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Preliminary Communication

η^3-Azatrimethylenemethane complexes of platinum. Structural characterization of $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(4\text{-}NC_6H_4NO_2)CHPh)$ ☆

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Abstract

η^3-Azatrimethylenemethane complexes of platinum, $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(NR)CHPh)$ (**1a**,**b**: R = $4\text{-}NO_2C_6H_4$ (**a**), $4\text{-}MeC_6H_4$ (**b**)), are conveniently prepared by reaction of $(PPh_3)_2Pt(C_2H_4)$ with RNH_2 and $PhC{\equiv}CCH_2OTs$ (Ts = $4\text{-}MeC_6H_4SO_2$) in CH_2Cl_2 at 0–25 °C, followed by deprotonation of the resulting η^3-2-aminoallyl products (**3**) with LiPh. The structure of **1a** was determined by X-ray crystallography. The Ph substituent on C(3) is oriented *syn* to the $NC_6H_4NO_2$ group. Other than that, the structure of **1a** closely resembles that of the analogous η^3-trimethylenemethane complex $(PPh_3)_2Pt(\eta_3\text{-}CH_2C\text{-}(C(CO_2Me)_2)CHPh)$ (V. Plantevin et al., *Organometallics, 13* (1994) 3651). Complexes **1** react with TsNCO to give cyclic ureas, $CH(Ph)N(Ts)C(O)N(R)C{=}CH_2$ (**6**).

Keywords: Azatrimethylenemethane complexes; Platinum complexes; Crystal structures; Cycloaddition reactions

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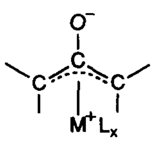
Heteroatom-substituted 'isoelectronic' analogues of trimethylenemethane complexes of transition metals are attracting considerable attention because of their applications in organic synthesis [1–3]. Several η^3-oxatrimethylenemethane metal complexes (I) have been isolated and characterized by X-ray diffraction techniques [4]. η^3-Azatrimethylenemethane complexes (II) have been also synthesized [5,6], but have not been crystallographically characterized. In this communication we report (i) a convenient general synthetic procedure for η^3-azatrimethylenemethane platinum(II) complexes (**1**), (ii) the characterization by X-ray diffraction analysis of $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(4\text{-}NC_6H_4\text{-}NO_2)CHPh)$ (**1a**), and (iii) preliminary reaction chemistry of **1**.



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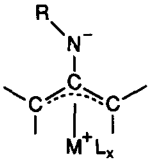
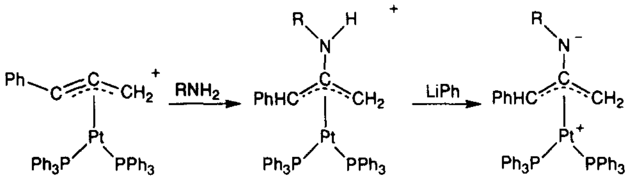


II

Complexes **1** were previously obtained by reaction of the η^3-propargyl/allenyl compound $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)](OTf)$ (**2**(OTf); Tf = CF_3SO_2) with primary amines (RNH_2), followed by deprotonation of the resultant $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(NHR)CHPh)](OTf)$ (**3**(OTf)) with LiPh [6]:



2 **3a-b** **1a-b**

a R = $4\text{-}NO_2C_6H_4$
b R = $4\text{-}MeC_6H_4$

Our new procedure [1] eliminates the need to synthesize and isolate the η^3-propargyl/allenyl complex **2** by furnishing **3** directly by the reaction of $(PPh_3)_2Pt(C_2H_4)$ with RNH_2 and $PhC{\equiv}CCH_2OTs$ (Ts = $4\text{-}MeC_6H_4SO_2$):

☆ This paper is dedicated to the memory of Professor Ugo Croatto.

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[1] This procedure is an adaptation of the one initially developed for η^3-trimethylenemethane and η^3-2-alkoxoallyl complexes of platinum, $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(C(CO_2R)_2)CHR')$ and $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C\text{-}(OR)CHR')]^+$, respectively [7].

