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Phosphorus Phenyl-Group Activation by Reduced Zirconium and Niobium Complexes Stabilized by the [P_2N_2] Macrocycle

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The activation of dinitrogen by transition metal complexes has been an active area of research for almost four decades.[1−3] Despite the considerable investment of effort and time, the synthesis of complexes that contain coordinated dinitrogen is still considered difficult and oftentimes fortuitous. The most widely used method is that of reduction whereby a metal complex in a relatively high oxidation state is combined with a strong reducing agent in the presence of dinitrogen. Depending on the ligands, the metal, the solvent and the reducing agent, sometimes a dinitrogen complex results. As part of our general program aimed at a better understanding of the mode of formation of dinitrogen complexes, we have been examining the reaction of group 4 and 5 transition metal complexes with reducing agents.[4,5] As already reported[6] reduction of [P_2N_2]$ZrCl_2$ (where [P_2N_2] = PhP($CH_2SiMe_2NSiMe_2CH_2$)$_2$PPh) under 4 atm of N_2 with potassium graphite (KC_8) results in the formation of the side-on bridged dinitrogen complex ([P_2N_2]Zr)$_2$(μ-η^2:η^2-N_2); similarly, reduction of [P_2N_2]NbCl[7] in the presence of N_2 with KC_8 generates the end-on derivative, ([P_2N_2]Nb)$_2$(μ-N_2).[8] Interestingly, when these reductions are performed in the absence of dinitrogen, phosphorus-phenyl activation occurs to generate highly activated arene-bridged derivatives. In this work we describe the preparation of two new bimetallic complexes in which arene activation occurs when dinitrogen is excluded.

During the preparation of dark blue ([P_2N_2]Zr)$_2$(μ-η^2:η^2-N_2), a small amount (<5%) of a yellow crystalline byproduct was sometimes observed. A Pasteur separation of a few crystals of this material allowed analysis by X-ray crystallography; the molecular structure and numbering scheme of the material is shown in Figure 1 along with selected bond lengths and bond angles.[9] What became evident is that this byproduct does not contain dinitrogen; instead, a phosphorus-phenyl group on one [P_2N_2]Zr unit is bound to the zirconium center of another [P_2N_2]Zr fragment.[10] When this reduction was performed in the absence of N_2 (either under argon or in a vacuum), good yields of ([P_2N_2]Zr)$_2$ (**1**) were obtained (eq 1).[11] The NMR spectroscopic parameters of **1** are consistent with this formulation, as are elemental analyses and mass spectrometric data. The ^{1}H NMR spectrum shows one set of phosphorus-phenyl resonances in the ratio 2:2:1 upfield shifted to 4.35, 4.20, and 3.30 ppm indicative of coordination. The ^{31}P{^{1}H} NMR spectrum is a AA′BB′ pattern due to coupling information being transmitted through the coordinated arene ring between metal centers.

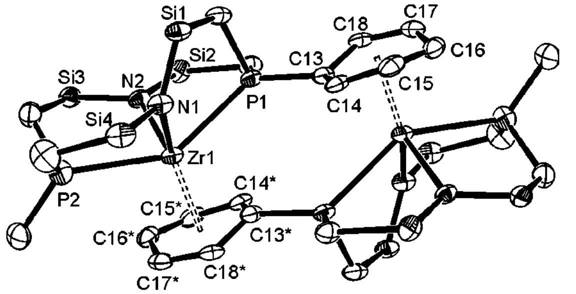
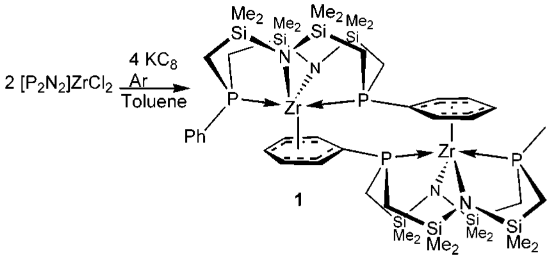


Figure 1. Molecular structure of ([P_2N_2]Zr)$_2$, **1**. Silyl methyl groups are omitted for clarity and only *ipso* carbons of phenyl rings are shown. Selected bond lengths (Å), angles (deg): Zr1−C13*, 2.352(3); Zr1−C14*, 2.460(3); Zr1−C15*, 2.542(3); Zr1−C16*, 2.401(3); Zr1−C17*, 2.528(3); Zr1−C18*, 2.551(3); Zr(1)−C_M, 2.03; C13−C14, 1.488(5); C14−C15, 1.384(5); C15−C16, 1.399(5); C16−C17, 1.447(5); C17−C18, 1.359(5); C13−C18, 1.439(4); P1−Zr1−C_M, 109.3.



