Short Communication

Synthesis and characterization of $MCl(CH_2COY)(PPh_3)_2$ (M = Pd, Pt; Y = C_6H_5, CH_3, CH_2Cl)

Keinosuke Suzuki*
College of Medical Technology, Nagoya University, Daikominami 1 chome, Higashi, Nagoya 461 (Japan)

and Hisashi Yamamoto
Inorganic Chemistry Laboratory, Faculty of Science, Nagoya University, Chikusa, Nagoya 464 (Japan)

(Received December 1, 1992)

Abstract

Complexes of the type $MCl(CH_2COY)(PPh_3)_2$ (M = Pd, Pt; Y = C_6H_5, CH_3, CH_2Cl) were synthesized by the reaction of $M(PPh_3)_4$ with a corresponding organic chloride and characterized by ^1H NMR and IR spectra. These complexes were less stable than the cyanomethyl derivatives. Both of the palladium complexes **2** and **3** have the *trans* configuration in the solid state but exist as a mixture of *cis* and *trans* isomers in $CDCl_3$ solution. The platinum analogues were isolated as a *cis* isomer and retain their geometry in solution. The values of ^2J(Pt–H), ^4J(Pt–H) and ν(M–Cl) are related with the *trans* influence of the ligand *trans* to the CH_2COY group or Cl atom.

Introduction

Oxidative addition reactions of organic halides with low valent transition metal complexes such as $Pd(PPh_3)_4$ are one of the well known methods to prepare compounds containing a metal carbon σ-bond. Previously we reported the reaction of $ClCH_2CN$ with $M(PPh_3)_4$ (M = Pd, Pt) to yield the cyanomethyl complexes [1, 2]. These cyanomethyl complexes were found to be stable both in the solid state and in solution. In addition the palladium complex $PdCl(CH_2CN)(PPh_3)_2$ reacts with TlC_5H_5 to yield a cyclopentadienyl complex $Pd(\eta^5\text{-}C_5H_5)(CH_2CN)(PPh_3)$ [3]. These results prompted us to investigate other substituted methyl derivatives in order to examine the effect of the substituent on the properties of the complexes formed. This paper describes the synthesis and IR and ^1H NMR spectra of complexes of the type $MCl(CH_2COY)(PPh_3)_2$ (M = Pd, Pt; Y = C_6H_5, CH_3, CH_2Cl).

Experimental

All the required starting chlorides $ClCH_2COY$ were available commercially and were used without further purification. $Pd(PPh_3)_4$ [4] and $Pt(PPh_3)_4$ [5] were prepared by literature methods. All the reactions were carried out under nitrogen but subsequent workup was performed in air. IR spectra were recorded on JASCO DS-402G and HITACHI EPI-2L spectrometers. ^1H NMR spectra were recorded on a Jeol-C-60H or JNM-PMX60Si spectrometer with TMS as an internal standard. Elemental analyses were determined by Wako Pure Chemical Industries, Ltd.

Preparation of trans-$PdCl(CH_2COC_6H_5)(PPh_3)_2$ (1a)

A solution of $C_6H_5COCH_2Cl$ (0.30 g, 2.14 mmol) in acetone (30 ml) was added to a suspension of $Pd(PPh_3)_4$ (2.0 g, 1.73 mmol) in acetone (100 ml) with stirring at room temperature. The mixture was stirred overnight and the yellow precipitate was filtered, washed with diethyl ether and dried *in vacuo* (1.1 g, 81%). *Anal.* Found: C, 67.69; H, 4.69. Calc. for $C_{44}H_{37}OClP_2Pd$: C, 67.27; H, 4.74%.

Preparation of trans-$PdCl(CH_2COCH_3)(PPh_3)_2$ (2)

$Pd(PPh_3)_4$ (10.0 g, 8.63 mmol) was added to an acetone solution (500 ml) of freshly distilled $ClCH_2COCH_3$ (5 ml excess). The mixture was stirred for 1.75 h at 50 °C and the resulting precipitate was filtered, washed with diethyl ether and dried *in vacuo* (4.0 g, 64%). *Anal.* Found: C, 64.92; H, 4.78. Calc. for $C_{39}H_{35}OClP_2Pd$: C, 64.74; H, 4.88%.