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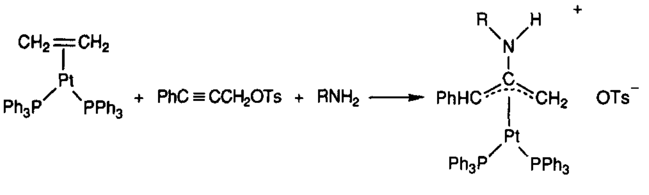


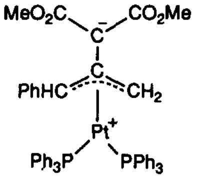
3(OTs)

The synthesis of 3a(OTs) ($R = 4\text{-}NO_2C_6H_4$) provides details of the new procedure. A solution of $4\text{-}NO_2C_6H_4NH_2$ (0.095 g, 0.680 mmol) and $(PPh_3)_2Pt(C_2H_4)$ (0.500 g, 0.669 mmol) in 10 ml of CH_2Cl_2 at 0 °C was treated dropwise over 5 min with $PhC{\equiv}CCH_2OTs$ (0.195 g, 0.680 mmol) in 1 ml of CH_2Cl_2. The resulting solution was stirred for 15 min at room temperature, and the volatiles were removed under reduced pressure. The orange residue (**3a**(OTs)) was washed with hexane (100 ml) and benzene (50 ml) and then dried under vacuum for 2 days. Yield 0.708 g (92%). The product was converted to **1a** by treatment with LiPh in THF. Spectroscopic data for **3a**(OTs) and **1a** were published earlier [6].

Since complexes **1** readily undergo protonation at nitrogen to regenerate **3**, an X-ray diffraction analysis of **1a** was undertaken to unequivocally establish the identity of this η^3-azatrimethylenemethane compound. It was further of interest to compare the structure of **1a** with that of the analogous η^3-trimethylenemethane and η^3-oxatrimethylenemethane complexes.

The molecular structure[2] of **1a** is shown in Fig. 1, and selected bond distances and angles are presented in Table 1.

Molecules of **1a** contain an azatrimethylenemethane (or 2-iminoallyl) ligand bonded to platinum in an η^3 fashion through the three carbon atoms C(1), C(2) and C(3). The phenyl substituent on C(3) is oriented *syn* to the $NC_6H_4NO_2$ group on C(2), in contrast to its *anti* position with respect to the $C(CO_2Me)_2$ group in the analogous η^3-trimethylenemethane complex **4** [11].



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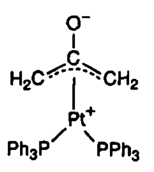

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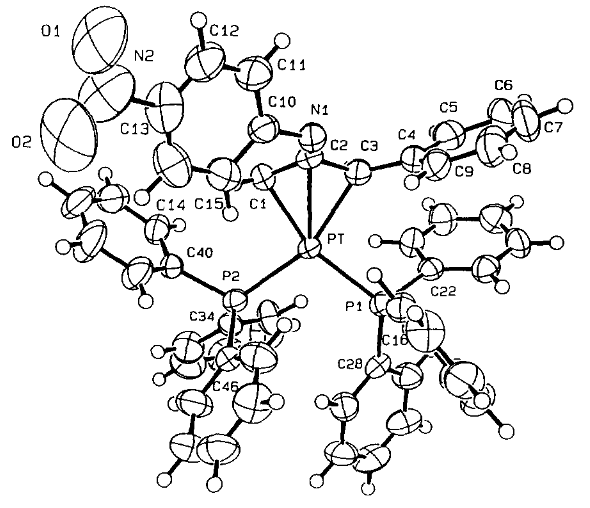

Fig. 1. ORTEP drawing of **1a** showing the atom-numbering scheme. The non-hydrogen atoms are represented by 50% probability thermal ellipsoids. The hydrogen atoms are drawn with an artificial radius.

Table 1
Selected bond distances (Å) and angles (°) for **1a**

Pt–P(1)	2.307(2)	C(1)–C(2)	1.440(12)
Pt–P(2)	2.287(2)	C(2)–C(3)	1.472(12)
Pt–C(1)	2.092(10)	C(3)–C(4)	1.465(12)
Pt–C(2)	2.421(8)	N(1)–C(2)	1.315(10)
Pt–C(3)	2.210(9)	N(1)–C(10)	1.367(11)
P(1)–Pt–P(2)	105.79(8)	C(2)–C(3)–C(4)	121.8(9)
C(1)–C(2)–C(3)	106.7(8)	C(2)–N(1)–C(10)	122.7(8)

