

Preliminary communication

A novel Lewis-acid-catalyzed 1,2-OMe shift reaction of an acetylenic ether on a dipalladium framework.

X-ray structure of $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-C}=\text{C}(\text{OMe})(\text{Me}))]$

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Abstract

Treatment of $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2]$ with $\text{MeOC}\equiv\text{CMe}$ in CH_2Cl_2 in the presence of catalytic amounts of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ led to the formation of $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-C}=\text{C}(\text{OMe})(\text{Me}))]$ via a 1,2-OMe shift reaction. The complex was characterized crystallographically.

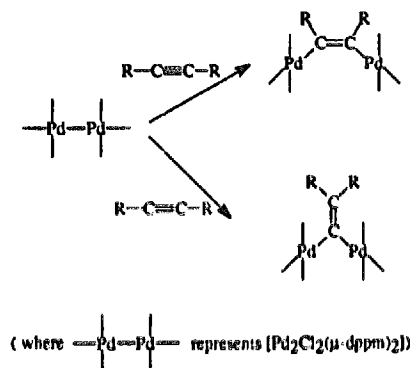
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1. Introduction

The dipalladium(I) complex, $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2]$, is known to react with acetylenes to form either 1,2-dimetalated olefins (acetylene adducts) or 1,1-dimetalated olefins (vinylidene complexes) [1–3] (Scheme 1). Formation of the latter involves a metal-assisted 1,2-shift reaction which, while relatively common for terminal acetylenes [4], is unusual in the case of acetylenes bearing heteroatomic substituents [3,5–13]. Reactions of acetylenes without electron-withdrawing groups with $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2]$ are slow and may be facilitated by Lewis-acid catalysis which leads to the formation of acetylene adducts [14].

We have recently reported that Lewis acids catalyze 1,2-SMe shifts in the reaction of $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2]$ with $\text{MeSC}\equiv\text{CSMe}$ [15]. In the presence of a Lewis acid only the vinylidene complex, $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-C}=\text{C}(\text{SMe})_2)]$, was formed while, in the absence of Lewis acid, exclusively the acetylene adduct, $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-MeSC}=\text{CSMe})]$, was produced. The acetylene adduct could then be rearranged to the corresponding vinylidene isomer by addition of catalytic amounts of a Lewis acid (Scheme 2).

The results with $\text{MeSC}\equiv\text{CSMe}$ parallel those obtained earlier from an investigation of the reactions of

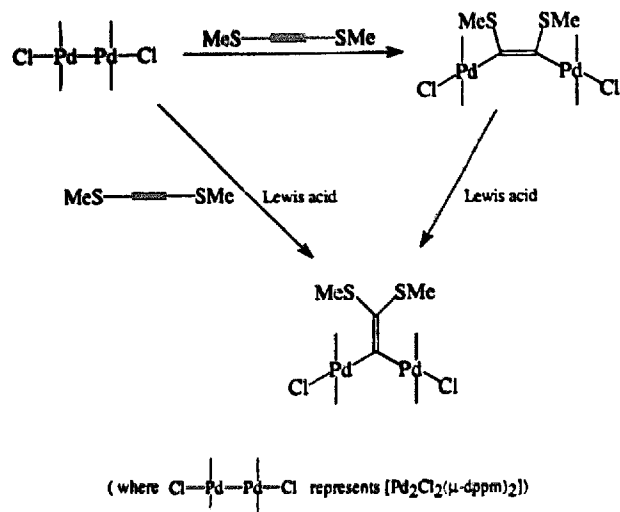


Scheme 1.

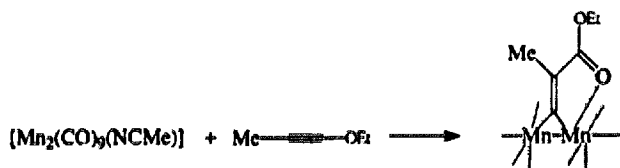
$[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2]$ with $\text{IC}\equiv\text{Cl}$ [3]. In both cases, vinylidene formation resulting from a 1,2-shift of a soft atom was observed. Work with $\text{Et}_2\text{NC}\equiv\text{CNEt}_2$, in contrast, revealed no evidence of a 1,2- NEt_2 shift in reactions with $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2]$ [16]. Accordingly, reactions of acetylenic ethers are of particular interest since the $-\text{OR}$ group could show similarities to $-\text{NR}_2$ (first row) or to $-\text{SR}$ (Group VI).

