Nucleophilicity of (Oxodimethylenemethane)-palladium and -platinum Complexes and Derivatization to π-Allyl Complexes with Ester and Ether Functionality at 2-Position

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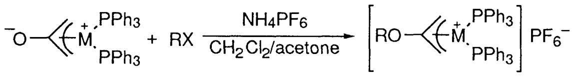
(Received November 6, 1995)

A novel kind of 2-oxy-substituted π-allyl palladium complexes as well as platinum complexes were synthesized by the reaction of the corresponding oxodimethylene-methane complexes with electrophiles such as acid halides and some organic halides. From these reactions, the correlation between electronic structure and nucleophilicity of the oxodimethylenemethane complexes was disclosed.

Oxodimethylenemethane transition metal complexes, including those of palladium and platinum,[1-3] are interesting in the structure, utilization to organic synthesis, and derivatization to new complexes. We have reported the novel synthesis and structure of the simplest (oxodimethylenemethane)-palladium and -platinum complexes.[2,3] As for the reactivities of these complexes, only acetonylidenation of strained olefins by [1+2] cycloaddition for palladium complex[2,4] and protonation at the 2-oxygen for these complexes of both metals have been reported.[2,5]

In this report, we investigated the nucleophilicity of these complexes and studied derivatization to novel π-allyl complexes having C-O bonding at its 2-position. Thus, we established synthetic method for the preparation of novel π-allyl complexes substituted with acyloxy or alkoxy moiety at its 2-position and disclosed the correlation of electronic structure and nucleophilicity beween the oxodimethylene-methane complexes. Only a few π-allyl platinum complexes with acyloxy or alkoxy group at the 2-position have been reported,[6] and nothing as for the corresponding palladium complex. Our method has another synthetic merit, since allyl halides substituted with acyloxy or alkoxy moiety at the 2-position, expected to react with Pd(0), are difficult to synthesize.

Complexes **1** reacted with electrophile such as acid halides and some kind of organic halides to afford esters or ethers. Thus, a CH_2Cl_2 solution of halides was added to a CH_2Cl_2 solution of oxodimethylenemethane complexes at room temperature. After 15 min, NH_4PF_6 in acetone was added to the mixture for anion exchange to afford precipitate of NH_4X (X = Cl, Br). The solution was evaporated to dryness and the residue was washed with hexane. The product was purified by recrystalization from dichloromethane/hexane.



1

2a: M = Pd, R = CH_3CO **5a**: M = Pd, R = Ts
2b: M = Pt, R = CH_3CO **5b**: M = Pt, R = Ts
3a: M = Pd, R = PhCO **6a**: M = Pd, R = $(PhO)_2PO$
3b: M = Pt, R = PhCO **6b**: M = Pt, R = $(PhO)_2PO$
4a: M = Pd, R = CH_3SO_2 **7a**: M = Pd, R = $PhCH_2$
4b: M = Pt, R = CH_3SO_2 **7b**: M = Pt, R = $PhCH_2$

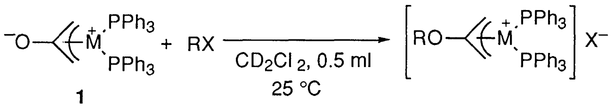
The synthesis of π-allyl complexes **2**-**7**[7] with acyloxy and alkoxy group at the 2-position is listed in the Table 1.

Table 1. π-Allyl complexes with ester and ether group at the 2-position

RX	M	Yield / %[a]			
		Pd		Pt	
MeCOCl		**2a**	56	**2b**	58
PhCOCl		**3a**	56	**3b**	65
$MeSO_2Cl$		**4a**	61	**4b**	69
TsCl		**5a**	61	**5b**	62
$(PhO)_2P(O)Cl$		**6a**	34	**6b**	46
$PhCH_2Br$[b]		**7a**	63	**7b**	66

[a] isolated yield. [b] see Ref. 8.

It is very interesting to clarify how the different bonding in the palladium and platinum complexes affects their nucleophilicity. The reaction rate with the acid chlorides, however, is too high to measure the differences between them. Chloromethyl ether also reacted with **1** very fast to afford an acetal derivative within 5 min, being tested in an NMR tube.[9]



25 °C

1
0.05 mmol 0.05 mmol RX = $PhCH_2OCH_2Cl$, $PhCH_2Br$

In the case of benzyl bromide, the reaction was slow enough to compare the reaction rates between **1a** and **1b**. Then the reaction was followed by ^1H NMR. The reactivity of **1a** was higher than that of **1b** as illustrated in Figure 1. Pseudo first order rate constants of this reaction were estimated to be 3.8×10^{-5} sec^{-1} and 6.7×10^{-6} sec^{-1} for **1a** and **1b**, respectively.[10]

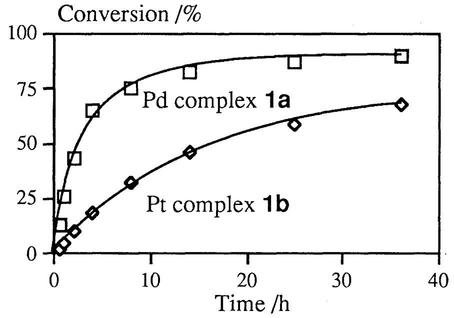


Figure 1. The reaction of oxodimethylenemethane complexes **1** (0.05 mmol) with benzyl bromide (0.05 mmol) in CD_2Cl_2 (0.5 ml) at 25 °C.