Preparation of trans-$PdCl(CH_2COCH_2Cl)(PPh_3)_2$ (3)

1,3-$ClCH_2COCH_2Cl$ (0.22 g, 1.73 mmol) was added to a stirred suspension of $Pd(PPh_3)_4$ (2.0 g, 1.73 mmol) in acetone (100 ml). The mixture was stirred for 1.5 h at room temperature and then filtered. The filtrate was concentrated to *c.* 20 ml to precipitate a yellow product which was filtered, washed with diethyl ether and dried *in vacuo* (0.57 g, 44%). *Anal.* Found: C, 62.46; H, 4.87. Calc. for $C_{39}H_{34}OCl_2P_2Pd$: C, 61.84; H, 4.87%.

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

Preparation of cis-$PtCl(CH_2COC_6H_5)(PPh_3)_2$ *(4)*

A solution of $C_6H_5COCH_2Cl$ (0.30 g, 1.94 mmol) in benzene (20 ml) was added to a suspension of $Pt(PPh_3)_4$ (2.0 g, 1.60 mmol) in benzene (100 ml) with stirring at room temperature. After a few hours, the yellow precipitate was filtered, and washed with diethyl ether. Recrystallization from dichloromethane/diethyl ether gave yellow crystals containing 0.5 CH_2Cl_2 (1.13 g, 77%). *Anal.* Found: C, 57.75; H, 4.06. Calc. for $C_{45}H_{38}OCl_2P_2Pt$: C, 58.30; H, 4.17%.

Preparation of trans-$PtCl(CH_2COCH_3)(PPh_3)_2$ *(5a)*

A mixture of *cis*-$PtCl(CH_2COCH_3)(PPh_3)_2$ (0.20 g, 0.25 mmol) and PPh_3 (0.05 g, 0.19 mmol) was refluxed in benzene (50 ml) for 2 h. After filtration the solution was concentrated to *c.* 10 ml and diethyl ether (30 ml) was added dropwise with stirring to precipitate a yellow product which was filtered, washed with diethyl ether and dried *in vacuo*. The ^1H NMR spectrum gave only a triplet for the methylene protons but its far-IR spectrum showed the presence of *cis*-$PtCl_2(PPh_3)_2$ (*c.* 40%).

Preparation of cis-$PtCl(CH_2COCH_3)(PPh_3)_2$ *(5b)*

Freshly distilled $ClCH_2COCH_3$ (1 ml excess) was added to a suspension of $Pt(PPh_3)_4$ (2.0 g, 1.60 mmol) in benzene (150 ml). The mixture was stirred for 25 h at room temperature and filtered. The filtrate was concentrated to *c.* 40 ml *in vacuo* followed by dropwise addition of diethyl ether (100 ml) to precipitate a yellow product. The product was filtered, washed with diethyl ether and dried *in vacuo* (0.79 g, 60%). *Anal.* Found: C, 57.97; H, 4.37. Calc. for $C_{39}H_{35}OClP_2Pt$: C, 57.67; H, 4.34%.

Preparation of cis-$PtCl(CH_2COCH_2Cl)(PPh_3)_2$ *(6)*

1,3-$ClCH_2COCH_2Cl$ (0.24 g, 1.89 mmol) was added to a suspension of $Pt(PPh_3)_4$ (2.0 g, 1.60 mmol) in benzene (100 ml) with stirring. After stirring for 2 h at room temperature the solution was concentrated to *c.* 30 ml and diethyl ether was added dropwise with stirring. The precipitate was filtered, washed with diethyl ether and dried *in vacuo* (1.0 g, 62%). *Anal.* Found: C, 55.76; H, 4.05. Calc. for $C_{39}H_{34}OCl_2P_2Pt$: C, 55.33; H, 4.03%.

