A Novel Synthesis of (Oxodimethylenemethane)-palladium and -platinum Complexes

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Treatment of π-allyl-palladium and -platinum complexes bearing a methoxymethoxy group at the 2-position with base give the corresponding oxodimethylenemethane complexes, in contrast to the formation of 2-hydroxy-substituted π-allyl complexes *via* acidic hydrolysis.

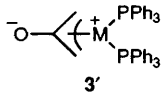
Functionalization of π-allylpalladium intermediates is envisaged to widen their synthetic utility. The π-allyl complex **2a** bearing an acetal function, methoxymethoxy group, at the 2-position seems to possess versatile reactive sites. This complex has been considered to be involved as a reaction intermediate in the catalytic allylation step in the acetonylation process using **1**.[1] We describe herein a novel and efficient synthesis of the oxodimethylenemethane complexes **3** from the palladium and platinum complexes **2**. Complex **3** is known to be the oxygen analogue of the trimethylenemethane complexes,[2] which have a high synthetic potential.

The π-allylpalladium complex **2a** was readily prepared as shown in Scheme 1. Treatment of this palladium complex **2a** with KOH–propan-2-ol at room temperature resulted in unexpected bond cleavage of the acetal moiety to give the oxodimethylenemethane complex **3a** (44% yield). Variable temperature ^{1}H NMR (400 MHz, $CDCl_3$) of **3a** showed the coalescence of methylene proton resonances at a higher temperature, 29 °C, compared with −20 °C for **3b**,† showing that the interconversion of the metallacyclobutanone ring of **3a** is slower than that of **3b**. Thus, palladacyclobutanone **3a** should be considered to have the higher contribution of the π-allylic canonical structure **3′** than the platinum analogue.[3]

It should be noted that this is the first case of the preparation of the unsubstituted parent (oxodimethylenemethane)palladium complexes.[4] The isolated complex **3a** reacted with an equivalent amount of norbornadiene to afford 3-acetyltricyclo[3.2.1.0^{2,4}]oct-6-ene quantitatively, supporting the fact that **3a** is proposed to be a reaction intermediate in the Pd(0)-catalysed cyclization of 1-acetoxy-3-(trimethylsilyl)propan-2-one and norbornadiene.[5]

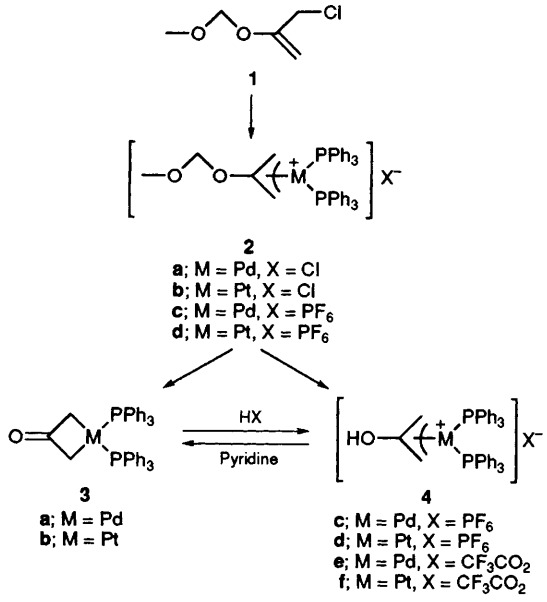
A similar reaction of **2b** with NaOH(aq.) led to the formation of the (oxodimethylenemethane)platinum complex **3b** in 93% yield.[3]

Complex **3a** in moistened organic solvent showed basicity *viz.* proton acceptability. The basicity of **3a**, pH = 9.7 (0.01 mmol in H_2O–acetone = 0.1 ml : 0.9 ml), was stronger than that of **3b** (pH = 8.6) under the same conditions. This result may support the above-mentioned assumption concerning the higher contribution of the allylic canonical structure in **3a** than in **3b**. Protonation of **3** with trifluoroacetic acid resulted in the formation of the novel 2-hydroxy-substituted π-allyl complexes **4e** and **f**.



3′

† Coalesced at −78 °C in [$^2H_8$]THF (400 MHz), see ref. 3.



