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Preliminary communication

REACTIONS OF BENZYLCHLOROBIS(TRIPHENYLPHOSPHINE)-PALLADIUM(II) WITH DIMETHYL ACETYLENEDICARBOXYLATE

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Summary

Benzylchlorobis(triphenylphosphine)palladium(II) reacted with dimethyl acetylenedicarboxylate to give $[\{Pd[C(CO_2Me)=C(CH_2Ph)(CO_2Me)]Cl(PPh_3)\}_2]$ (II) and $[(Ph_3P)ClPd\{\mu\text{-}C(CO_2Me)=C(CO_2Me)\}PdCl(PPh_3)]$ (III). Complexes II and III reacted with Tl(acac) to afford $[Pd\{C(CO_2Me=C(CH_2Ph)(CO_2Me)\}\text{-}(acac)(PPh_3)]$ and $[(Ph_3P)(acac)Pd\{\mu\text{-}C(CO_2Me)=C(CO_2Me)\}Pd(acac)(PPh_3)]$, respectively.

Clark et al. [1, 2] studied systematically the insertion reactions of substituted acetylenes into hydrido- and methyl-platinum(II) complexes. Tohda et al. reported that dimethyl acetylenedicarboxylate (dmadc) was inserted into a carbon—palladium bond in $[PdRX(PEt_3)_2]$ [R = C≡CPh, X = Cl or Br; R = Me, X = I] [3] or into a hydrido—palladium bond in $[Pd(C{\equiv}CPh)H(PEt_3)_2]$ (prepared in situ) [4] to afford [1,2-bis(methoxycarbonyl)vinyl]bis(triethylphosphine)palladium(II) complexes. A hydridopalladium(II) complex, $[PdH(NO_3)(PCy_3)_2]$ (Cy = cyclohexyl) also reacted with substituted acetylenes to give the corresponding insertion products [5]. Moreover, a chloro-bridged cyclopalladated complex derived from *N,N*-dimethylbenzylamine or 8-methylquinoline reacted with hexafluoro-2-butyne and diphenylacetylene to yield a chloro-bridged mono-insertion product and a mononuclear bis-insertion one, respectively [6]. In this communication, we wish to describe new types of palladium(II) complexes produced from the reactions between benzylchlorobis(triphenylphosphine)palladium(II) (I) [7] and dmadc.

A benzene solution of I (1.05 mmol) and dmadc (3.19 mmol) was stirred at room temperature for 48 h. The resulting suspension was filtered to yield a yellow precipitate and a yellow filtrate. The filtrate was concentrated and chromatographed with dichloromethane/diethyl ether (4/1) as an eluent. A yellow

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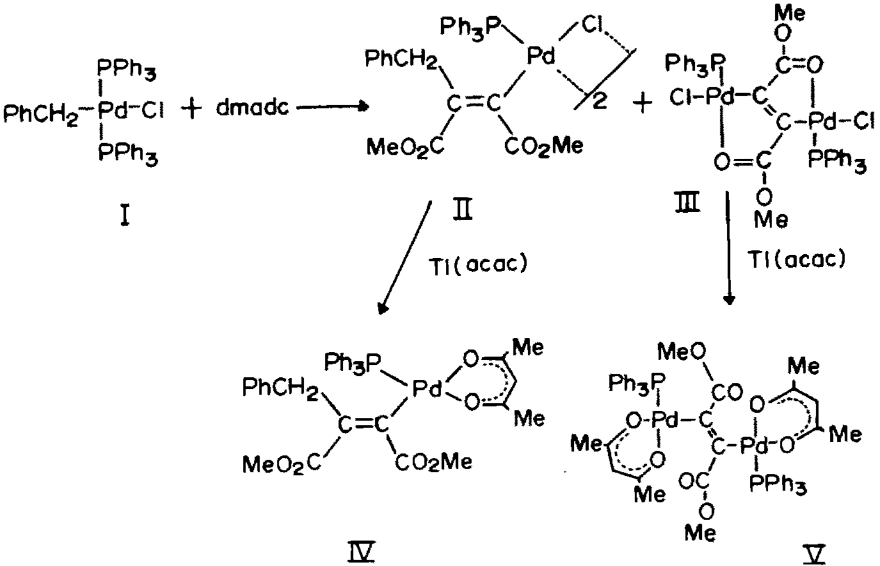
fraction gave a pale yellow powder, [{Pd[C(CO_2Me)=C(CH_2Ph)(CO_2Me)]Cl(PPh_3)}$_2$] (II). The yellow precipitate was recrystallized from dichloromethane/diethyl ether to give a pale yellow solid, [(Ph_3P)ClPd{μ-C(CO_2Me)=C(CO_2Me)}-PdCl(PPh_3)] (III). At a molar ratio of dmadc to I of 4, II was obtained in 57% yield without the isolation of III.

