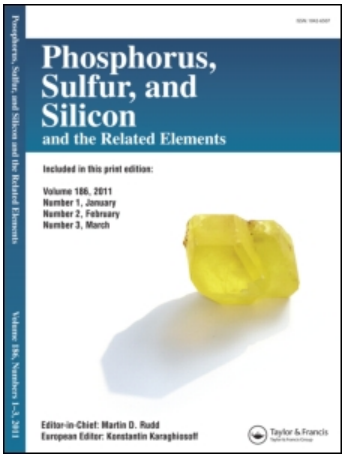

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Novel Reactivity of a Dinuclear d^{10}-d^{10} Palladium Complex

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To cite this Article Landtiser, Richard , Pan, Youlin and Fink, Mark J.(1994) 'Novel Reactivity of a Dinuclear d^{10}-d^{10} Palladium Complex', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 393 — 394
To link to this Article: DOI: 10.1080/10426509408021872
URL: http://dx.doi.org/10.1080/10426509408021872

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93-94, pp. 393-394
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NOVEL REACTIVITY OF A DINUCLEAR d^{10}-d^{10} PALLADIUM COMPLEX

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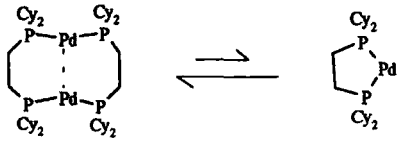
Abstract The novel dinuclear complex, $Pd_2(\mu\text{-dcpe})_2$, exists as a monomer-dimer equilibrium in solution. Stereoelectronic factors which control the reactivity of this system are discussed.

The novel complex, $Pd_2(\mu\text{-dcpe})_2$ (1), is readily generated via the photolysis of (dcpe)Pd(oxalate) in acetonitrile (dcpe = $Cy_2PCH_2CH_2PCy_2$). Although the solid state structure of 1 shows a significant interaction between the palladium atoms (*d*(Pd-Pd) = 2.76 Å), the complex (1) readily dissociates in solution and exists in equilibrium with the reactive monomer (dcpe)Pd ,(2), as shown below.[1]

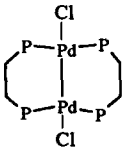


1 2

The dinuclear complex (1) is found to be the predominate species in room temperature solutions; however, the reaction chemistry of this equilibrium system is largely, but not entirely, controlled by the high reactivity of the monomer (2). The high reactivity of the monomer, which is isolobal with singlet methylene,[2] is similar to the previously reported platinum analog, (dcpe)Pt.[3] Another factor which favors the monomer as the more reactive species in solution is the highly hindered nature of the dimer. The palladium atoms of this complex are well sheilded by the cyclohexyl groups of the phosphine ligand, leaving a relatively small cleft for reaction with substrates. Therefore, it is anticipated that reaction chemistry resulting directly from the dimer may be favored only for the very smallest substrates.

The profound effect of sterics on the product distribution is amply demonstrated from the reaction of 1 with halogens in hydrocarbon solution. Bromine and iodine react to give the colorless complexes (dcpe)$PdBr_2$ and (dcpe)PdI_2, respectively. However, the reaction with chlorine gives exclusively the bright yellow Pd(I)-Pd(I) complex, (3).

While the reaction with bromine and iodine apparently proceed through the monomer, the smaller chlorine molecule is able to attack the dinuclear palladium species directly.



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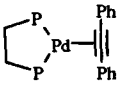

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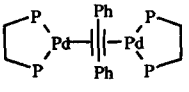

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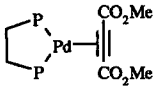

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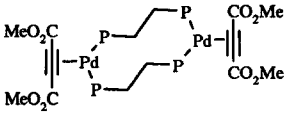

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Another example of a substrate affecting the product distribution is found in the reaction with acetylenes. Diphenylacetylene reacts predominately with the monomer to give the π complexes **4** and **5**. However, DMAD reacts with both the monomer and dimer to give (dcpe)Pd(η^2-MeOOCC≡CCOOMe), (**6**) and {(μ_2-dcpe)Pd}$_2$(η^2-MeOOCC≡CCOOMe)$_2$, (**7**), in 80% and 20% yields respectively. An X-ray structure of the colorless bisacetylene adduct shows that the palladium atoms are decidedly non-bonding with a Pd-Pd distance of 6.7 Å. It may be argued that DMAD is sterically less challenging than diphenylacetylene but other factors may also be important for their difference in chemistry.

In most cases, however, solutions of **1** are a convenient and mild source of the reactive (dcpe)Pd species. This typically allows the synthesis and isolation of nominally unstable palladium species. For example, the reaction of **1** with hydrosilanes and hydrodisilanes afford some of the few examples of simple palladium bis(silyls).[4] Also, the reaction of diphenyldisulfide and diphenyldiselenide with **1** give (dcpe)Pd(SPh)$_2$ and (dcpe)Pd(SePh)$_2$ as relatively rare examples of bisthio- and bisseleno- palladium complexes, respectively.

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