Scheme 1 *Reagents and conditions*: for **2a** : **1** (1 equiv.), $Pd_2(dba)_3$ (0.4 equiv.), PPh_3 (2.1 equiv.) CH_2Cl_2–acetone (*in situ*), 20 °C; for **2b**: $Pt(PPh_3)_4$ (0.8 equiv.), C_6H_6, 20 °C; for **2c,d** : **2a,b** (1 equiv.), NH_4PF_6 (1.1 equiv.), CH_2Cl_2–acetone, 20 °C; for **3a** : **2a** (1 equiv.), 0.1 mol dm^{-3} KOH–Pr^iOH (1.1 equiv.), CH_2Cl_2–acetone, 20 °C; for **3b** : **2b** (1 equiv.), 0.1 mol dm^{-3} NaOH (aq.) (1.1 equiv.), tetrahydrofuran (THF), 20 °C; for **4c,d** : **2c,d** (1 equiv.), 60% HPF_6 (aq.) (excess), CH_2Cl_2, 20 °C; for **4e,f** : **3a,b** (1 equiv.), CF_3CO_2H (excess), CD_2Cl_2, 20 °C; (H_4dba = dibenzylideneacetone)

Complexes **4c** and **d** were prepared by acidic hydrolysis of the π-allyl complexes **2c** and **d**, respectively. Complexes **3** and **4** are intertransferable because the regeneration of **3** was achieved by treatment of **4c** and **d** with pyridine.

In summary, complexes **2** showed high reactivity under both basic and acidic conditions to provide an efficient route to unsubstituted oxodimethylenemethane and 2-hydroxy π-allyl complexes.‡

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‡ Satisfactory elemental analysis (C, H, Cl) for **2c**, **3a**, **3b** and **4c** was obtained.

Melting point (°C) and ^1H NMR data [600 MHz, solvent $CDCl_3$ (unless stated otherwise), 25 °C] are as follows: **2b**; m.p. 228–232 (dec.); δ 3.03 (br, 2H, *syn*-CH_2C), 3.30 (s, 2H, *anti*-CH_2C), 3.42 (s, 3H, OCH_3), 4.94 (s, 2H, OCH_2O), 7.28 (m, 24H, *o,m*-Ph), 7.38 (t, 6H, *p*-Ph). **2c**: m.p. 200–204 (dec.); δ 3.22 (m, 2H, *syn*-CH_2C), 3.44 (s, 2H, *anti*-CH_2C), 3.38 (s, 3H, OCH_3), 4.88 (s, 2H, OCH_2O), 7.24 (m, 24H, *o,m*-Ph), 7.38 (t, 6H, *p*-Ph). **2d**: m.p. 196–201 (dec.); δ 2.75 (dd, 2H, $^2J_{PtH}$ 42, $^3J_{PH}$ 9.1, $^2J_{HH}$ 4.8 Hz, *syn*-CH_2C), 3.27 (d, 2H, $^2J_{HH}$ 4.8 Hz, *anti*-CH_2C), 3.42 (s, 3H, OCH_3), 4.92 (s, 2H, OCH_2O), 7.28 (m, 24H, *o,m*-Ph), 7.38 (t, 6H, *p*-Ph). **3a**: m.p. 165–175 (dec.); δ 2.40 (br, 2H, *syn*-CH_2), 2.80 (br, 2H, *anti*-CH_2), 7.20 (m, 24H, *o,m*-Ph), 7.28 (t, 6H, *p*-Ph); δ (30 °C) 2.58 (br, 4H, CH_2). **3b**: m.p. 222–226 (dec.); δ 2.35 (d, 4H, $^2J_{PtH}$ 48, $^3J_{PH}$ 3.0 Hz, CH_2), 7.18 (t, 12H, *m*-Ph), 7.27 (m, 18H, *o,p*-Ph). **4c**: m.p. 173–193 (dec.); δ (CD_2Cl_2) 2.68 (m, 2H, *syn*-CH_2), 3.40 (s, 2H, *anti*-CH_2), 7.20 (dd, 12H, *o*-Ph), 7.26 (t, 12H, *m*-Ph), 7.38 (t, 6H, *p*-Ph). **4d**: m.p. 180–185 (dec.), δ (CD_2Cl_2) 2.30 (dd, 2H, $^2J_{PtH}$ 46, $^3J_{PH}$ 10, $^2J_{HH}$ 4.3 Hz, *syn*-CH_2), 3.24 (d, 2H, $^2J_{HH}$ 4.3 Hz, *anti*-CH_2), 7.24 (m, 24H, *o,m*-Ph), 7.36 (t, 6H, *p*-Ph). **4e**: δ (CD_2Cl_2) 2.62 (m, 2H, *syn*-CH_2), 3.45 (s, 2H, *anti*-CH_2), 7.20 (dd, 12H, *o*-Ph), 7.28 (t, 12H, *m*-Ph), 7.38 (t, 6H, *p*-Ph). **4f**: δ (CD_2Cl_2) 2.45 (dd, 2H, $^2J_{PtH}$ 46, $^3J_{PH}$ 10, $^2J_{HH}$ 4.3 Hz, *syn*-CH_2), 3.15 (d, 2H, $^2J_{HH}$ 4.3 Hz, *anti*-CH_2), 7.22 (dd, 12H, *o*-Ph), 7.26 (t, 12H, *m*-Ph), 7.40 (t, 6H, *p*-Ph).

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