Complex II (0.38 mmol) reacted with thallium(I) acetylacetonate (0.82 mmol) in dichloromethane at room temperature for 24 h to give a pale yellow solid, [Pd{C(CO_2Me)=C(CH_2Ph)(CO_2Me)}(acac)(PPh_3)] (IV). Similarly, III was treated with thallium(I) acetylacetonate in benzene at room temperature for 48



SCHEME 1

TABLE 1

YIELDS AND SELECTED SPECTROSCOPIC DATA

Complex	Yield (%)	Mp.[a] (°C)	IR data[b]		^{1}H NMR data[c]		
			ν(C=O)	ν(C=C)	CH_3[d]	CH_2	CH[d]
II	9	126—127	1706	1604	3.25(6H)[e] 3.31(2H) 3.39(4H)	3.06d[f](0.7H) 4.01d[f](0.7H) 4.21d[g](1.3H)	—
III	12	209—213	1702	1553	2.85(6H)	—	—
IV	74	107—110	1710	1580	1.48(3H) 1.99(3H) 3.40(6H)	3.06d[g](1H) 3.99d[g](1H)	5.26(2H)[h]
V	49	215—217	1680 1700	1570	0.97(6H)[i] 1.34(6H) 3.15(6H)	—	4.76(2H)

[a] With decomposition. [b] In cm^{-1} in KBr disk. [c] δ value (ppm) from TMS. In $CDCl_3$, unless otherwise noted. Aromatic protons are omitted. [d] Appearing as a singlet. [e] In a mixed solvent (CD_2Cl_2:C_6D_6 = 10:1). [f] J(HH) = 13 Hz. [g] J(HH) = 14 Hz. [h] Overlapping with methylene protons of solvating molecule (1/2 CH_2Cl_2). [i] In CD_2Cl_2.

h to afford a pale greenish yellow solid, [$(Ph_3P)(acac)Pd\{\mu$-$C(CO_2Me)=C(CO_2Me)\}Pd(acac)(PPh_3)$] (V). The elemental analyses of II—V were satisfactory. The yields and selected spectroscopic data are shown in Table 1.

The IR spectra of II—V showed a band near 1590 cm^{-1}, assignable to ν(C=C). Furthermore, the retention of the ester groups and PPh_3 ligands was confirmed by a ν(C=O) band near 1700 cm^{-1} and a ν[P—C(aromatic)] one near 1435 cm^{-1}, respectively. In addition, IV and V exhibited three bands near 1580, 1515, and 1400 cm^{-1}, characteristic of an *O,O′*-chelating acetylacetonato ligand.

The ^{1}H-NMR spectrum of IV showed two doublets at δ 3.06 and 3.99 (an AB type, ^2J(HH) = 14 Hz), ascribable to benzyl methylene protons, indicating that the rotation of the benzyl group was restricted, probably by steric requirement of neighboring ester groups and the PPh_3 ligand. Two kinds of methoxy protons resonated as a singlet at δ 3.40 ppm, owing to accidental overlapping. Taking into account the restricted rotation of the benzyl group, the two ester groups must be in *cis* positions to each other, as shown in Scheme 1. In addition, the plane which the olefinic moiety forms together with the two ester-carbonyl carbons, the methylene one and the palladium atom is located perpendicularly to the palladium coordination plane.

The ^{1}H-NMR spectrum of II showed three doublets at δ 3.06, 4.01, and 4.21 ppm ascribable to methylene protons of benzyl groups.* Methoxy protons resonated as three singlets at δ 3.25 (6H), 3.31 (ca. 2H), and 3.39 ppm (ca. 4H). The $^{13}C\{^1H\}$-NMR spectrum of II in CD_2Cl_2 showed two sets of signals; large singlets at δ 43.8 (CH_2), 51.4 and 51.6 (OCH_3)**, and 164.1 and 169.7 ppm (C=O): small ones at δ 44.6 (CH_2), 54.2 (OCH_3)***, and 158.5 and 169.2 ppm (C=O). These data indicate unambiguously that II involves two nonequivalent 1,2-bis(methoxycarbonyl)-3-phenyl-1-propenyl moieties. The molecular weight of II in CH_2Cl_2 was 1386 (calcd. 1274.8), implying a dimeric structure†. A σ,π-vinyl-bridged structure for II was ruled out by the fact that palladium(II) species such as di-μ-chloro-dichlorobis(triphenylphosphine)dipalladium(II) did not form a stable complex with dimethyl maleate, a model compound of the 1,2-bis(methoxycarbonyl)-3-phenyl-1-propenyl moiety. Then, II was ascribed a chloro-bridged dimeric structure (Scheme 1). It has been determined that the two coordination planes in a chloro-bridged dimeric palladium(II) complex are situated with a dihedral angle of about 121° [8, 9]. Assuming that the chloro-bridged structure of II has a similar dihedral angle and that the olefinic moieties in II are coordinated to palladium atoms in a similar way to that in IV, there are three possible configurations, A, B, and C, as shown in Fig. 1. These three configurations involve two nonequivalent 1,2-bis(methoxycarbonyl)-3-phenyl-1-propenyl moieties with respect to the directions of the olefinic double bond. On the basis of these discussions, II was assigned to a mixture of the configurational isomers A, B, and C. It is noteworthy that I liberates one of the two PPh_3 ligands during the reaction with dmadc to give the chloro-bridged binu-