(1)

The solid state structural data show that the bridging phosphorus-phenyl rings are highly distorted and bind in a η^3:η^3 fashion. The bonding in this complex can be viewed as the interaction of a Zr(IV) fragment with the phenyl ring acting as a bis(allyl) dianion.[12] The coordinated phenyl ring is no longer planar and adopts a “boat” conformation with a dihedral angle of 29.9° between the planes defined by C13−C14−C18 and C15−C16−C17. The allyl units on each activated P-phenyl group correspond to C14−C15−C16 and C17−C18−C13 on the basis of shorter C−C bond lengths in the range of 1.359(5) to 1.439(4) Å. The C13−C14 and C16−C17 bond lengths of 1.488(5) and 1.447(5) Å, respectively, are longer and approximate the single C−C bonds that connect the two allyl moieties within each ring.

In the analogous high-yield preparation of the paramagnetic, end-on niobium dinitrogen complex, ([P_2N_2]Nb)$_2$(μ-N_2), similar byproducts are not observed. However, if reduction of [P_2N_2]NbCl is performed in the absence of dinitrogen, a pale green, diamagnetic solid is obtained in good yield (eq 2). In addition to resonances from the [P_2N_2] macrocycle, the ^{1}H NMR spectrum displays three upfield-shifted phosphorus-phenyl resonances with 1:2:2 integration at 5.24, 3.99, and 3.58 ppm suggesting a coordinated arene ligand.[13,14] The ^{31}P{^{1}H} NMR spectrum consists of a broad pair of doublets at 44.94 and 18.16 ppm, suggesting coupling between two inequivalent phosphorus environments; any second-order effects are masked by the quadrupolar niobium center. If one assumes that

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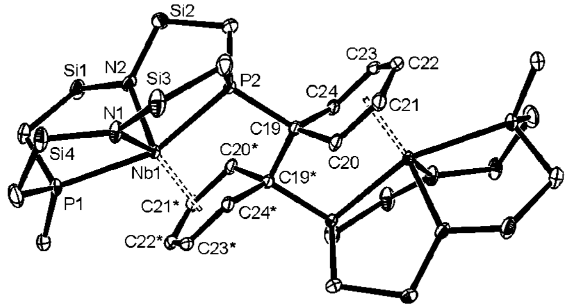
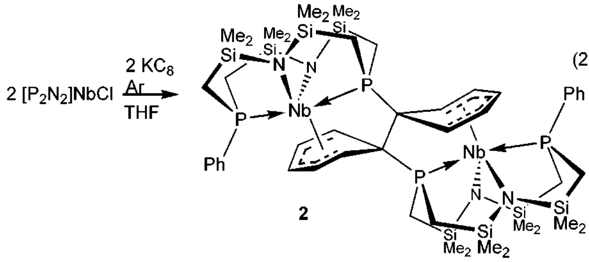


Figure 2. Molecular structure of $([P_2N_2]Nb)_2$, **2**. Silyl methyl groups are omitted for clarity and only *ipso* carbons of phenyl rings are shown. Selected bond lengths (Å), angles (deg): Nb1−C20*, 2.313(3); Nb1−C(21)*, 2.367(3); Nb1−C22*, 2.415(3); Nb1−C23*, 2.390(3); Nb1−C24*, 2.340(3); Nb1−C$_{\mathrm{M}}$, 1.925; C19−C19*, 1.542(5); C19−C20, 1.5294; C20−C21, 1.429(4); C21−C22, 1.408(4); C22−C23, 1.396(4); C23−C24, 1.427(4); C24−C19, 1.520(4); Nb1−C$_{\mathrm{M}}$−C22*, 101.29; P2−C19−C19*, 98.4(2).

the structure of niobium dimer **2** is identical to that of zirconium dimer **1**, then the diamagnetism of the former is not easily reconciled; the two niobium(IV) centers would have to be strongly antiferromagnetically coupled to produce a diamagnetic ground state.