Results and discussion

Oxidative addition reactions of a molecule of $ClCH_2COY$ with $M(PPh_3)_4$ gave the substituted methyl complexes $MCl(CH_2COY)(PPh_3)_2$ with *cis* or *trans* configuration. These complexes could be handled in air in the solid state but in solution they were unstable and gradually decomposed. This instability made it difficult to recrystallize the complexes from organic solvents like CH_2Cl_2 or $(CH_3)_2CO$ because the recrystallization usually led to the formation of $MCl_2(PPh_3)_2$. This behaviour is especially pronounced for the palladium complexes and quite different from that of the cyanomethyl analogue. The ^1H NMR and IR spectra of the complexes are summarized in Tables 1 and 2.

$MCl(CH_2COC_6H_5)(PPh_3)_2$

The ^1H NMR spectrum of the palladium complex **1a** in $CDCl_3$ showed a triplet (δ 2.70 ppm) for the

TABLE 1. Selected ^1H NMR spectral data for the complexes[a]

Complex	M–CH_2			Others
	$\delta(CH_2)$	$^3J(PH)$	$^2J(Pt–H)$	
1a	2.70t	6.0		7.06[b]
1b	2.70t	6.0		7.06[b]
2	2.20t 2.87dd	6.0 13.0, 6.0		1.30s (CH_3 *trans*) 2.37s (CH_3 *cis*)
3	2.05t 2.83dd	7.5 12.0, 5.0		2.95s (CH_2Cl *trans*) 4.65s (CH_2Cl *cis*)
4	3.00dd	11.0, 5.0	79.0	7.06[b]
5a	2.16t	7.5	90.0	1.13s (CH_3) 10.0 {$^4J(Pt–H)$}
5b	2.70dd	12.0, 6.0	79.5	2.30s (CH_3) 6.0 {$^4J(Pt–H)$}
6	2.66dd	11.0, 5.0	81.0	4.53s (CH_2Cl) 7.5 {$^4J(Pt–H)$}

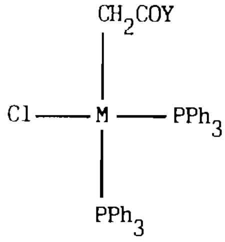
[a] Measured in $CDCl_3$; s = singlet, t = triplet, dd = doublet of doublets; δ in ppm with respects to $SiMe_4$; J in Hz. [b] See text.

TABLE 2. Selected IR spectral data (cm^{-1})[a]

Complex	$\nu(CO)$	550 ± 5[b]	$\nu(M–Cl)$
1a	1615vs	530m	280s
1b	1643vs (1621s)[c]	534vs	302m (333w)
2	1680s	537sh	265m
3	1670s	535sh	287m
4	1650vs (1633s)	548vs	306m (333w)
5a	1690s	b	276s
5b	1643s	547vs	298s (320w)
6	1684s	550vs	303s (323w)

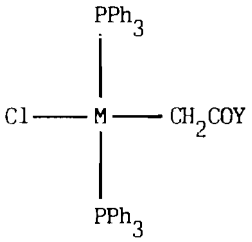
[a] Nujol mulls. [b] See text. [c] Absorptions in parentheses are observed but their assignment is uncertain. vs = very strong, s = strong, m = medium, w = weak.