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*Another methylene proton signal was not distinguished owing to overlapping with the methoxy proton ones.

**Olefinic carbon signals were not distinguished owing to overlapping with aromatic carbon ones.

***Another methoxy carbon signal was not found owing to overlapping with solvent signals.

†Molecular weights were determined with a Corona Model 114 molecular weight apparatus.

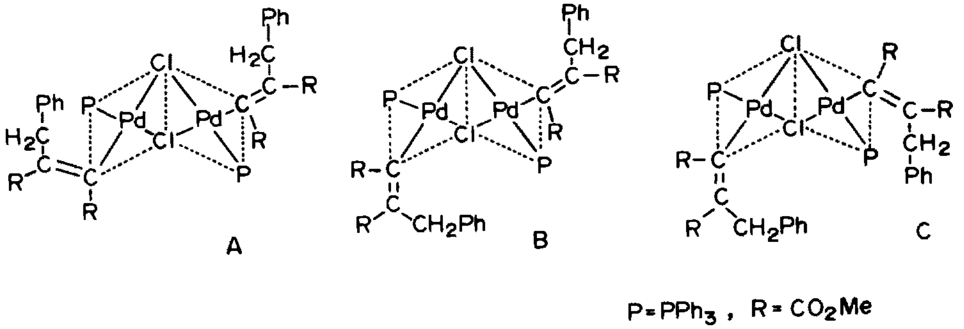

Fig. 1. The three isomers of II.

clear complex, II, in contrast to the normal insertion products reported previously [3—5]. It seems that the ready dissociation of the PPh_3 ligand from palladium is attributable to poor σ-donating ability as compared with trialkylphosphines [10].

The ^{1}H-NMR spectrum of III showed a singlet at δ 2.85 ppm attributable to methoxy protons, as well as a multiplet in the range of δ 7.0—7.8 ppm (aromatic protons), but lacked a benzyl-methylene proton resonance. The molecular weight of III in 1,1-dichloroethane was 980 (calcd. 950.39). Complex III reacted with dry hydrogen chloride in dichloromethane at room temperature to afford dimethyl fumarate (11%, detected by GLPC) and di-μ-chloro-dichlorobis(triphenylphosphine)dipalladium(II) (15%, isolated yield). These facts and the elemental analysis indicate that III is dimethyl 1,2-bis[chloro(triphenylphosphine)palladio(II)] fumarate, as shown in Scheme 1. This structure is a sharp contrast to the normal insertion products [1—5]. It has been reported that $[ClPd(\mu\text{-}Ph_2PCH_2PPh_2)_2PdCl]$ and $[Ru(\eta^5\text{-}C_5H_5)(CH_3)(CO)(PPh_3)]$ reacted with the disubstituted acetylenes to give 1,2-di[metallo(II)]ethylene-type complexes $[ClPd(\mu\text{-}Ph_2PCH_2PPh_2)_2(\mu\text{-}CY{=}CY)PdCl]$ (Y = CO_2Me or CF_3) [11] and $[(Ph_3P)(OC)(\eta^5\text{-}C_5H_5)Ru\{\mu\text{-}C(CF_3){=}C(CF_3)\}Ru(\eta^5\text{-}C_5H_4C_6H_4PPh_2\text{-}o)(CO)]$ [12], respectively.

As for V, the two ν(C=O) bands and the simple ^{1}H-NMR spectrum suggest that V consists of two isomers with C_i- and a C_2 symmetries at low temperature, and that the two isomers exchange with each other rapidly on the NMR time scale at room temperature. No ^{1}H-NMR spectrum could be obtained at low temperature owing to its fairly low solubility.

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