69$ Å was used. Crystals were sealed in 0.5-mm capillaries under N_2. A Rigaku AFC6-S four-circle diffractometer was employed to collect the data ($4.5° < 2\theta < 50°$). The solution was obtained and refined employing the TEXSAN software package running on a VAX 3520 workstation. The positions of the hydrogen atoms were calculated and their contributions included but not refined. Refinement: 2313 data $I > 3\sigma(I)$, 316 variables, $R = 0.0535$, $R_w = 0.0538$.

[10] (a) The only known Zr–phosphinidene complex was described in: Ho, J.; Stephan, D. W. *Organometallics* **1991**, *10*, 3001. (b) Ho, J.; Hou, Z.; Drake, R. J.; Stephan, D. W. *Organometallics*, submitted for publication.

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weaker bonding interaction arises from the overlap of the Li(2s) and the N($2p_y$) orbitals. The calculations as well as the structural data imply that the primary interaction results in a negligible perturbation of the N–N bonding. The calculations are consistent with the intuitive notion that such a bonding interaction between Li and N_2 is weak. However, it is interesting to note that calculations for a model in which the N_2 bridges the Li centers in an end-on fashion predicted a significantly higher total energy. A similar side geometry has also been predicted for $Li_2C{\equiv}C$.[14]

The preparation of **1** has been repeated at least 8–10 times with varying scales. The identity of the crystalline product has been confirmed for four of these batches by determination of the unit cell parameters. Nontheless, compound **1** is thermally unstable and extremely air-sensitive as a result of the facile loss of N_2 from the dication and the ease of oxidation of Zr(III) in the dianion. The compound is stable when sealed in a capillary under an N_2 atmosphere. However, when a sample of **1** was cooled to 77 K and placed under a vacuum ($<10^{-3}$ Torr) and allowed to warm to 25 °C, gas evolution began. Heating to 50 °C for 20 min and subsequent cooling to 25 °C results in the liberation of 1.00 equiv of gas.[13] GC experiments showed that the released gas was N_2.[13] Placement of a sample of **1** under dynamic vacuum for less than 5 min resulted in the total loss of N_2. In a similar sense, facile loss of side-bound N_2 has been described for $(Cp^*{}_2Sm)_2(\mu\text{-}N_2)$.[5]

Despite the plethora of Li-complex cations known, **1** is the first to reveal a simple, unsupported Li–N_2 interaction. Apparently the fortuitous use of the Zr–phosphinidene dianion results in solid-state effects which favor the Li_2–N_2 dication instead of fully solvated counterions. Ligand systems designed to enhance the stability of this dication are being pursued while an examination of Zr–phosphinidene chemistry continues.

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Supplementary Material Available: Experimental data; Pluto drawings of the dianion and dication of **1**; tables of crystallographic data, thermal and hydrogen atom parameters, bond distances and angles (12 pages); listing of observed and calculated structure factors for **1** (16 pages). Ordering information is given on any current masthead page.

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(12) Molecular orbital calculations were performed employing extended Huckel, Fenske–Hall and Gaussian-80 (ab initio) programs running on a VAX workstation 3520. Models were constructed employing the idealized geometries derived from the structural parameters.

(13) Combustion analyses for C and H were satisfactory. In gas evolution and GC experiments, blank tests demonstrated no systematic error. Attempts to prepare **1** under an Ar atmosphere have not yielded crystalline product.

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