Convenient Preparation of Novel Palladium–π-Olefin Complexes from Bis(dibenzylideneacetone)palladium(0)

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Summary Bis(dibenzylideneacetone)palladium(0) reacts with various olefins in the presence of various ligands to give stable π-olefin–palladium(0) complexes.

Zerovalent palladium–olefin complexes so far have been isolated only with ligands such as phosphines or phosphites.[1] We now report that various zerovalent palladium–olefin complexes can be synthesized more conveniently *via* bis(dibenzylideneacetone)palladium(0) [$(dba)_2Pd$],[2] which is quite stable in the air.

In the absence of ligand, $(dba)_2Pd$ reacted with olefins in acetone solution, but stable olefin–palladium complexes could not be isolated since they decomposed at room temperature to give metallic palladium and free dba. However, in the absence of olefins, treatment of $(dba)_2Pd$ with excess of ligand gave $(dba)PdL_n$ [L = bipyridyl (bipy), *o*-phenanthroline (ophen), and pyridine (py)], but other ligands such as *NN*-tetramethylethylenediamine (tmeda) did not afford $(dba)PdL_n$ complexes which were stable enough to be isolated. In the presence of both olefin and ligand, $(dba)_2Pd$ gave the corresponding olefin–palladium complexes.

When excess of bipyridyl was added to a suspension in acetone of $(dba)_2Pd$ under nitrogen, the colour of the solution changed from dark red to orange, and further addition of olefin [*e.g.* dimethyl fumarate (mf)] caused a colour change from orange to yellow. Yellow crystals then precipitated which were fairly stable in air and in benzene solution but rather unstable in chloroform. The complexes were identified by their i.r. and n.m.r. spectra, and elemental analyses.†

Yields were quite high and free dba was recovered quantitatively. Among olefins examined, stable complexes were isolated only from acrylonitrile (an), dimethylfumarate, dimethyl maleate (mm), and maleic anhydride (ma), all of which have an *e*-value[3] above 1·2. Olefins with *e*-values below 1·2 did not afford stable olefin complexes and complexes such as (dba)Pd(bipy) were obtained as major products in most cases.

Table

Complex	Yield (%)	Decomp. (°C)
(ma)Pd(bipy)	97	229—231
(ma)Pd(ophen)	95	>200
$(ma)Pd[P(OPh)_3]_2$	96	132—133[a]
$(ma)Pd[P(OMe)_3]_2$	94	92—93[a]
(mm)Pd(bipy)		
(mm)Pd(ophen)	73	171—172
(mf)Pd(bipy)	74	195—198
(mf)Pd(ophen)	69	210—212
(dvs)Pd(bipy)[b]	60	143—145
(dvs)Pd(ophen)[b]	81	168—171

[a] M.p. [b] dvs = divinyl sulphone.

Ligands examined included bipy, *o*-phen, PPh_3, tmeda, $P(OPh)_3$, and $P(OMe)_3$. With tmeda, $P(OPh)_3$, and $P(OMe)_3$, only maleic anhydride formed stable olefin–palladium complexes, and with phosphine as ligand, no olefin–palladium complex was isolated.

The complexes thus obtained were very stable in the crystalline state and almost insoluble in common organic solvents except methanol or chloroform, in which they slowly decomposed. Only acetone was of use as solvent for *N*-donor ligands or benzene for *P*-donor ligands. Typical examples are given in the Table.

Olefins with electronegative functional groups form relatively stable complexes. Good σ-donor and poor π-acceptor ligands such as bipy and *o*-phen may give olefin complexes with more olefins than poor σ-donor ligands [*i.e.*, $P(OPh)_3$ and $P(OMe)_3$].

We thank Dr. Kenji Itoh for helpful suggestions.

(*Received*, 1*st March* 1972; *Com.* 346.)

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† *E.g.* (mf)(bipy)Pd^0 showed $\nu_{C=O}$ (KBr disc): 1696 and 1680 cm^{-1}; τ ($CDCl_3$): 6·46 (6H, OMe) and 6·15 (2H, =CH).

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