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NEW MIXED OLEFIN COMPLEXES OF PALLADIUM(0). A STABILIZATION OF THE Pd(0) STATE WITH A COMBINATION OF ELECTRON-DONATING AND ELECTRON-WITHDRAWING OLEFINS

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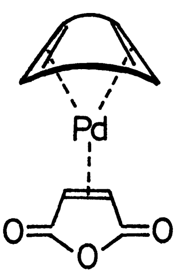
Mixed olefin complexes of Pd(0) are prepared by a ligand substitution of (dibenzylideneacetone)$_3$Pd$_2$(CHCl$_3$) (**1**) or (tribenzylideneacetylacetone)$_3$Pd$_3$(CHCl$_3$) (**2**) with a judicious combination of both electron-donating and electron-withdrawing olefin ligands.

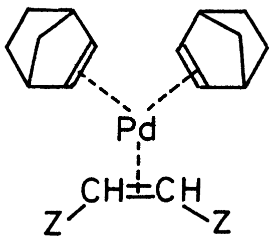
We report the formation of several new mixed olefin complexes of palladium(0) with an appropriate combination of electron-donating and -withdrawing olefin ligands. Although few olefin complexes of zerovalent palladium which did not involve any supporting ligands such as phosphines or phosphites were reported recently, for example, highly stable [Ph-CH=CH-CO-CH=CH-Ph]$_3$Pd$_2$(CHCl$_3$) (**1**)[1] and [Ph-CH=CH-CO-C(=CH-Ph)-CO-CH=CH-Ph]$_3$Pd$_3$(CHCl$_3$) (**2**)[2], as well as thermally unstable (1,5-cyclooctadiene)$_2$Pd[3,4] and (ethylene)$_3$Pd[3], no mixed olefin complex of Pd(0) is known. It seems important to prepare zerovalent palladium complexes without donor ligands of group V or VI elements, which cover a wide range of thermal stability and catalytic activity. For this purpose a control of the reactivity of the zerovalent state of palladium atom with different olefin ligands is an attractive project which will produce new mixed olefin complexes showing an extended phase of catalytic activity.

The present synthesis depends on a ligand substitution of air-stable and readily available Pd(0) complexes, **1** and **2**, with several combinations of both electron-donating and electron-withdrawing olefins. An appropriate choice of olefin ligands brings about a delicate balance of electrons around the palladium atom to give novel three-coordinate mixed olefin complexes.

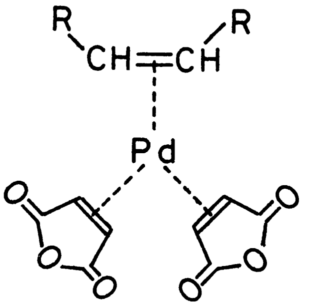
When an acetone(10 ml) suspension of 1(0.87 mmol), maleic anhydride(MAH; 5.86 mmol), and 1,5-cyclooctadiene(COD; 14.15 mmol) was stirred under argon at room temperature for 30 min., the mixture turned to a greenish yellow homogeneous solution which was filtered and was concentrated to ca. 1 ml under reduced pressure. Addition of ethyl ether gave yellow prisms of (COD)(MAH)Pd (3a) in 32% yield. The yield of 3a increased to 51% with 2 instead of 1. 3a: Mp 102-105°C, dec. IR(KBr) 1802 and 1731 cm^{-1}(C=O); NMR(acetone-d_6) δ=5.84(4H,m, COD olefin), 4.40(2H,s, MAH olefin), 2.48(8H,m). Found: C, 45.82; H, 4.48%. Calcd for $C_{12}H_{14}O_3Pd$: C, 46.10; H, 4.51%. Several new mixed olefin complexes of Pd(0) were prepared similarly and results are summarized in Table 1.



Cyclic diene =
1,5-Cyclooctadiene (3a)
Norbornadiene (3b)



Z-CH=CH-Z =
Maleic anhydride (3c)
Dimethyl fumarate (3d)



R-CH=CH-R =
Norbornene (4c)
Cyclopentene (4d)

Although the reaction of 1 or 2 with a large excess of norbornene(NBE) in the presence of an equivalent amount of MAH gave $(NBE)_2(MAH)Pd$ (3c) as pale yellow prisms in 29 and 88% yield, respectively, [run 4 and 5; 3c: NMR($CDCl_3$) δ=4.72(4H,s, NBE olefin), 4.60(2H,s, MAH olefin), 3.18(4H,m, bridgehead), 1.6-2.0(12H,m). Found: C, 54.82; H, 5.89%. Calcd for $C_{18}H_{22}O_3Pd$: C, 55.04; H, 5.65%], a treatment of an excess of MAH with 1 or 2 unexpectedly resulted in the formation of $(NBE)(MAH)_2Pd$ (4c) as silver needles [4c: NMR($CDCl_3$) δ=4.61(2H,brs, NBE olefin), 7.00(4H,s, MAH olefin) and proton signals of NBE at 3.05(bridgehead), 0.9-1.9. Found: C, 45.43; H, 3.59%. Calcd for $C_{15}H_{14}O_6Pd$: C, 45.42; H, 3.56%].