methylene protons indicating its *trans* geometry. This triplet and a sharp resonance (δ 7.06 ppm) ascribable to some of the phenyl protons of the coordinated phenacyl group decreased in intensity with the concomitant appearance of a resonance (δ 2.61 ppm) assignable to the methyl protons of a newly formed actophenon. However the signals which indicate the existence of *cis*-$PdCl(CH_2COC_6H_5)(PPh_3)_2$ were not detected. The decomposition was complete after one day. The complex **1a** in the solid state also possesses the *trans* geometry which was determined by comparison of the IR spectrum of **1a** with that of **1b** discussed later. In contrast to **1a** the ^1H NMR spectrum of the platinum analogue **4** showed a doublet of doublets (δ 3.00 ppm) for the methylene protons indicating its *cis* geometry. In fact *trans*-$Pt(C_6H_5)(CH_2COC_6H_5)(PPh_3)_2$ prepared by heating *trans*-$Pt(C_6H_5)(OH)(PPh_3)_2$ with $CH_3COC_6H_5$ showed a triplet for the methylene protons as found in the ^1H NMR spectrum of **1a** [6]. The far-IR spectrum of **4** showed a strong band at 547 cm^{-1} which also supports its *cis* geometry because the band at 550 ± 5 cm^{-1} in the IR spectrum of $PtXY(PPh_3)_2$ is strong in *cis* complexes and weak in *trans* [7]. Thus complex **4** exists as a *cis* isomer in the solid state and in solution.



(cis)

	M	Y
1b	Pd	C_6H_5
4	Pt	C_6H_5
5b	Pt	CH_3
6	Pt	CH_2Cl



(trans)

	M	Y
1a	Pd	C_6H_5
2	Pd	CH_3
3	Pd	CH_2Cl
5a	Pt	CH_3

Although *cis*-$PdCl(CH_2COC_6H_5)(PPh_3)_2$ was not detected in $CDCl_3$ as mentioned above it is worthwhile to comment here that the compound **1b**, which is supposed to be *cis*-$PdCl(CH_2COC_6H_5)(PPh_3)_2$ on the basis of its IR spectrum (4000–200 cm^{-1}), was isolated only once under the same conditions as that used for the preparation of **1a** (*Anal.* for **1b**: C, 66.46, H, 4.72. Calc.: C, 67.27; H, 4.74%) and its IR spectrum was similar to that of **4** but quite different from that of **1a** as the selected spectral data given in Table 2 indicate, thus leading us to assign the *cis* geometry for **1b**. In particular, the appearance of a very strong absorption at 538 cm^{-1} is important because this band seems to correspond to the absorption which is characteristic for *cis*-$PtXY(PPh_3)_2$ and appears at 550 ± 5 cm^{-1} [7]. Interestingly its ^1H NMR spectrum in $CDCl_3$ resembles that of **1a** but the resonance due to the *cis* isomer was not detected again. This suggests that rapid isomerization of **1b** occurs when it is dissolved in $CDCl_3$. The comparison of ν(M–Cl) of **1a** (280 cm^{-1}) and **1b** (302 cm^{-1}) indicates that the *trans* influence of the phenacyl group is a little larger than that of PPh_3 in accord with the *trans* influence series found for the platinum complexes [8]. Although the isolation of the square planar complexes of palladium(II) with two PPh_3 in *cis* position is relatively rare, recently the crystal structure of *cis*-$Pd(C_6F_5)_2(PPh_3)_2$ has been reported [9]. A phenacyl complex of Ir(III) has been prepared by a quite different route, i.e. the reaction of phenyl oxide with $Ir(I)(PMe_3)_4Cl$ [10].

