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Trimethylsilyldiazomethane as a diazomethane equivalent in the synthesis of $(\alpha$ -halomethyl)platinum(II) complexes

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Abstract

The reaction between $[PtX_2L_2]$ (X = Cl, Br, I; $L_2 = 1,5$ -cyclo-octadiene (cod), 2PPh₃, 2PMePh₂, Ph₂PCH₂CH₂PPh₂, S,S-Ph₂PCHMeCH₂CHMePPh₂ (S,S-skewphos)) and an excess of Me₃SiCHN₂ in a CH₂Cl₂/Me₂CO/H₂O solvent mixture gives the complexes $[Pt(CH_2X)_2L_2]$. When $[PtX_2(cod)]$ is treated with Me₃SiCHN₂ in a CH₂Cl₂/Me₂CO/D₂O solvent mixture, the complexes $[Pt(CHDX)_2(cod)]$ are formed exclusively. The mechanism of these reactions is discussed.

Keywords: Diazoalkane; Platinum complexes; Halomethyl complexes

1. Introduction

Halogenomethyl complexes of transition metals have attracted attention because they can be used as precursors to other organometallic complexes containing M-CH2OH, M-CH₂OR, M-CH₂PR₃, M=CH₂ or M-CH₂-M [1]. The insertion of the CH2 group derived from CH2N2 into Pt-X bonds is the conventional route to Pt-CH₂X complexes [2,3] but this suffers from the disadvantage of requiring the use of the potentially hazardous diazemethane [4]. Trimethylsilyldiazomethane [5] is routinely used as a safe CH₂N₂ equivalent for many organic transformations [6] but it has rarely been used in this way in organometallic chemistry [7]. In this paper we show that Me₃SiCHN₂ can replace CH₂N₂ in the synthesis of (a-halomethyl)platinum(II) complexes. A preliminary account of some of this work has appeared [8] and some of the compounds synthesised by our new route have been previously prepared by McCrindle et al. [3] or us [2].

2. Results and discussion

We [8,9] and others [10] have previously reported that the reaction of $[PtX_2L_2]$ (X = Cl, Br, I; L_2 = 1,5-cyclo-octadiene (cod) or diphosphine) with an excess of Me₃SiCHN₂ in CH₂Cl₂ gives the chiral mono-insertion products [PtX(CHXSiMe₃)L₂] and when L₂ is an optically active diphosphine, a pair of diastercoisomers is obtained, see Eq. (1). During our experiments with [PtCl₂(S,S-skewphos)], we noticed that in the presence of aqueous acetone the complex [Pt(CH₂Cl)₂(S,S-skewphos)] (1) was formed, as shown by elemental analysis (Table 1), NMR spectroscopy (Tables 2–4) and X-ray crystallography [8]. We have now extended this procedure to the synthesis of other phosphine halomethyl complexes 2, 3 and 4a–c, see Eq. (2).

	с	н		
1	50.40 (50.70)	4.85 (4.65)		
2	48.15 (48.45)	4.27 (4.35)		
3	55.50 (55.75)	4.25 (4.20)		
4a	47.75 (48.60)	4.05 (4.10)		
4b	40.35 (40.20)	3.25 (3.45)		
4c	38.10 (38.40)	3.25 (3.20)		
5a	30.17 (29.90)	3.92 (4.00)		
5b	24.50 (24.45)	3.30 (3.30)		
5c	20.65 (20.55)	2.75 (2.75)		
5a'	29.75 (29.70)	4.15 (4.45)		
5b'	24.45 (24.35)	3.20 (3.70)		
5c'	21.00 (20.45)	3.00 (3.10)		
6+7°	47.90 (47.80)	3.89 (3.85)		

* Calculated values in parentheses.

b These isomers were not separated.

