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Preparation and properties of alkylpalladium(II) and -platinum(II) alkynyl complexes

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Abstract

Reaction of methylpalladium alkoxide complex, $PdMe(OCH(CF_3)_2)(dppe)$ (dppe = 1,2-bis(diphenylphosphino)ethane) with phenylacetylene gives PdMe(C≡CPh)(dppe) (I). Methylpalladium and -platinum alkoxide complexes having PMe_3 ligands also react with phenylacetylene to give *trans*-$PdMe(C≡CPh)(PMe_3)_2$ (II) and *trans*-$PtMe(C≡CPh)(PMe_3)_2$ (III), respectively. The complexes were characterized by IR and NMR spectroscopy as well as by elemental analyses. Thermolysis of complexes **I–III** causes reductive elimination of MeC≡CPh in 97–98% yields. Reaction of I with CO at 1 atm gives MeC≡CPh while the reaction with CO at 10 atm gives a mixture of MeCOC≡CPh and MeC≡CPh. Complex **III** does not react with CO at 1 atm.

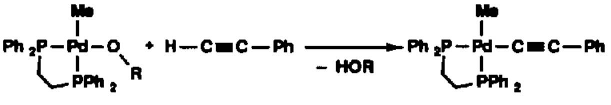
1. Introduction

Transition metal alkynyl complexes have recently attracted attention [1–7] as the intermediates of (a) metal-promoted dimerization or oligomerization of alkynes and of (b) addition of various reagents on the C≡C triple bond [8]. Although alkynyl complexes of palladium and platinum were already reported [9–12], there have been few reports on the reactivity of the alkynyl ligand bonded to these metals. During our study on transition metal alkoxide complexes [13] we have observed that methylpalladium and -platinum alkoxide complexes with tertiary phosphine ligands react smoothly with phenylacetylene to give methylpalladium and -platinum alkynyl complexes, respectively. Thermolysis of the complexes as well as reaction with CO were carried out. Here we report the preparation and chemical properties of the alkynylpalladium and -platinum complexes.

2. Results and discussion

2.1. *Preparation and characterization of the methylpalladium and platinum alkynyl complexes*

Reaction of $PdMe(OCH(CF_3)_2)(dppe)$ (dppe = 1,2-bis(diphenylphosphino)ethane) with phenylacetylene at room temperature gives PdMe(C≡CPh)(dppe) (**I**) in 94% yield. $PdMe(OCH(CF_3)Ph)(dppe)$ also reacts with phenylacetylene to give complex **I** (eqn. (1)).



(1)

(I)

(R = $CH(CF_3)_3$, $CH(CF_3)Ph$)

The reaction proceeds very cleanly and does not give any other palladium compounds such as $Pd(OCH(CF_3)_2)(C≡CPh)(dppe)$ or $Pd(C≡CPh)_2(dppe)$ that might be formed by protonation of the methyl ligand.

Complex **I** was characterized by IR and NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectroscopy as well as by elemental analysis. The IR spectrum shows a band due to ν(C≡C) vibration at 2100 cm^{-1}. Table 1 summarizes the NMR data. The $^{13}C\{^1H\}$ NMR spectrum shows the signal due to the methyl ligand as a doublet of doublets at −2.1 ppm. The signals due to the alkynyl carbons appear at 119.7 and 113.0 ppm, respectively. The former signal, assigned to the carbon bonded to palla-

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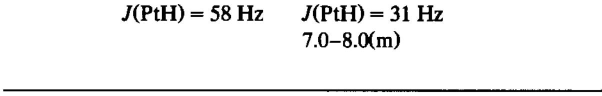
TABLE 1. NMR data of complexes I–III [a]