$MCl(CH_2COCH_3)(PPh_3)_2$

The ^1H spectrum of **5b** obtained from the reaction of $ClCH_2COCH_3$ with $Pt(PPh_3)_4$ in benzene showed a doublet of doublets for the methylene protons, thus indicating the *cis* geometry. The far-IR spectrum of **5b** exhibited a very strong band at 547 cm^{-1} which also supports the *cis* geometry as mentioned above. To obtain the corresponding *trans* isomer, **5b** was heated with PPh_3 in refluxing benzene. The ^1H NMR spectrum of the product showed a triplet for the methylene protons showing the formation of the expected *trans* isomer. However its far-IR spectrum showed absorption bands ascribable to *cis*-$PtCl_2(PPh_3)_2$ (550, 318, 298 cm^{-1}), together with the band at 270 cm^{-1} assignable to ν(Pt–Cl) of the *trans* isomer, thus indicating that the product is really a mixture of *trans*-$PtCl(CH_2COCH_3)(PPh_3)_2$ and *cis*-$PtCl_2(PPh_3)_2$. We failed to isolate the *trans* isomer in the pure state but the spectra of the product (mixture) allowed us to extract the ^1H NMR and IR spectral data of the *trans* isomer **5b** given in Tables 1 and 2. The intensity of the band at 550 ± 5 cm^{-1} for **5a** is uncertain because the product contains *cis*-$PtCl_2(PPh_3)_2$ which has a strong absorption at 550 ± 5 cm^{-1}. However if we use the bands at 318 and 298 cm^{-1} as internal standards for intensity comparison, we may suggest that the intensity of the band at 550 ± 5 cm^{-1} for **5a** is weak. The coupling constant ^2J(Pt–H) of **5a** (90.0 Hz) is larger than that of **5b** (79.5 Hz) as expected from the geometry of these complexes and the *trans* influence of PPh_3 and Cl because the ^2J(Pt–H) of the Pt–CH_2 bond is larger when the bond is *trans* to the ligand with a smaller *trans* influence [8]. The methyl protons of these two platinum complexes also coupled with the ^{195}Pt nucleus. The coupling constant $^4J(^{195}Pt–H)$ (10.5 Hz) of the *trans* isomer **5a** is larger than that (6.0 Hz) of the *cis* isomer **5b**. This result may indicate that ^4J(Pt–H) is also affected by the ligand *trans* to the Pt–CH_2 bond. The ν(Pt–Cl) (276 cm^{-1}) of the *trans* isomer **5a** is considerably lower than that of the *cis* isomer **5b** (303 cm^{-1}) indicating the larger *trans* influence of a carbon atom than that of a phosphorus atom [8].

The treatment of $Pd(PPh_3)_4$ with $ClCH_2COCH_3$ in acetone formed complex **2** whose IR spectrum resembles that of *trans*-$PtCl(CH_2COCH_3)(PPh_3)_2$ (**5a**) (Table 2) suggesting its *trans* geometry. However the ^{1}H NMR spectrum of **2** showed a doublet of doublets (δ 2.87 ppm) together with a triplet (δ 2.19 ppm) for the methylene protons and two singlets (δ 1.29, 2.37 ppm) for the methyl protons as shown in Fig. 1. This result clearly indicates the presence of an equilibrium mixture of *cis* and *trans* isomers in solution. Since the palladium complex **2** in the solid state seems to be the *trans* isomer alone, this result clearly demonstrates that the *trans* isomer **2** partially isomerized to the *cis* isomer although the *trans* isomer is still the major species. This is not surprising because some palladium complexes, which exist in only one form in the solid state, form a *cis–trans* equilibrium mixture in solution [11]. The ^{1}H NMR spectrum of **2** also showed a sharp singlet (δ 2.61 ppm) which is due to the formation of CH_3COCH_3 and gradually increased in intensity at the expense of the resonance due to the methyl and methylene protons of both *cis* and *trans* isomers. This spectral change also shows the instability of the palladium complex. The platinum analogue also decomposed in $CDCl_3$ but more slowly.

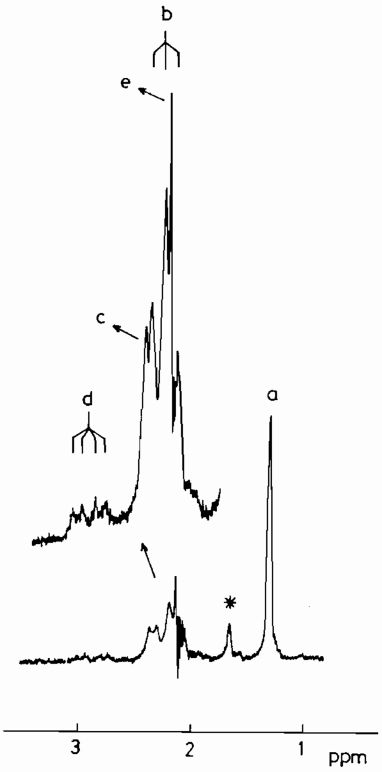


Fig. 1. ^{1}H NMR spectrum of $PdCl(CH_2COCH_3)(PPh_3)_2$ in deuterochloroform. Peak labelling: a = CH_3 (*trans*), b = Pd–CH_2 (*trans*), c = CH_3 (*cis*), d = Pd–CH_2 (*cis*), e = $(CH_3)_2CO$, * = H_2O.