We now wish to report the formation of $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-C}=\text{C}(\text{OMe})(\text{Me}))]$ in the reaction of $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2]$ [17] with $\text{MeOC}\equiv\text{CMe}$ [18] in the presence of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$. This reaction represents the first Lewis-acid-catalyzed 1,2-shift of an acetylene bearing an alkoxy group. To the best of our knowledge only

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Scheme 2.



Scheme 3.

one somewhat-related example of a 1,2-shift reaction of an acetylene containing an oxygen functional group has so far been described [9,10]. The reaction differs from that reported here since, in the reaction of $[\text{Mn}_2(\text{CO})_9(\text{NCMe})]$ with $\text{EtOC}\equiv\text{CMe}$, the 1,2-OEt rearrangement was accompanied by CO insertion (Scheme 3).

2. Results and discussion

Treatment of a solution of $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2]$ in CH_2Cl_2 with two equivalents of $\text{MeOC}\equiv\text{CMe}$ in the presence of catalytic amounts of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ led, over a period of 20 h, to the formation of a light yellow solid which settled out of solution and proved to be air stable. It was washed with cold CH_2Cl_2 , dried in vacuo, and recovered in ca. 71% yield, based on palladium. (Anal. Found: C, 55.6; H, 4.5, for $\text{C}_{54}\text{H}_{50}\text{Cl}_2\text{O}_4\text{Pd}_2$. Calc.: C, 57.7; H, 4.5%. NMR (CDCl_3): ($^{31}\text{P}\{^1\text{H}\}$) AA'BB' δ 10.5–14 (^1H) δ 1.0 (s, 3H, CH_3), 2.9 (s, 3H, OCH_3), 6.9–8.1 (m, 40H, C_6H_6), 2.7 (m, 2H, PCH_2P), 3.3 (m, 2H, PCH_2P). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , rel. to 85% H_3PO_4) showed the AA'BB' splitting pattern expected for an unsymmetrical dinuclear species, centered at 12.5 ppm. This value proved to be very close to that observed for the related, sulfur-containing vinylidene complex, $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-C}=\text{C}(\text{SMe})(\text{Me}))]$ (AA'BB' centered at 12 ppm) [13].

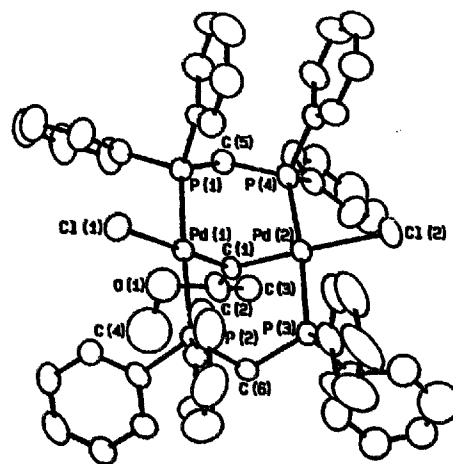


Fig. 1. ORTEP diagram of $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-C}=\text{C}(\text{OMe})(\text{Me}))]$, showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Pd(1)–Cl(1) 2.417(1), Pd(2)–Cl(2) 2.403(2), Pd(1)–P(1) 2.312(1), Pd(1)–P(2) 2.318(1), Pd(2)–P(3) 2.300(1), Pd(2)–P(4) 2.313(1), Pd(1)–C(1) 1.991(5), Pd(2)–C(1) 1.991(5), C(1)–C(2) 1.325(8), C(2)–O(1) 1.547(7), C(2)–C(3) 1.40(1), O(1)–C(4) 1.447, Pd(1)···Pd(2) 3.2248(5); Cl(1)–Pd(1)–P(1) 92.33(5), Cl(1)–Pd(1)–P(2) 95.72(5), Cl(1)–Pd(1)–C(1) 177.0(2), P(1)–Pd(1)–P(2) 171.59(5), P(1)–Pd(1)–C(1) 86.5(1), P(2)–Pd(1)–C(1) 85.3(1), C(2)–Pd(2)–P(3) 92.41(5), C(2)–Pd(2)–P(4) 94.72(5), C(2)–Pd(2)–C(1) 177.6(1), P(3)–Pd(2)–P(4) 171.18(6), P(3)–Pd(2)–C(1) 86.7(1), P(4)–Pd(2)–C(1) 86.0(1), Pd(1)–C(1)–Pd(2) 108.2(2), Pd(1)–C(1)–C(2) 125.0(4), Pd(2)–C(1)–C(2) 126.8(4), C(1)–C(2)–O(1) 116.6(5), C(1)–C(2)–C(3) 123.3(7), C(2)–O(1)–C(4) 109.7(2).