Complex	^{1}H [b]		^{31}P{^{1}H} [c]	^{13}C{^{1}H} [d]		
	M–C*H*$_3$	phosphine ligands		M–*C*H$_3$	P–*C*H$_2$ or P–*C*H$_3$	M–C$_\alpha$≡C$_\beta$
I	0.60(t, 3H) *J*(PH) = 6 Hz	1.9–2.7(m) 7.0–8.1(m)	35.7(d), 51.0(d)	−2.1(dd) *J*(PC) = 102, 3 Hz	25.7(dd), 29.4(dd) [e] *J*(PC) = 20, 16 Hz	119.7(dd, C$_\alpha$) [e] *J*(PC) = 153, 22 Hz 113.0(d, C$_\beta$) *J*(PC) = 30 Hz
II	−0.34(t, 3H) *J*(PH) = 7 Hz	1.47(t) *J*(PH) = 3 Hz 7.0–8.1(m)	−14.0(s)	−8.8(t) *J*(PC) = 8 Hz	15.3(t) *J*(PC) = 15 Hz	122.5(t, C$_\alpha$) [f] *J*(PC) = 22 Hz 109.5(s, C$_\beta$)
III	0.02(t, 3H) *J*(PH) = 7 Hz *J*(PtH) = 58 Hz	1.57(t) *J*(PH) = 4 Hz *J*(PtH) = 31 Hz 7.0–8.0(m)	−19.4(s) *J*(PtH) = 2574 Hz	−5.5(t) *J*(PC) = 8 Hz *J*(PtC) = 473 Hz	22.6(t) *J*(PC) = 19 Hz *J*(PtC) = 43 Hz	126.8(t, C$_\alpha$) [g] *J*(PC) = 153, 22 Hz 115.1(s, C$_\beta$) *J*(PtC) = 225 Hz

[a] Abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet. [b] 100 MHz in CD_2Cl_2. [c] 40 MHz in CD_2Cl_2. Ppm downfield from external 85%H_3PO_4. [d] 125 MHz in CD_2Cl_2. [e] Signals due to the phenyl carbons are observed in the range 129–134 ppm. [f] Signals due to the phenyl carbons are observed at 125, 128, 130, and 131 ppm, respectively. [g] Signals due to the phenyl carbons are observed at 133, 137, 138, and 139 ppm, respectively.

dium, is split as a doublet of doublets (*J*(CP) = 153 and 22 Hz), while the latter signal appears as a doublet (*J*(CP) = 30 Hz). These ^{13}C{^{1}H} NMR results as well as ^{31}P{^{1}H} NMR spectrum, showing two doublets, indicate the square-planar configuration of I having the methyl and alkynyl ligands at mutually *cis* positions.

Reaction of *trans*-PdMe(OCH(CF_3)Ph)(HOCH(CF_3)Ph)(PMe_3)$_2$ with phenylacetylene at room temperature gives *trans*-PdMe(C≡CPh)(PMe_3)$_2$ (II) in 76% yield (eqn. (2)).

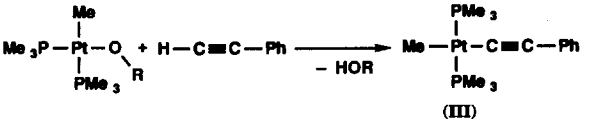

$$\mathrm{Me{-}Pd(PMe_3)_2{-}OR} + \mathrm{H{-}C{\equiv}C{-}Ph} \xrightarrow[-\,2\ \mathrm{HOR}]{} \mathrm{Me{-}Pd(PMe_3)_2{-}C{\equiv}C{-}Ph} \quad (2)$$

(II)

(R = CH(CF_3)Ph)

The structure of **II** was confirmed by NMR and IR spectra. The ^{1}H and ^{13}C{^{1}H} NMR spectra show the signals due to the methyl ligand as triplets. The PMe_3 signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra appear as apparent triplets due to virtual coupling [14]. All these data agree with a *trans* structure for the complex.

The platinum alkoxide complex, *cis*-PtMe(OCH(CF_3)$_2$)(PMe_3)$_2$, reacts with phenylacetylene to give the alkynyl complex, *trans*-PtMe(C≡CPh)(PMe_3)$_2$ (**III**) (eqn. (3)).


$$\mathrm{Me_3P{-}Pt(Me)(PMe_3){-}OR} + \mathrm{H{-}C{\equiv}C{-}Ph} \xrightarrow[-\,\mathrm{HOR}]{} \mathrm{Me{-}Pt(PMe_3)_2{-}C{\equiv}C{-}Ph} \quad (3)$$

(III)

(R = CH(CF_3)$_2$)

^{1}H and ^{13}C{^{1}H} NMR spectra of the complex **III**, showing signals of the PMe_3 hydrogens and carbons as apparent triplets due to virtual coupling, unambiguously indicate that the complex has *trans* configuration. The reaction (3) involves *trans–cis* isomerization. Since the starting *cis* alkoxide complex does not undergo transformation into the *trans* isomer [13c], the isomerization seems to have occurred during the reaction or after formation of *cis*-PtMe(C≡CPh)(PMe_3)$_2$. Carbonylation of *cis*-PtMe(OCH(CF_3)$_2$)(PMe_3)$_2$ giving *trans*-PtMe(COOCH(CF_3)$_2$)(PMe_3)$_2$ was reported to proceed through initial formation of the *cis* alkoxycarbonyl intermediate followed by its isomerization into the *trans* product [13c].

