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Communications to the Editor

Facile Reductive Elimination of Ethane from Strained Dimethylpalladium(II) Complexes

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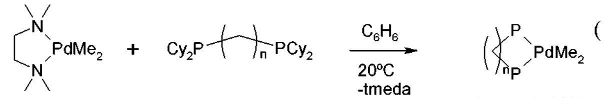
Complexes of the type $L_2Pd(0)$ are often implicated in textbook mechanisms as essential intermediates in various palladium-catalyzed carbon−carbon coupling[1] and cross-coupling reactions,[2] and have fundamental and practical significance (L = monodentate phosphine P or $^1/_2$ chelating bisphosphine P−P). Stable complexes P_2Pd have been studied for some time,[3] but their chelated counterparts, (P−P)Pd, are known only as reactive intermediates. The high reactivity of (P−P)Pd has been attributed to the acute P−Pd−P bond angle that spawns an isolobal relationship to singlet methylene.[4] One fate of these zerovalent intermediates is their dimerization to complexes in which the bidentate ligands bridge the two metal centers.[5] We have shown that the stable complex, $[(\mu\text{-dcpe})Pd]_2$, dissociates readily and reversibly in solution to give highly reactive (dcpe)Pd(0) fragments.[6] Accordingly, other dimeric complexes of this type could serve as "bottled" sources of catalytically active (P−P)Pd. For example, complexes such as $[(\mu\text{-dippe})Pd]_2$,[7] $[(\mu\text{-dppm})Pd]_2$,[8] and $[(\mu\text{-d}^t\text{bpm})Pd]_2$[9] have been implicated in chemically reacting systems but never isolated. The only reports of isolated examples, thus far, are for $[(\mu\text{-dcpe})Pd]_2$[6a,10] and $[(\mu\text{-dippm})Pd]_2$.[11] We now report an unusual chelate ring-size-dependent reductive elimination of ethane from dimethylpalladium(II) complexes bearing electron-rich chelating bisphosphines to afford the complexes $[(\mu\text{-dcpm})Pd]_2$ and $[(\mu\text{-d}^t\text{bpm})Pd]_2$ under extremely mild conditions.

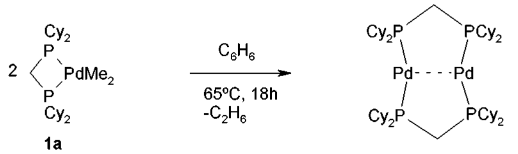
Recently, Pörschke et al. showed that displacement of the tmeda ligand in $(tmeda)PdMe_2$[12] by phosphines affords P_2PdMe_2 complexes which may undergo facile reductive elimination of ethane to give zerovalent palladium species.[13] We have found that $(tmeda)PdMe_2$ reacts with bisphosphines $Cy_2P(CH_2)_nPCy_2$ (n = 1−4) in benzene at room temperature to afford dimethyl palladium complexes **1a**−**d** as air-stable, white, crystalline solids (eq 1).[14] An X-ray crystal structure of **1a** indicates a highly strained chelate ring system with the P−Pd−P bond angle being only 73.34(4)°.[15]



(1)

1a: n = 1 (82%)
1b: n = 2 (73%)
1c: n = 3 (60%)
1d: n = 4 (65%)

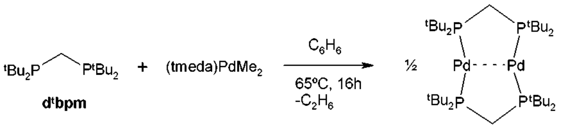
Colorless **1a** decomposed cleanly in benzene at 20 °C (days) or more conveniently at 65 °C (18 h) to give ethane (δ_H = 0.80) and the red dipalladium(0) complex $[(\mu\text{-dcpm})Pd]_2$, **2** (eq 2). The formation of **2** likely proceeds through the dimerization of (dcpm)-Pd(0) generated by the reductive elimination of ethane from **1a**. The related analogue $[(\mu\text{-d}^t\text{bpm})Pd]_2$, **3**, was obtained as bright orange crystals from the direct reaction between $(tmeda)PdMe_2$ and d^{t}bpm in hot benzene (eq 3). The intermediate $(\mu\text{-d}^t\text{bpm})$-$PdMe_2$ could not be isolated, presumably because rapid elimination of ethane occurs under the reaction conditions necessary for its formation.[16] The air-sensitive complexes **2** and **3** each gave



(2)

1a

2 (88%)



(3)

3 (81%)

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(14) The structural assignment of the compounds **1a**−**d** are entirely consistent with spectroscopic data. The mononuclear nature of these species is established by a combination of mass spectral techniques including FAB, electrospray, and chemical ionization.

