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Preliminary communication

REACTIONS OF DIMETHYL ACETYLENEDICARBOXYLATE WITH HYDRIDOALKYNYL COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

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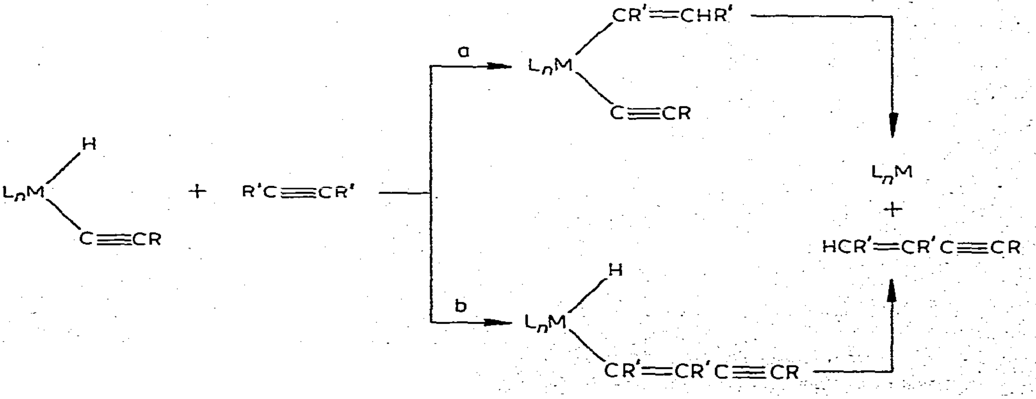
Summary

Reaction of *trans*-$HM(PEt_3)_2(C{\equiv}CC_6H_5)$ (M = Pt, Pd) with dimethyl acetylenedicarboxylate has given *trans*-$\{(CH_3O_2C)HC{=}C(CO_2CH_3)\}M(PEt_3)_2(C{\equiv}CC_6H_5)$. It is suggested that oligomerization of a terminal acetylene proceeds through an alkynylalkenyl derivative.

A hydridoalkynylmetal complex, which is formed by oxidative addition of a terminal acetylene group to the metal, is considered to be an intermediate in oligomerizations of terminal acetylenes catalyzed by low valent transition metal complexes [1]. Hydrido (path a) or alkynyl groups (path b) of such an intermediate may add to acetylenes [2] to form an alkynylalkenyl or a hydridoalkenyl complex, respectively, which can subsequently undergo reductive elimination to the dimer and reform the starting low valent complex (eq. 1). Since the question of whether path a or path b is preferred remains unanswered, it should be of interest to examine the reactions of such hydridoalkynyl complexes with acetylenes. Although the reaction of acetylenes with a variety of hydrido- and



(1)

alkynyl-metal complexes [3, 4] have been reported, the reaction with hydridoalkynyl complexes has not yet been investigated.

A dioxane solution (40 ml) of *trans*-$HPt(PEt_3)_2(C{\equiv}CPh)$ (I)* (356 mg) and dimethyl acetylenedicarboxylate (dma) (190 mg) was stirred for 2 h at 25°C. Chromatography of the reaction mixture provided the major product as colorless crystals (II) (224 mg, yield 45%, m.p. 89—91°C after recrystallization from methanol). Mass spectrum (m/e): P^+ 675, $[Et_3PC(CO_2CH_3){=}CH(CO_2CH_3)]^+$ 261, $[Et_3PC{\equiv}CC_6H_5]^+$ 219; IR ($\nu(C{\equiv}C)$ 2100s, $\nu(C{=}O)$ 1690 s cm^{-1} in Nujol) and proton NMR (see Table 1) confirm the complex as *trans*-$[(CH_3O_2C)HC{=}C(CO_2CH_3)]Pt(PEt_3)_2(C{\equiv}CC_6H_5)$ (II). In due consideration of the difference of the *trans*-effect between $Pt{-}H$ and $Pt{-}C{\equiv}CC_6H_5$ moieties of I, $HPt(PEt_3)_2Cl$ (III) and $(PhC{\equiv}C)Pt(PEt_3)_2Cl$ (IV) were treated with dma for 2 h at 100°C in dioxane, respectively (eq. 3 and 4). The results suggest that the order of increasing reactivity for the insertion of acetylenes is $Pt{-}H > Pt{-}C{\equiv}CC_6H_5$, regardless of the *trans* ligand.

$$\underset{\text{(I)}}{\textit{trans}\text{-}HPt(PEt_3)_2(C{\equiv}CPh)} + CH_3O_2CC{\equiv}CCO_2CH_3 \xrightarrow[\text{dioxane}]{\text{room temp., 2 h,}}$$

$$\underset{\text{(II)}}{\textit{trans}\text{-}HC(CO_2CH_3){=}C(CO_2CH_3)Pt(PEt_3)_2(C{\equiv}CPh)} \qquad (2)$$

$$\textit{trans}\text{-}HPt(PEt_3)_2Cl + CH_3O_2CC{\equiv}CCO_2CH_3 \xrightarrow[\text{dioxane}]{100^\circ C,\ 2h}$$

$$\underset{\text{(III)}}{HC(CO_2CH_3){=}C(CO_2CH_3)Pt(PEt_3)_2Cl} \qquad (3)$$

yield 76%; m.p. 172—174°C; P^+ 609 m/e; NMR (see Table 1; IR $\nu(C{=}O)$ 1710, $\nu(Pt{-}Cl)$ 294 cm^{-1})

$$\textit{trans}\text{-}(PhC{\equiv}C)Pt(PEt_3)_2Cl + CH_3O_2CC{\equiv}CCO_2CH_3 \xrightarrow[\text{dioxane}]{100^\circ C,\ 2\ h} \text{no reaction} \qquad (4)$$