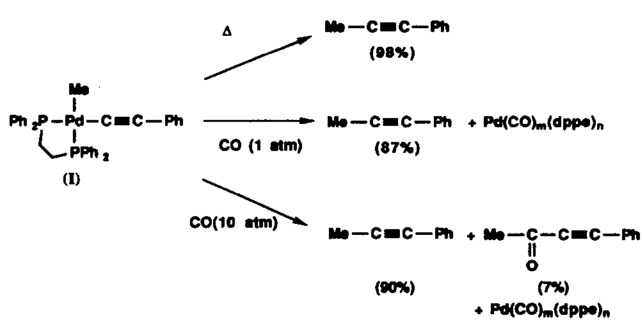
In the reactions (1–3) substitution of the alkoxide ligand by the alkynyl group occurred smoothly to give the alkynyl complexes. Insertion of the C≡C triple bond of the alkyne into the Pd–O and Pt–O bond was not observed at all, although facile insertion of olefin into the Pt–O and Pt–N bonding has been reported [15,16]. The methylpalladium and -platinum alkoxide complexes (I–III) did not undergo substitution of the methyl ligand by the alkynyl ligand even when excess phenyl acetylene was added.

Previously Bryndza, Bercaw and their co-workers reported that Cp*Ru(OH) (Cp* = pentamethylcyclopentadienyl) reacts with phenylacetylene to give the corresponding alkynyl complex [17]. They also established the reversibility of the reaction whose equilibrium is shifted towards the formation of the thermodynamically more stable alkynyl complex. Reaction of PdMe(OCH(CF_3)Ph)(PMe_3)$_2$ with phenol was reported to cause substitution of the alkoxide ligand giving $PdMe(OPh)(PMe_3)_2(HOCH(CF_3)Ph)$ rather than protonation of the methyl ligand [13b]. Also in the present reactions the alkoxide ligand underwent substitution by the alkynyl group.

2.2. Thermolysis and reaction with CO of the complexes I–III

Thermolysis of **I** gives methylphenylacetylene in 98% yield. Amounts of the other coupling products such as ethane and diynes are negligible. On the basis of these results the reaction seems to have proceeded through intramolecular reductive elimination. Thermolysis of complexes **II** and **III** also gives methylphenylacetylene in 98% and 97%, respectively. These complexes having *trans* configuration are considered to undergo a configurational change to give a *cis* intermediate prior to the C–C coupling reaction.

Reaction of **I** with CO at 1 atm gives methylphenylacetylene in 87% yield. The inorganic product was identified as a mixture of palladium carbonyl complexes based on the IR spectrum showing a broad band due to ν(CO) near 1700 cm^{-1} [18]. In the reaction CO seems to have promoted coupling of the methyl and alkynyl ligands at room temperature similarly to the previously reported coupling of the acylnickel carboxylate complexes [19]. Reaction of **I** with CO at 10 atm gives a mixture of methylphenylacetylene (90%) and methyl(phenylethynyl) ketone (7%). The latter product was formed through initial insertion of CO into a Pd–C bond [20] to give an acylpalladium intermediate which undergoes rapid reductive elimination of the product. The previous study on carbonylation of methylpalladium phenoxide complex showed that CO underwent insertion into the Pd–methyl bond at 10 atm [20d]. Since the Pd–alkynyl bond is stronger than the Pd–methyl bond, the reaction is considered to proceed through CO insertion into the Pd–methyl bond rather than into the Pd–alkynyl bond. Complex **III** does not react with CO at 1 atm. Scheme 1 summarizes these reactions of **I**.



Scheme 1. Reactions of alkynylpalladium complex.