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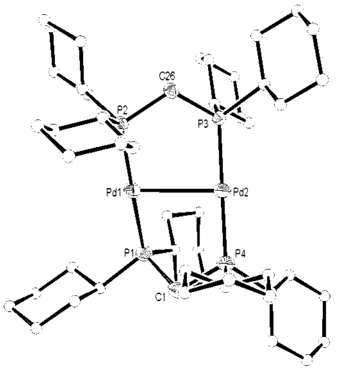
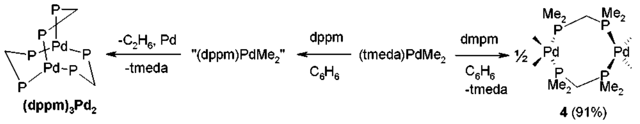


Figure 1. ORTEP drawing of **2** with thermal ellipsoids drawn at 30% probability except for the cyclohexyl carbons which are shown as arbitrary spheres for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−Pd(2), 2.8582(6); Pd(1)−P(1), 2.268(1); Pd(1)−P(2), 2.259(1); Pd(2)−P(3), 2.281(1); Pd(2)−P(4), 2.262(1); P(1)−Pd(1)−P(2), 178.56(5); P(3)−Pd(2)−P(4), 178.68(5); P(1)−C(1)−P(4), 112.7(3); P(2)−C(26)−P(3), 114.7(2); P(1)−Pd(1)−Pd(2)−P(3), 148.50(5); P(2)−Pd(1)−Pd(2)−P(4), 148.59(5).

rise to sharp singlets in $^{31}P\{H\}$ NMR spectra at δ_P 28.59 and 62.87, respectively, and exhibit molecular ions in the corresponding high-resolution mass spectra. The X-ray crystal structure of **2** shows that the two dcpm ligands that bridge the dipalladium core are highly twisted relative to each other (P1−P4−P3−P2 ≈ 45°) (Figure 1), an arrangement that minimizes interactions between the cyclohexyl groups.[17] The Pd−Pd interatomic distance of 2.8582(6) Å is slightly longer than that found for the related complex $[(\mu\text{-dcpe})Pd]_2$ (Pd−Pd = 2.7611(5) Å),[6a] but considerably longer than formal single bonds in Pd(I)−Pd(I) complexes.[18] The weak Pd−Pd interaction has been ascribed to d−p mixing in the σ bonding orbital.[19] Accordingly, the long wavelength $d\sigma^* \rightarrow p\sigma$ electronic absorption[20] for **2** (λ_{max} = 480 nm) is somewhat lower in energy than that for $[(\mu\text{-dcpe})Pd]_2$ (λ_{max} = 456 nm) consistent with the reduced orbital overlap associated with a longer Pd−Pd distance.

Surprisingly, complexes **1b**−**d** do not eliminate ethane under the experimental conditions found for **1a**. Facile reductive elimination of ethane from **1a** is likely facilitated via the formation of a three-coordinate "T-shaped" intermediate[21] following initial dissociation of one phosphine "arm",[22] a step that is much more favored for the dcpm ligand in strained **1a** than those ligands in the unstrained analogues **1b**−**d**.

Scheme 1. Reactions with Other Bisphosphines



The reaction between equimolar amounts of dppm and (tmeda)-PdMe$_2$ in benzene afforded a very sparingly soluble white solid whose mass spectrum indicated the formation of (dppm)PdMe$_2$. Attempts to purify and characterize this complex, however, were prevented by the extremely rapid reductive elimination of ethane in polar and nonpolar solvents to give the well-known $(\mu\text{-dppm})_3Pd_2$[23] (Scheme 1).[24] Although it is also likely that divalent (dppm)Pd is formed initially, the detailed mechanism for the formation of $(\mu\text{-dppm})_3Pd_2$ is uncertain at this time since we were unable to detect any intermediates by NMR.

The addition of less sterically demanding dmpm to (tmeda)-PdMe$_2$ unexpectedly furnished dimeric $[(dmpm)PdMe_2]_2$, **4**, in high yield. An X-ray crystal structure of **4** showed that it is comprised of two square-planar *cis*-PdMe$_2$ units bridged by two dmpm ligands in a "twist saddle" conformation, a structural motif observed previously for related platinum(II) complexes.[5a,25] The eight-member ring system of **4** is thermally stable and does not eliminate ethane in solution.

We have demonstrated an unusual dependence of the reductive elimination of ethane from dimethylpalladium complexes bearing bisphosphine ligands on the size of the chelate ring. Reductive elimination of ethane from highly strained dimethyl palladium complexes containing chelating bisphospinomethane ligands may be a practical and highly efficient route to certain stable $d^{10}-d^{10}$ dipalladium species, $[(\mu\text{-(P−P)})Pd]_2$. We are currently exploring the scope of these elimination reactions and the potential of these unique dinuclear complexes to serve as "bottled" sources of highly reactive 14 electron (P−P)Pd fragments.

Acknowledgment. We thank Dow Corning Corporation for financial support of this work and Aldrich Chemical Co. for generous gifts of PdCl$_2$ and phosphines. We also thank Sarah Shealy and David Bostwick of Georgia Institute of Technology for their assistance with mass spectrometry.

Supporting Information Available: Full experimental details and compound characterizations; tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1a**, **2**, and **4** (PDF). Three X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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