As the palladium analog of I is unstable, we used the following system as a precursor of the hydridoalkynyl complex. n-BuLi (1 mmol) in hexane solution was added at −78°C to 1 mmol (479 mg) of *trans*-$ClPd(PEt_3)_2(C{\equiv}CC_6H_5)$ in 30 ml of ether. After allowing the temperature to rise gradually to 20°C, 1.5 mmol of dma in ether (10 ml) were added and the reaction mixture was stirred for 1 h under nitrogen. The gas evolved was identified as 1-butene by GLPC analysis. Chromatography of the product provided the major product as colorless crystals (IV, 326 mg, 52%, m.p. 87—88°C after recrystallization from hexane). Mass spectrum (m/e): P^+ 586, $[Et_3PC(CO_2CH_3){=}CH(CO_2CH_3)]^+$ 261, $[Et_3PC{\equiv}CPh]^+$ 219, proton NMR (see Table 1) and IR-spectrum ($\nu(C{=}O)$ 1720s, 1710s, 1690s, $\nu(C{\equiv}C)$ 2100 cm^{-1} in Nujol) confirm the complex IV as *trans*-$[(CH_3O_2C)HC{=}C(CO_2CH_3)]Pd(PEt_3)_2(C{\equiv}CC_6H_5)$.

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*This complex was prepared by the reaction of $HPt(PEt_3)_2Cl$ with $NaC{\equiv}CC_6H_5$ [5] in benzene, yield 45%. Physical and spectral data agreed with those of the literature [6]. *trans*-Configuration of this complex has been well confirmed by the characteristic 1:4:6:4:1 quintet for methyl resonances of the PEt_3 group [7].

$$trans\text{-}ClPd(PEt_3)_2(C{\equiv}CC_6H_5) \xrightarrow{\text{n-BuLi}}$$

$$trans\text{-}CH_3CH_2CH_2CH_2Pd(PEt_3)_2(C{\equiv}CC_6H_5) \xrightarrow[-\text{ 1-butene}]{+\text{ dma}}$$

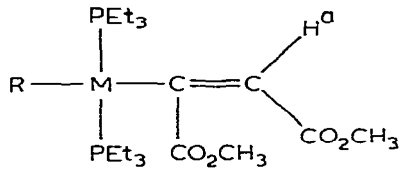
$$\underset{\text{(IV)}}{trans\text{-}[(CH_3O_2C)HC{=}C(CO_2CH_3)]Pd(PEt_3)_2(C{\equiv}CC_6H_5)} \xrightarrow{\text{HCl/ether}}$$

$$\underset{\text{(V)}}{trans\text{-}[(CH_3O_2C)HC{=}C(CO_2CH_3)]Pd(PEt_3)_2Cl}$$

Treatment of IV with hydrogen chloride in ether at 25°C for 1 h gave colorless crystals (V, m.p. 158—162°C after alumina chromatography followed by recrystallization from hexane/ether, yield 84%). Mass spectrum (m/e): P^+ 520, $[Et_3PC(CO_2CH_3){=}CH(CO_2CH_3)]^+$ 261, $[Et_3PCl]^+$ 153, proton NMR (see Table 1), and IR (ν(C=O) 1715, 1720, ν(C—O) 1205, 1190, 1155, ν(Pd—Cl) 298 cm^{-1}) confirm V as $trans\text{-}[(CH_3O_2C)HC{=}C(CO_2CH_3)]Pd(PEt_3)_2Cl$.

TABLE 1

PROTON NMR DATA FOR



[a]

R	M	P—C$\underline{H}_2$—CH$_3$	P—CH$_2$C$\underline{H}_3$	COOC$\underline{H}_3$	=C<$\underline{H}$	Ph	^3J(PtH^a) (Hz)	^4J(PH^a)^d (Hz)
PhC≡C	Pt	1.9 m	1.11 qu^b	3.60 s	6.74	7.05 m	82.0	2.1
Cl	Pt	1.9 m	1.12 qu^b	3.65 s 3.72^c	5.73 t		99.6	1.5
PhC≡C	Pd	1.9 m	1.15 qu^b	3.58 s 3.60 s	5.58 t	7.06 m		0.5
Cl	Pd	1.9 m	1.13 qu^b	3.60 s 3.64 s	5.56 s			0

[a] Spectra were recorded on Hitachi Perkin—Elmer R20 in CCl$_4$. Chemical shifts (δ) are in ppm downfield from TMS and coupling constants (J) are given in Hz. Multiplicity d = doublet, t = triplet, qu = quintet, m = multiplet. [b] Characteristic 1:4:6:4:1 quintet for methyl resonances of the *trans*-PEt$_3$. [c] ^5J(PtH) 3.2. [d] The geometry of the platinum complexes can also be determined from the magnitude of ^3J(PtH^a) and ^4J(PH^a) values [8].

Although we cannot yet provide detailed mechanisms for the oligomerization of terminal acetylenes, the above results indicate that the reaction of acetylenes with hydridoalkynyl complexes may produce the alkenylalkynyl derivatives (path a in eq. 1), regardless of the gross geometry of the central metal.

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