$[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2]$ was found to be unreactive towards $\text{MeOC}\equiv\text{CMe}$ in the absence of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction solution recorded after 48 h stirring in CH_2Cl_2 at room temperature exhibited one signal which corresponded to the starting material. After removal of the solvent only starting material was recovered.

Since $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2]$ as well as $\text{MeOC}\equiv\text{CMe}$ separately react with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$, the sequence of the acid-catalyzed reaction is unclear.

Single crystals were grown by slow evaporation of the solvent CH_2Cl_2 . X-ray analysis revealed the formation of a dinuclear vinylidene complex (Fig. 1).

Crystal data: $\text{C}_{54}\text{H}_{50}\text{Cl}_2\text{O}_4\text{Pd}_2$; $M = 1122.60$; tetragonal, $P4_3$; $a = 21.184(4)$ Å, $c = 14.233(2)$ Å; $V = 6387(3)$ Å³; $Z = 4$; $D_c = 1.17$ g cm⁻³; $\lambda(\text{MoK}\alpha) = 0.71073$ Å; $\mu = 7.7$ cm⁻¹; $F(000) = 2272$; $T = 213 \pm 1$ K; yellow crystal, prism, $0.50 \times 0.35 \times 0.20$ mm³, mounted on a glass fiber, Enraf–Nonius CAD4 diffractometer, graphite monochromator. ω - θ scan technique, unit cell constants from the setting angles of 25 reflections in the range $12 < \theta < 13^\circ$, empirical absorption correction (min. correction 0.819, max. 1.210), maximum $2\theta = 52.0^\circ$, $0 < h < 26$; $0 < k < 26$; $0 < l < 17$; anisotropic decay (from 0.950 to 1.078 on l), reflection averaging $R(\text{int}) = 2.3\%$, 6905 total reflections measured, 6541 unique, 5631 reflections with $F_o^2 > 3.0\sigma(F_o^2)$, solution by direct methods, refinement by

full-matrix least squares, function minimized was $\sum w(|F_o| - |F_c|)^2$, weight w is defined as $4F_o^2/\sigma^2(F_o^2)$; coordinates fixed, multiplicity set to 0.5 for O1, O1a, C4 and C4a of disordered vinylidene moiety, isotropic thermal parameters refined for O1, O1a, C3, C3a and C4 of vinylidene moiety, one phenyl ring found to be disordered, multiplicity for carbon atoms C33, C33a, C34, C34a, C35, C35a, C36 and C36a of this phenyl ring set to 0.5 and isotropic thermal parameters refined, anisotropic thermal parameters refined for all other non-hydrogen atoms, hydrogen atoms refined with $U_{iso} = 1.3 \times U$ (bonding atom), 547 refined parameters, $R = 0.033$, $wR = 0.043$, $S = 1.42$, largest shift 0.03σ , high peak in final difference map $0.57(9)e\text{\AA}^{-3}$, low peak $-0.08(9)e\text{\AA}^{-3}$. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974).

The metal centers were held together by two mutually trans dppm ligands. The α -carbon (C(1)) of the vinylidene moiety symmetrically bridged the palladium atoms; trans to the vinylidene moiety were two chloride ligands, completing the approximately square-planar coordination geometry around palladium in this 'A-frame' complex. The vinylidene moiety was unsymmetrical. The two different substituents (Me and OMe) on the β -carbon (C(2)) were found to be disordered over a two-fold axis. The distance of $1.325(8)\text{\AA}$ between C(1) and C(2) of the vinylidene moiety is consistent with sp^2 hybridization. The bridging vinylidene moiety is not supported by any significant metal-metal bonding interaction ($\text{Pd}(1) \cdots \text{Pd}(2) = 3.2248(5)\text{\AA}$).

The formation of $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{C}(\text{OMe})(\text{Me}))]$ indicates that Lewis-acid catalysis of 1,2-heteroatom shift reactions of acetylenes is not limited to sulfur groups. It represents the first straightforward 1,2-OMe rearrangement of an acetylene (see Scheme 3). The mechanism of the Lewis-acid-catalyzed acetylene-vinylidene isomerization is under investigation.

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