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Table 2 Selected ¹H NMR data ^a

	$\delta(CH-Pt)$	² J(PtH)	J(PH)	Cod resonances b
1	3.68 °	45.5	7.8	
	3.54	44.8	7.8	
2	3.66	43.5	8.7	
3 ª	3.68	44.5	8.9	
4a ^d	3.96	48.4	7.4, 2.8	
4b	3.72	40.1	8.6, 1.5	
4c	3.05	34.9	8.8	
5a °	3.83	60.0		5.34 (42.3), 2.48
				(17.6)
5Ъ °	3.62	48.4		5.32 (41.7), 2.51
				(17.4)
5c	2.96	43.4		5.25 (40.6), 2.53
				(17.2)
5a'	3.82	60.2		5.35 (41.9), 2.48
				(17.5)
5b′	3.60	48.5		5.32 (41.7), 2.50
				(17.4)
5c'	2.93	43.5		5.25 (40.7), 2.53
				(17.1)
6	4.35	48.6	7.2	• •
7	4 10	49.2	6.5	

^a Spectra measured in CDCl₃. Chemical shifts in ppm (± 0.01) to high frequency of Si(CH₃)₄; coupling constants in Hz (± 0.1).

^b The data for the vinylic protons (given first) and allylic protons; chemical shifts are followed by J(PtH) in brackets.

^c The CH₂ protons are diastereotopic ²J(HH) 7.8 Hz.

^d The data agree with the values given in Ref. [3].

* The data agree with the values given in Ref. [11].



The complexes $[Pt(CH_2X)_2(cod)]$ are useful intermediates to a variety of phosphine complexes $[Pt(CH_2X)_2L_2]$ where L_2 is a diphosphine or two monophosphines [2,11]. We have found that treatment of $[PtX_2(cod)]$ with Me₃SiCHN₂ in a mixture of CH₂Cl₂/Me₂CO/H₂O (3:1:1 by volume) gives [Pt(CH₂X)₂(cod)], where X = Cl (5a), Br (5b) or I (5c), as the only platinum-containing products, see Eq. (2).

The complexes **4a** [11] and **4b** have been made also by treatment of **5a** or **5b** with dppe, see Eq. (3). Treatment of **5a** with dppm gave the two products **6** and **7** in the ratio 1:4. From its ³¹P NMR spectrum, the minor product was identified as the expected four-membered chelate **6** which we have previously described [2]. The major product is assigned the isomeric five-membered chelate structure **7** (Eq. (4)) on the basis of its characteristic ³¹P NMR spectrum (Table 4).



We propose the mechanism shown in Scheme 1 to explain the formation of products $1-5^1$. The five-coordinate platinum-carbene species A are the proposed intermediates in the reactions of Me₃SiCHN₂ with dihaloplatinum(II) complexes (step i). The hydrodesilylation of A by water to give B (step ii) is the critical step in the mechanism: this is shown in Scheme 1 as a concerted addition of H-OH to the Si-C bond via C but may equally proceed by sequential addition of H⁺ and OH⁻. Migration of the halo ligand to the CH₂ ligand (step iii) completes the transformation of Pt-X to PtCH₂X.

The above mechanism is supported by the following observations. (a) When the reaction shown in Eq. (5) was carried out in a CH₂Cl₂/Me₂CO/D₂O solvent mixture, the products are specifically di-deuterated, [Pt(CHDX)₂(cod)] (5a'c'). The complexes 5a'-c' have been fully characterised (Tables I-3) and the ¹³C spectra are particularly informative; for example, in the ¹³C NMR spectrum of 5a' (see Fig. 1), the PtCHDCl signals are 1:1:1 triplets due to coupling to a

¹ Previously McCrindle and McAlees [10] detected small quantities of 5a when [PCI(CHCISiMe₉)(cod)] was treated with N₂CHSiMe₉ and they postulated a mechanism involving the attack of adventitious water on a carbene intermediate to explain this.



Scheme 1. Proposed mechanism for the hydrodesilylation (see text for discussion of steps i-vii).



Fig. 1. ¹³C NMR spectrum (50.3 MHz) of [Pt(CHDCl)₂(cod)] (**5a**') in CDCl₃ with expansions showing: (i) the two alkenyl signel⁴ of the coordinated cod with ¹⁹⁵Pt satellites; (ii) the PtCHDCl signal at 42.1 ppm with one of the ¹⁹⁵Pt satellites (the other is partly masked by an impurity having resonances around 32 ppm).

