

## Metallacycloalkane Chemistry: Synthesis of the First Palladacyclopentane Derivative and its Transformation into a $\eta^3$ -Butenyl Cationic Complex

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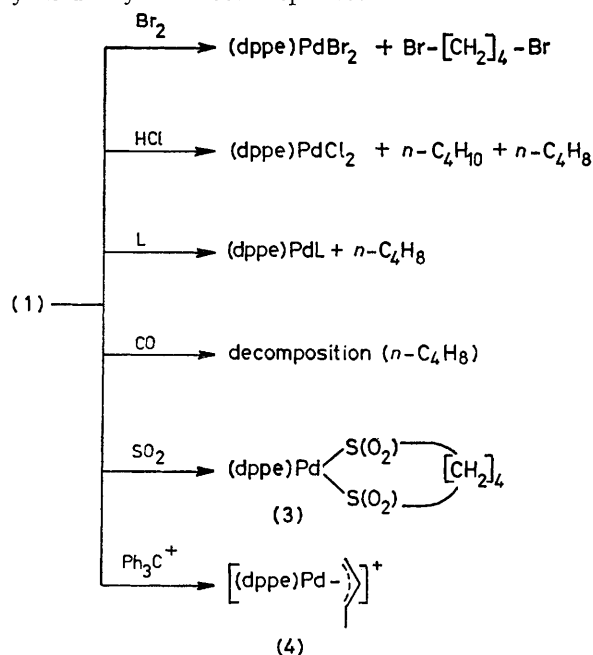
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*Summary* The preparation and some reactions of the palladacyclopentane complex (**1**) are reported including reaction with  $\text{Ph}_3\text{C}^+$  which transforms (**1**) into the  $\eta^3$ -

butenyl cationic derivative (**4**); a qualitative comparison of the thermal stability of (**1**) with that of the related di-n-butyl complex (**2**) is also reported.

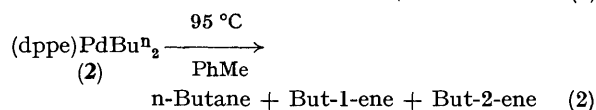
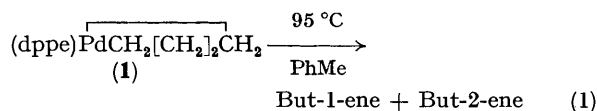
As a part of our study of transition metal metallocycles,<sup>1</sup> we now report the preparation and properties of (dppe)-PdCH<sub>2</sub>[CH<sub>2</sub>]<sub>2</sub>CH<sub>2</sub> (**1**) [dppe = 1,2-bis(diphenylphosphino)ethane]. Compound (**1**) was prepared in *ca.* 40% yield by the reaction of an excess of 1,4-dithiobutane with (dppe)-PdCl<sub>2</sub> in diethyl ether at -70 °C. The temperature was then raised to 20 °C and the resulting yellow solid was isolated and recrystallized from toluene-*n*-pentane to give pure, off-white, moderately air-stable crystals of (**1**).

In order to compare the thermal stability of (**1**) with that of a related dialkyl compound, the hitherto unknown (dppe)PdBu<sub>n</sub><sub>2</sub> (**2**) was prepared in *ca.* 35% yield by the reaction of (dppe)PdCl<sub>2</sub> with *n*-butyl-lithium, under the experimental conditions described above. Compound (**1**) is thermally very stable considering that it is an alkyl-palladium derivative containing β-hydrogen atoms available for hydride elimination; it decomposes slowly in toluene (*ca.* 12 h) while (**2**) requires only 1 h for complete decomposition. A similar difference in the thermal stability of some platinum metallocycles and analogous acyclic dialkyls has been reported.<sup>2</sup>



SCHEME. L = dppe, dimethyl maleate, dimethyl acetylenedicarboxylate, or *p*-benzoquinone.

Amongst the decomposition products of (**1**) and (**2**) [equations (1) and (2)], a small but significant amount of ethylene was always present. However, any implication of a carbon-carbon bond rupture must be ruled out on the basis of thermogravimetric analysis of (**1**) and (**2**). In both cases, in addition to the fragmentation of the aliphatic group, cleavage of the two phosphorus-carbon bonds of dppe also occurs resulting in the formation of ethylene.

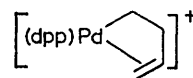


It is interesting to note that the already known<sup>2</sup> isostructural (dppe)PtCH<sub>2</sub>[CH<sub>2</sub>]<sub>2</sub>CH<sub>2</sub> thermally decomposes giving the same volatile products as (**1**), while (dppe)-NiCH<sub>2</sub>[CH<sub>2</sub>]<sub>2</sub>CH<sub>2</sub> essentially undergoes cyclobutane elimination.<sup>3</sup>

Some reactions of (**1**) are outlined in the Scheme. On treatment with ligands such as dppe or activated unsaturated molecules, (**1**) gives palladium(0) derivatives of general formula (dppe)PdL with the concurrent formation of *n*-butenes. In this respect also (**1**) behaves quite differently from some nickelacyclopentane derivatives which have been reported<sup>4</sup> to undergo reductive elimination of cyclobutanes on reaction with activated olefins.

On reaction with CO at room temperature in benzene, (**1**) gives only decomposition products (*n*-butenes); no insertion or keto products are observed. On the contrary, reaction with liquid SO<sub>2</sub> at -40 °C gives the stable crystalline cyclic complex (**3**) which appears to be the only reported example of SO<sub>2</sub> insertion into the metal-carbon σ-bonds of a metallacycloalkane derivative. The difference in the reactivity between CO and SO<sub>2</sub> can be attributed to the greater electrophilicity of the latter.

When (**1**) is treated with Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature, the η<sup>3</sup>-allylic compound [Pd(dppe)(η<sup>3</sup>-CH<sub>2</sub>-CHCHCH<sub>3</sub>)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (**4**) is obtained in high yield. The reverse reaction, *i.e.* the transformation of the allylic derivatives into metallacycloalkanes *via* nucleophilic attack by H<sup>-</sup>, has already been reported.<sup>5</sup>



(5)

An initial β-hydrogen abstraction by the trityl cation<sup>6</sup> would give the intermediate (**5**) which could rearrange to the more stable η<sup>3</sup>-allylic derivative (**4**). Such a rearrangement has some precedent by analogy with a related iron system.<sup>7</sup> Such a β-hydrogen abstraction appears to be closely related to the mechanism of thermal decomposition of (**1**) to give *n*-butenes, which could proceed *via* an inter- or intramolecular abstraction of hydrogen from one of the β-carbons.

All the compounds were characterized by <sup>1</sup>H n.m.r., i.r., and mass spectra (where appropriate), and by elemental analysis.

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<sup>6</sup> M. L. H. Green and P. L. I. Nagy, *J. Organometallic Chem.*, 1963, **1**, 58.

<sup>7</sup> M. L. H. Green and M. J. Smith, *J. Chem. Soc. (A)*, 1971, 3220, and references therein.