Dimethyl fumarate(MF) can be used as an electron-withdrawing olefin component in the reaction of 2 with an excess of NBE(run 6) to give $(NBE)_2(MF)Pd$ (3d) [3d: NMR($CDCl_3$) δ=4.33(2H,s, MF olefin), 4.26 and 4.79(each 2H,brs, NBE olefins under a different environment each other), 3.07 and 2.84(4H,brs, bridgehead), 3.67(6H,s,

Table 1. New Mixed Pure-olefin Complexes of Palladium(0)[a]

Run	Donor Olefin (mmol)	Acceptor Olefin (mmol)	Starting Pd(0) Complex(mmol)	Product	Yield (%)	Mp (°C; dec.)	IR($\nu_{C=O}$) (cm^{-1})
1	COD(14.15)	MAH(5.86)	1 (0.87)	(COD)(MAH)Pd (3a)	32	102-105	1802, 1731
2	COD(8.15)	MAH(1.08)	2 (0.19)	(3a)	51		
3	Norbornadiene (NBD; 6.68)	MAH(1.08)	1 (0.23)	(NBD)(MAH)Pd[b] (3b)	73	130-132	1815, 1750
4	NBE(8.01)	MAH(2.61)	1 (0.16)	$(NBE)_2(MAH)Pd$ (3c)	29	60-62	1809, 1795
5	NBE(11.71)	MAH(0.53)	2 (0.16)	(3c)	88		
6	NBE(9.88)	MF(0.69)	2 (0.17)	$(NBE)_2(MF)Pd$ (3d)	30	104-105	1703
7	NBE(1.64)	MAH(2.67)	1 (0.16)	$(NBE)(MAH)_2Pd$ (4c)	41	132-134	1825, 1765
8	NBE(1.70)	MAH(1.75)	2 (0.07)	(4c)	63		
9	Cyclopentene (5.35)	MAH(1.88)	1 (0.20)	() $(MAH)_2Pd$[c] (4d)	49	90-94	1825, 1750
10	COD(5.37)	TCNE(0.39)	1 (0.15)	(COD)(TCNE)Pd (3e)	46	202-203	-

a. Used acetone(10 ml) as a solvent. b. 3b: Found: C, 44.38; H, 3.58%. Calcd for $C_{11}H_{10}O_3Pd$: C, 44.55; H, 3.40%. c. Used dichloromethane (4 ml) as a solvent. 4d: Found: C, 42.13; H, 3.22%. Calcd for $C_{13}H_{12}O_6Pd$:C, 42.13; H, 3.22. Extremely unstable in solution.

ester methyl), 0.89-1.84(10H,m), 0.51(2H,brs, bridge)]. The preparation of **3d** was feasible only with **2** as a starting material. Dimethyl maleate did not give a similar complex. Tetracyanoethylene(TCNE) reacted analogously as an electron-withdrawing olefin in the reaction of **1** with COD to yield highly stable and insoluble complex, (COD)(TCNE)Pd (**3e**)[5] [run 10 in 46% yield. **3e**: IR(KBr) 2265 and 2225 cm^{-1}($C\equiv N$). Found: C, 51.76; H, 3.26; N, 15.10%. Calcd for $C_{14}H_{12}N_4Pd$: C, 52.41; H, 3.30; N, 15.28%].

The stabilization of the zerovalent palladium state by a combination of both electron-donating and electron-withdrawing olefin ligands is closely related to the first step of a palladium-catalyzed cyclocotrimerization between two molecules of dimethyl acetylenedicarboxylate which may be considered to be an electron-withdrawing ligand and norbornene or norbornadiene[6].

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5) The possibility of an oligomeric structure remains in the case of **3b** and **3e** because of their insolubilities to most organic solvents. Most complexes listed in Table 1 were highly unstable in solution or under vacuum, therefore, molecular weight determinations were impossible.

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