Reactions of Zerovalent Palladium Complexes with Dimethyl Acetylenedicarboxylate; Ligand Effects on the Formation of Palladiacyclopentadiene Complexes

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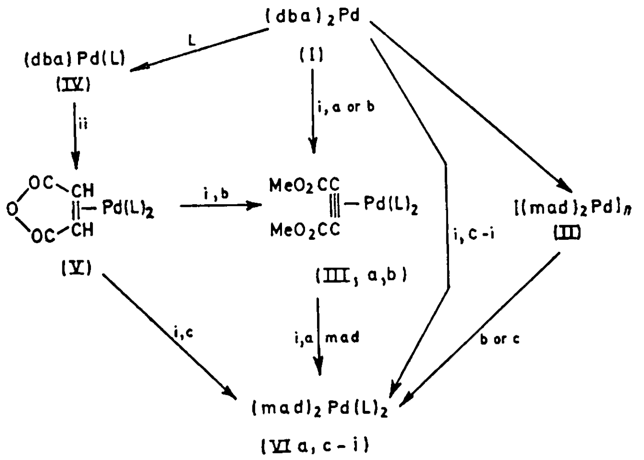
Summary Bis(dibenzylideneacetone)palladium(0) reacts with dimethyl acetylenedicarboxylate to give either palladiacyclopentadiene complexes or π-bonded acetylene complexes, according to the ligands.

IN view of recent reports by Maitlis *et al.*[1,2] we report related results. Treatment of bis(dibenzylideneacetone)palladium(0) [$(dba)_2Pd$] (I) with dimethyl acetylenedicarboxylate (mad) in acetone under nitrogen gave the palladiacyclopentadiene complex (II) which reacted with excess of ligand [L = bipy or $P(OPh)_3$] to give the monomeric palladiacyclopentadiene complexes (VI), in agreement with Maitlis' results.[3] More conveniently, palladiacyclopentadiene complexes (VI) could be prepared by the simultaneous addition of ligands and mad to a suspension of $(dba)_2Pd$ in acetone.



a; L = PPh_3
b; L = $P(OPh)_3$
c; L = bipy
d; L = ophen
e; L = tmeda
f; L = py
g; L = dmg
h; L = dte
i; L = badn

Reagents: i, mad; ii, C(:O)·CH = CH·C(:O)·O.

Palladiacyclopentadiene complexes such as (II) or (VI) could be formed *via* a zerovalent π-acetylene–palladium intermediate. Thus, addition of mad to excess of $P(OPh)_3$ and $(dba)_2Pd$ in benzene solution gave $[P(OPh)_3]_2Pd(mad)$ (IIIa), m.p. 136—138° (*ca.* 50%), which was identified by n.m.r. and i.r. spectroscopy and elemental analyses [$\nu_{C\equiv C}$ 1845 cm^{-1} (KBr disc), τ ($CDCl_3$) 6·57 (6H, s, OMe) and 2·9 (30H, m, Ph). (IIIa) is surprisingly stable in air and in benzene or chloroform solution. Further addition of mad to (IIIa) did not afford the expected (VI; L = $P(OPh)_3$] which was prepared independently *via* (II).

However, with PPh_3 as ligand, the stepwise reactions (I) → (IIIb) and (IIIb) → (VIb) were successful. A similar complex (IIIb; L = PPh_3)[4] gave (VI; L = PPh_3) by addition of a second molecule of mad in benzene solution at room temperature, strongly suggesting that the π-complex (IIIb) is an intermediate in the formation of (VIb).

Complex (Va) obtained as in the preceding communication,[5] gave (IIIa) quantitatively on reaction with mad in benzene at room temperature, but (Vc), which has a more basic ligand, gave directly the corresponding palladiacyclopentadiene complex (VIc); (L = bipy) with mad.

In conclusion, intermediate π-complexes (III) are more stabilized as the π-acceptor character of L increases, in the order: bipy ~ *o*-phen $\ll$ PPh_3 < $P(OPh)_3$: indicating the following: (i) intermediate (III) would be stabilized by π-acceptor ligand such as $P(OPh)_3$ and would thus not give (VI); (ii) the less stable intermediate (IIIb; L = PPh_3) could afford (VI). Other basic ligands such as bipy, *o*-phenanthroline (ophen), tetramethylenediamine (tmeda), pyridine (py), dimethylglyoxime (dmg), 1,2-bis(methylthio)-ethane (dte), and biacetyldianil (badn) gave directly the corresponding palladiacyclopentadiene complexes (VIc—i), respectively.

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[3] Y. Takahashi, Ts. Ito, S. Sakai, and Y. Ishii, *Chem. Comm.*, 1970, 1065.
[4] E. O. Greaves and P. M. Maitlis, *J. Organometallic Chem.*, 1966, **6**, 104.
[5] Ts. Ito, Y. Takahashi, and Y. Ishii, preceding communication.