3. Experimental section

All manipulations of the complexes were performed under a nitrogen or argon atmosphere using standard Schlenk techniques. $PdMe(OCH(CF_3)_2)(dppe)$, $PdMe(OCH(CF_3)Ph)(dppe)$, *trans*-$PdMe(OCH(CF_3)Ph)(HOCH(CF_3)Ph)(PMe_3)_2$, and *cis*-$PtMe(OCH(CF_3)_2(PMe_3)_2$ were prepared according to the literature [13].

Elemental analyses were carried out by Dr. Masako Tanaka of our laboratory with a Yanagimoto CHN autocorder, Type MT-2. NMR spectra were recorded on JEOL FX-100 and GX-500 spectrometers by Dr. Yoshiyuki Nakamura, Ms. Ryoko Ito, and Ms. Ayako Kajiwara of our laboratory. IR spectra were recorded on a JASCO IR-810 spectrophotometer.

3.1. Preparation of PdMe(C≡CPh)(dppe) (I)

To a THF (8 ml) solution of $PdMe(OCH(CF_3)_2)(dppe)$ (**I**) (330 mg, 0.48 mmol) was added phenylacetylene (140 mg, 1.35 mmol) by a syringe. The initially colourless solution turned red on stirring at room temperature. After reaction for 6 h, a pale brown solid was precipitated. The product was filtered, washed with pentane, and recrystallized from THF-pentane to give crystals of **I** (280 mg, 94%). IR: $\nu(C\equiv C)$ 2100 cm^{-1}. Anal. Found: C, 67.6; H, 5.3. Calcd. for $C_{35}H_{32}P_2Pd$: C, 67.7; H, 5.2%.

Reaction of phenylacetylene with $PdMe(OCH(CF_3)Ph)(dppe)$ also gave complex **I** in 90% yield.

3.2. Preparation of trans-PdMe(C≡CPh)(PMe$_3$)$_2$ (II)

To an Et_2O (8 ml) solution of *trans*-$PdMe(OCH(CF_3)Ph)(HOCH(CF_3)Ph)(PMe_3)_2$ (460 mg, 0.74 mmol) was added phenylacetylene (150 mg, 1.5 mmol). After stirring for 2 h at room temperature the reaction mixture was cooled at −70°C to yield yellow precipitates which were filtered and dried *in vacuo*. Recrystallization from Et_2O gave yellow crystals of **II** (210 mg, 76%). IR, $\nu(C\equiv C)$ 2100 cm^{-1}. Anal. Found: C, 47.6; H, 7.0. Calcd. for $C_{15}H_{26}P_2Pd$: C, 48.1; H, 7.0%.

3.3. Preparation of trans-PtMe(C≡CPh)(PMe$_3$)$_2$ (III)

To an Et_2O (3 ml) solution of *cis*-$PtMe(OCH(CF_3)_2(PMe_3)_2$ (170 mg, 0.32 mmol) was added phenylacetylene (60 mg, 0.64 mmol). After stirring for 24 h at room temperature the reaction mixture was cooled to −80°C to give colourless crystals which were filtered and dried *in vacuo*. Recrystallization from Et_2O gave crystals of **III** (110 mg, 74%). IR, $\nu(C\equiv C)$ 2100 cm^{-1}. Anal. Found: C, 38.6; H, 5.8. Calcd. for $C_{15}H_{26}P_2Pt$: C, 38.9; H, 5.7%.

3.4. Thermolysis of I, II, and III

A Schlenk flask containing a solution in diphenylmethane (2 ml) of complex **I** (60 mg, 0.097 mmol) was evacuated, and then heated at 150°C for 3 h. GLC analysis of the gaseous and liquid products using propane and mesitylene as internal standards showed formation of ethane (< 1%) and methylphenylacetylene (98%).

Thermolysis of **II** and **III** was carried out analogously to give methylphenylacetylene in 98 and 97% yields, respectively.

3.5. Reaction of CO with I

Complex **I** (100 mg, 0.16 mmol) was dissolved in THF (4 ml) at room temperature. After evacuation of the system, CO (1 atm) was introduced. The initially colourless reaction mixture gradually turned dark red. After stirring the mixture for 12 h GLC analysis showed the formation of methylphenylacetylene (87%).

Reaction of **I** (80 mg, 0.12 mmol) under 10 atm of CO was carried out in a stainless steel autoclave to give a mixture of MeC≡CPh (90%) and MeCOC≡CPh (7%), the latter of which was confirmed by GC-MS.

The platinum complex **III** does not react with CO (1 atm) at all.

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