(2)

The structure of complex **2** was clarified by a single-crystal X-ray analysis; the numbering scheme and ORTEP are shown in Figure 2 along with selected bond lengths and bond angles.[9] The structure shows that a phosphorus-phenyl ring of one $[P_2N_2]Nb$ unit is coordinated to another niobium center, analogous to that found in **1**. However, there are major differences in arrangement of the bridging arene units. The niobium complex undergoes a one-electron reduction of the P-phenyl ring to generate a cyclohexadienyl moiety via C−C bond formation between the ipso carbons of the two phenyl groups. Thus, each P-phenyl ring binds in a η^5-cyclohexadienyl fashion. The C19−C19* bond length of 1.542(5) Å is consistent with single bond character. In the niobium complex, this rationalizes the diamagnetism observed since the oxidation state of each metal in **2** can be described as low-spin Nb(III). These compounds bear resemblance to the previously reported diaryl complexes of yttrium and holmium obtained by coupling of aryllithium reagents.[15] The bonding formalism in **1** and **2** differs from that observed in some low-valent lanthanide[16,17] and early transition metals stabilized by arene ligands[10,18−23] where the arene has sometimes been described as a neutral donor.

Both complexes **1** and **2** are inert to reaction with small molecules such as H_2 and N_2. This suggests that in neither case are these products intermediates toward dinitrogen complex formation. In fact, the niobium analogue is remarkably stable to oxidation in the solid state and shows no decomposition in air over several days.

The two systems described above illustrate the complexity that can result by the use of strong reducing agents in the preparation of dinitrogen complexes. Because dinitrogen is not a particularly good ligand,[24] highly reduced complexes can undergo other competing reactions rather than activate N_2. In the zirconium case, this is certainly true, although higher pressures of dinitrogen can minimize the formation of dimer **1**. For the niobium analogue, dimer **2** is not observed even when the reduction of $[P_2N_2]NbCl$ is carried out at 1 atm pressure of N_2; nevertheless, the similarity between the two bimetallic species is remarkable and suggests that similar but as yet unknown mechanisms are operative in these processes.

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Supporting Information Available: Experimental details and spectroscopic and X-ray structural data for **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystal data for **1**: $[C_{48}H_{84}N_4P_4Si_8Zr_2$ (fw = 1248.24)], brown block, monoclinic $P2_1/n$ (no. 14), $a = 9.3696(10)$ Å, $b = 16.114(2)$ Å, $c = 19.9855(19)$ Å, $\beta = 92.9202(9)°$, $V = 3013.5(4)$ Å^3, $D_{\mathrm{calc}} = 1.376$ g/cm^3 ($Z = 2$), $R = 0.080$, $Rw = 0.085$ (on F^2, all data), $R = 0.050$, $Rw = 0.043$ (on F, $I > 3\sigma(I)$), GOF = 2.69. Crystal data for **2**: $[C_{48}H_{84}N_4P_4Si_8Nb_2$ (fw = 1251.61)], green platelet, triclinic $P\bar{1}$ (no. 2), $a = 10.1860(6)$ Å, $b = 11.2073(6)$ Å, $c = 13.2219(7)$ Å, $\alpha = 86.865(2)°$, $\beta = 92.9202(9)°$, $\gamma = 86.208(4)°$, $V = 1503.4(1)$ Å^3, $D_{\mathrm{calc}} = 1.382$ g/cm^3 ($Z = 1$), $R = 0.043$, $Rw = 0.093$ (on F^2, all data), $R = 0.035$, $Rw = 0.086$ (on F, $I > 2\sigma(I)$), GOF = 1.05. All other details are reported in the Supporting Information.
(10) For a similar bonding mode in a Zr complex see: Cotton, F. A.; Wojtczak, W. A. *Inorg. Chim. Acta* **1994**, *217*, 187.
(11) A byproduct of this reaction is the toluene adduct $[P_2N_2]Zr(\eta^3{:}\eta^3\text{-}C_7H_8)$ usually evident in 5−15% yield.
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