$MCl(CH_2COCH_2Cl)(PPh_3)_2$

The reaction of $ClCH_2COCH_2Cl$ with $Pd(PPh_3)_4$ or $Pt(PPh_3)_4$ gave a result similar to those obtained for the acetonyl complexes: the palladium complex **3** is *trans* and the platinum analogue **6** is *cis* in the solid state. Again the ^{1}H NMR spectrum of **3** showed the existence of both *cis* and *trans* isomers. Although the resonance of Pd–CH_2 of the *cis* isomer partially overlapped with the CH_2Cl resonance of the *trans* isomer, its isomer ratio (*cis*/*trans*) was evaluated to be *c.* 1:1 in $CDCl_3$. Complex **3** is also unstable in solution and decomposed forming $ClCH_2COCH_3$ as shown by the appearance of two resonances (CH_3 δ 2.31 ppm, CH_2Cl δ 4.09 ppm). The methylene protons of the CH_2Cl group of **6** are also coupled to the ^{195}Pt nucleus as was observed for the acetonyl complex mentioned above (**5a**, **5b**). The ^4J(Pt–H) of **6** is similar in magnitude to that found for complex **5b**. This result supports the idea that the *trans* influence of the ligand *trans* to the Pt–CH_2 bond affects the value of $^4J(^{195}Pt–CH_2)$ as found in **5a** and **5b**. The *trans* isomer of Pt(II) was not obtained even when the *cis* isomer **6** was heated in refluxing benzene with excess of PPh_3.

ν(M–Cl)

A comparison of ν(Pd–Cl) indicates that the *trans* influence of the carbon ligands studied here decreases in the order $CH_2COCH_3 > CH_2COC_6H_5 > CH_2COCH_2Cl \sim CH_2CN$. The ν(Pt–Cl) for **4**, **5b** and **6** spans a narrow range, i.e. 298–306 cm^{-1}. This is probably due to the fact that the *trans* ligand to the Pt–Cl bond is always PPh_3.

References

1 K. Suzuki and H. Yamamoto, *J. Organomet. Chem., 54* (1973) 385.
2 K. Suzuki, H. Yamamoto and S. Kanie, *J. Organomet. Chem., 73* (1974) 131.
3 K. Suzuki and H. Hanaki, *Inorg. Chim. Acta, 20* (1976) L15.
4 D. R. Coulson, *Inorg. Synth., 13* (1972) 121.
5 R. Ugo, F. Cariati and G. La Monica, *Inorg. Synth., 11* (1968) 105.
6 T. Yoshida, T. Okano and S. Otsuka, *J. Chem. Soc., Dalton Trans.,* (1976) 993.
7 S. H. Mastin, *Inorg. Chem., 13* (1974) 1003.

8 T. G. Appleton and M. A. Bennett, *Inorg. Chem.*, *17* (1978) 738.

9 (a) K. Miki, N. Kasai and H. Kurosawa, *Acta Crystallogr., Sect. C, 44* (1988) 1132, and refs. therein; (b) R. Usón, J. Forniés, P. Espinet, F. Martinez and M. Tomás, *J. Chem. Soc., Dalton Trans.*, (1981) 463.

10 D. Milstein and J. C. Calabrese, *J. Am. Chem. Soc., 104* (1982) 3773.

11 A. T. Hutton and C. P. Morely, in G. Wilkinson, R. D. Gillard and J. A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Vol. 5, Pergamon, Oxford, 1987, pp. 1157–1170.