	δ(PtCH)	¹ J(PtC)	¹ J(DC)	δ(<i>C</i> H= <i>C</i> H)	J(PtC)	δ(CH ₂ CH=CH)
5a ^b	42.5	992		105.6	68.0	30.0
5b ^b	30.0	1018		105.9	65.9	30.2
5c	-1.5	1017		104.5	64.6	30.7
5a'	42.1	990	23	105.67 °	67.5	30.4
				105.61	67.8	
5b'	29.7	1016	23	105.89 ^b	65.5	30.4
				105.91	65.5	
5c′	-1.8	1014	23	104.5	64.5	31.2

Table 3 ¹³C NMR data for the cod complexes *

^a Spectra measured in CDCl₃. Chemical shifts in ppm (± 0.1) to high frequency of Si(CH₃)₄; coupling constants in Hz (± 0.1).

^b The data agree with the values given in Ref. [3].

^c Two closely similar signals observed (see Fig. 1 and text).

Table 4

31P NMR data *

	δ(Ρ)	J(PtP)
1	14.06	1847
2	3.73	1925
3 ^h	24.03	1973
4a ^b	43.60	1894
4Ь	43.06	1912
4c	44.50	1971
6	- 33.15	1673
7°	12.56 (54)	2372
	45.13	54

^a Spectra measured in CDCl₃. Chemical shifts in ppm (± 0.1) to high frequency of 85% H₃PO₄; coupling constants in Hz (± 1).

^b The data agree with the values given in Ref. [3].

^c Two $\delta(P)$ values for 7; the first is for the P coordinated to Pt with J(PP) in brackets.

single ²H and there are two signals observed for the alkenyl carbons, consistent with the presence of two diastereoisomers of 5a' (arising from the RR/SS and RS configurations at the a-carbons). This labelling experiment confirms that water is the source of the H in the reaction and is consistent with step ii in Scheme 1. (b) The presence of (Me₃Si)₂O was detected by GC/MS in the product reaction mixture, as predicted [12] in step iv of Scheme 1. (c) In the absence of acetone, the only platinum-containing product observed by ³¹P NMR spectroscopy was [PtX(CHXSiMe₁)(cod)] (step v) and thus the role of acetone is probably to increase the concentration of water in the solution of the platinum complex. (d) Me₃SiCHN₂ remains unchanged (¹H NMR evidence) when treated with the aqueous acetone/dichloromethane mixture showing that, in the absence of the platinum complex, free CH₂N₂ is not generated in detectable quantities under the reaction conditions used. (e) 5a is the only platinum-containing product from the reaction of [PtCl(CH₂Cl)(cod)] with Me₃SiCHN₂ in aqueous acetone/dichloromethane showing that [PtCl(CH2Cl)(cod)] could be an intermediate in the reaction (step vi), (f) [PtCl(CHClSiMe₂)(cod)] remains unchanged when treated with the aqueous acetone/ dichloromethane mixture even under reflux (or in the presence of NaF or LiF, Section 3) showing that $[PtCl(CHClSiMe_3)(cod)]$ is not an intermediate in the reaction (step vii).

In conclusion, chloromethylplatinum(II) complexes can be conveniently made using commercially available Me_3SiCHN_2 in place of CH_2N_2 via a hydrodesilylation reaction effected by water.

3. Experimental

All reactions were carried out in air. The phosphines and Me₃SiCHN₂ solution were used as purchased from Aldrich. The complexes $[PtX_{2L_2}]$ (L_2 =dppm, dppe, S_s -skewphos, 2PPh₃, 2 PMePh₂) were made by substitution of cod from $[PtX_2(cod)]$ [13]. ³¹P{¹H} (81 MHz), ¹³C{¹H} (50 MHz) and ¹H (200 MHz) spectra were measured using a Bruker AM200 spectrometer at 22 °C. GC/MS was performed using a Hewlett Packard 5889E GC (capillary column 5% diphenyl–95% dimethyl-polysiloxane) and a Hewlett Packard 5989B mass spectrometer.