The difference of the reactivities reflected the difference in the bonding. The structures of oxodimethylenemethane complexes are contributed by metallacyclobutanone **A** and π-allylic **B** canonical forms, the latter of which has negative charge at oxygen atom. The palladium complex **1a** had a larger contribution of π-allylic character than the platinum complex **1b** in solution and crystalline states.[3]

A **B**

These complexes showed basicity, being stronger for **1a** than **1b** reflecting the larger contribution of **B** for palladium complex **1a** compared with **1b**.[2,3] In other words, palladium complex **1a** was more nucleophilic than platinum complex **1b**, showing larger contribution of π-allylic structure **B** for **1a** than **1b** as one of probable main reasons.

In conclusion, clarified was the relationship between the electronic structure and the nucleophilicity of oxodimethylenemethane complexes and also established was a synthetic method for the preparation of novel π-allyl transition metal complexes substituted with an acyloxy or an alkoxy group at the 2-position.

This work was supported by Grants-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236104 from the Ministry of Education, Science, and Culture of Japan.

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7 Melting point (°C), IR (cm^{-1}), and ^{1}H, ^{31}P (85% H_3PO_4 aq. as an external reference) NMR (600, 162 MHz, $CDCl_3$, 25 °C) data are as follows: **2a**: mp 174 (dec.); ν(CO) 1770; δ = 7.38, 7.30-7.23, 3.66 (CH_2), 3.57 (CH_3), 2.22 (CH_2) ppm; δ = 24.3, -143.6 ppm. **2b**: mp 203 (dec.); ν(CO) 1775; δ = 7.38, 7.31-7.24, 3.45 (CH_3), 3.12 (CH_2), 2.24 (CH_2) ppm; δ = 16.3, -143.6 ppm. **3a**: mp 182 (dec.); ν(CO) 1740; δ = 8.04, 7.76, 7.60, 7.38, 7.29-7.23, 3.81 (CH_2), 3.75 (CH_2) ppm; δ = 24.4, -143.6 ppm. **3b**: mp 211 (dec.); ν(CO) 1735; δ = 8.04, 7.77, 7.60, 7.37, 7.30-7.24, 3.65 (CH_2), 3.28 (CH_2) ppm; δ = 16.6, -143.7 ppm. **4a**: mp 174 (dec.); δ = 7.39, 7.30-7.15, 3.74 (CH_2), 3.68 (CH_2), 3.21 (CH_3) ppm; δ = 24.7, -143.7 ppm. **4b**: mp 222 (dec.); δ = 7.38, 7.33, 3.28-3.24 (CH_2, CH_3) ppm; δ = 16.8, -143.7 ppm. **5a**: mp 188 (dec.); δ = 7.65, 7.38, 7.34, 7.29-7.23, 3.58 (CH_2), 3.54 (CH_2), 2.45 (CH_3) ppm; δ = 24.9, -143.7 ppm. **5b**: mp 195 (dec.); δ = 7.66, 7.39, 7.33, 7.31-7.15, 3.40 (CH_2), 3.24 (CH_2), 2.44 (CH_3) ppm; δ = 16.9, -143.7 ppm. **6a**: mp 200 (dec.); δ = 7.35-7.33, 7.27-7.20, 7.12, 3.75 (CH_2), 3.71 (CH_2) ppm; δ = 24.7, -19.3 (P(OPh)), -143.6 ppm. **6b**: mp 207 (dec.); δ = 7.39-7.33, 7.29-7.21, 7.14, 3.56 (CH_2), 3.26 (CH_2) ppm; δ = 16.0, -19.9 (P(OPh)), -143.6 ppm. **7a**: mp 185 (dec.); δ = 7.43-7.35, 7.28-7.19, 4.57 (CH_2Ph), 3.36 (CH_2), 3.23 (CH_2) ppm; δ = 25.4, -143.7 ppm. **7b**: mp 215 (dec.); δ = 7.42-7.37, 7.28-7.21, 4.64 (CH_2Ph), 3.18 (CH_2), 3.23 (CH_2) ppm; δ = 17.4, -143.7 ppm. Satisfactory elemental analysis (C, H) for **2**-**7** has been obtained. All complexes were also characterized by ^{13}C NMR.

8 Complexes **7** were prepared by the reaction between **1** and large excess (100 eq.) of benzyl bromide.

9 ^{1}H NMR (CD_2Cl_2, 600 MHz, 25 °C).
$[M(\eta^3\text{-}CH_2C(OCH_2OCH_2Ph)CH_2)(PPh_3)_2]Cl$: M = Pd; δ = 7.46-7.39, 7.31-7.17, 4.97 (CH_2Ph), 3.53 (CH_2), 2.87 (CH_2) ppm. M = Pt; δ = 7.45-7.37, 7.28-7.19, 4.99 (CH_2Ph), 3.34 (CH_2), 2.51 (CH_2) ppm.
$[M(\eta^3\text{-}CH_2C(OCH_2Ph)CH_2)(PPh_3)_2]Br$: M = Pd; δ = 7.54-7.19, 4.72 (CH_2Ph), 3.52 (CH_2), 3.05 (CH_2) ppm. M = Pt; δ = 7.41-7.17, 4.66 (CH_2Ph), 3.21 (CH_2), 2.86 (CH_2) ppm.

10 Reaction conditions for measurement of pseudo first order rate constants in ^{1}H NMR: Complex **1** (0.05 mmol), $PhCH_2Br$ (0.5 mmol), CD_2Cl_2 (0.5 ml) at 25 °C.