3.1. Preparation of [Pt(CH₂Cl)₂(S,S-skewphos)](1)

A 2 M hexane solution of Me₃SiCHN₂ (0.425 cm³, 0.85 mmol) was added dropwise over 2 min to [PtCl₂(*S*,*S*-skewphos)] (60 mg, 0.085 mmol) dissolved in a biphasic mixture of CHCl₃ (1.5 cm³), Me₂CO (0.6 cm³) and H₂O (0.6 cm³) and the mixture rapidly stirred. After 3 h, water (10 cm³) and CHCl₃ (10 cm³) were added and then the organic layer was separated, dried over Na₂SO₄, filtered and then reduced to dryness to give the crude product (58 mg, 93%). Recrystaliisation was performed by layering a CH₂Cl₂ solution with Et₂O. The complexes 2, 3 and 4c were made similarly in yields of over 90% (see Tables 1–4 for characterising data).

3.2. Preparation of [Pt(CH₂X)₂(cod)] (5a-c)

A 2 M hexane solution of Me_3SiCHN_2 (0.50 cm³, 1.0 mmol) was added dropwise over 2 min to [PtX₂(cod)] (0.2 mmol) dissolved in a biphasic mixture of CH₂Cl₂ (6 cm³),

Me₂CO (2 cm³) and H₂O (2 cm³) and the mixture rapidly stirred. The solution darkened and gas was evolved for a few minutes. (A small aliquot of the solution ($\sim 0.5 \text{ cm}^3$) was dried over MgSO₄ and then analysed by GC/MS and hexamethyldisiloxane was identified by comparison with a genuine sample; characteristic peaks (EI) at m/z 147 $[M - CH_3]^+$; 73 $[Me_3Si]^+$). After 2 h, the volatiles were stripped off and then CH₂Cl₂ (20 cm³) added. The solution was dried over Na₂SO₄, filtered and then reduced to dryness to give an oil (X = Cl, 92%) or solid (X = Br, 92%; X = I,83%). The identity and purity of the products were confirmed by ¹H NMR spectroscopy and elemental analysis (see Tables 1 and 3). The isotopomers [Pt(CHDX)₂(cod)] (5a', 5b', 5c') were made in the same way (all in \sim 90% yield) using D₂O in the place of H₂O. Complex 5a was also made from [PtCl(CH₂Cl)(cod)] as follows. A solution of [PtCl(CH₂Cl)(cod)] (40 mg, 0.10 mmol) in a mixture of CH_2Cl_2 (3 cm³), Me₂CO (1 cm³) and H₂O (1 cm³) was treated with Me₃SiCHN₂ in n-hexane (0.25 cm³, 0.5 mmol) and worked up as above to yield 32 mg, 80% of 5a.

3.3. Preparation of [Pt(CH2Cl)2(dppe)] (4a)

A solution of dppe (45 mg, 0.124 mmol) in CH₂Cl₂ (3 cm³) was added dropwise to a solution of [Pt(CH₂Cl)₂(cod)] (5a) (50 mg, 0.124 mmol) in CH₂Cl₂ (3 cm³) and the mixture was stirred for 30 min. The solvent was then evaporated to give a white solid product 4a (82 mg, 96%) which was triturated with MeOH (5 cm³) and then filtered off. The following were made similarly from the appropriate [Pt(CH₂X)₂(cod)] (5a or b) and ligand in the indicated yields: 4b (75%), 6 and 7 (1:4 mixture) (70%).

3.4. Attempted hydrolysis of [PtCl(CHClSiMe_3)(cod)]

[PtCl(CHClSiMe₃)(cod)] (50 mg, 0.10 mmol) was dissolved in a mixture of CH₂Cl₂ (6 cm³), Me₂CO (2 cm³) and H₂O (2 cm³) and refluxed for 5 h. The reaction mixture was then worked up as above and the starting material was recovered unchanged (40 mg, 80%). We also attempted to promote desitylation by performing similar reactions in the presence of LiF (2 mmol, 20 equiv.), or NaF and 18-crown-6 (0.5, 5 equiv.), but in each case the complex [PtCl(CHClSiMe₃)(cod)] was recovered unchanged and in high yield.

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