With the exception of the aforementioned stereochemical difference, the structures of **1a** and **4** are remarkably similar. They also closely resemble the structures of several η^3-oxatrimethylenemethane platinum(II) complexes [12], including that of $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(O)CH_2)$ (**5**) [13], investigated by Kemmitt and co-workers. Thus, for example, the C(1)–C(2)–C(3) bond angle of 106.7(8)° in **1a** may be compared with that of 107.0(9)° in **4** and 107.7(10)° in **5**. The dihedral angle between the planes C(1)–Pt–C(3) and C(1)–C(2)–C(3) is 54.0° in **1a**, 59.9° in **4**, and 51.0° in **5**. The coordination environment of C(1), C(3), P(1) and P(2) around the platinum center in **1a** is essentially square planar, as reflected by the values of the dihedral angle between the C(1)–Pt–C(3) and P(1)–Pt–P(2) planes of 2.0°. This angle measures 3.2° in **4** and 5.5° in **5**. The average C–C bond distance in the C_3 fragment of **1a** (1.456(12) Å) compares well with that in **4** (1.45(1) Å) and **5** (1.484(20) Å). Furthermore, as already noted for **4** [11] and **5** [13], the Pt–C(2) bond is significantly longer than the Pt–C(1) and Pt–C(3) bonds. The average Pt–C(terminal) bond distance of 2.151(10) Å may be compared with the Pt–C(central) bond distance of 2.421(8) Å, a difference of 0.27 Å for **1a**. This difference is 0.21 Å for **4** and 0.29 Å for **5**. The C(2)–N(1) bond

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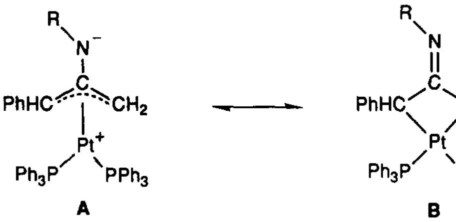
[2] Crystal data for **1a**: $M = 971.94$, triclinic, $P\bar{1}$, $a = 9.630(1)$, $b = 10.851(1)$, $c = 21.277(2)$ Å, $\alpha = 86.166(8)$, $\beta = 80.109(8)$, $\gamma = 75.970(7)$°, $V = 2124.3(4)$ Å^3, $Z = 2$, $D_{calc} = 1.52$ g cm^{-3}; Mo Kα_1 (0.70930 Å), ambient temperature, Rigaku AFC5S diffractometer. The data were corrected for absorption by the empirical Ψ-scan method [8] and linear decay based on average decrease in intensity of 17.2% for six standards. The position of the Pt atom was obtained from a Patterson map and was used as a phasing model in DIRDIF [9]. The three C_3 hydrogens were refined isotropically, while the other hydrogen atoms are in calculated positions (C–H = 0.98 Å). Full-matrix least-squares refinements on F were done in TEXSAN [10]. For the 4991 intensities with $I > 3\sigma(I)$ and the 535 variables, $R = 0.047$ and $R_w = 0.034$.

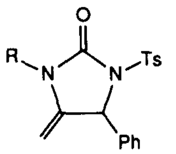
distance in **1a** (1.315(10) Å) is substantially shorter than a typical C–N single bond (1.47 Å [14]).

The foregoing metrical data for **1a** may be rationalized by two contributing resonance descriptions: a zwitterionic η^3-iminoallyl structure **A** and a platinacyclic structure **B**. Similar resonance structures have been proposed for η^3-trimethylenemethane platinum(II) [11] and η^3-oxatrimethylenemethane platinum(II) complexes [12,13], and their relative importance has been discussed.



R = 4-$NO_2C_6H_4$

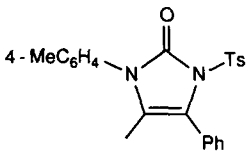
1a reacts with ~3 equiv. of TsNCO in benzene solution at room temperature to afford a cyclic urea, **6a**[3], and an as yet uncharacterized platinum-containing product. An analogous reaction occurs between **1b** and TsNCO to yield **6b**[4], which isomerizes to **7**[5] upon overnight storage in $CDCl_3$ solution. These reactions are similar to those reported by Murai and co-workers [5], who isolated several cyclic ureas, $Me_2\overline{CN(Ar)C(O)N(Ar)C}=CH_2$ (Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$NO_2C_6H_4$), by treating $Me_2\overline{COC(O)OC}=CH_2$ with ArNCO and 5 mol.% $(PPh_3)_2Pt(C_2H_4)$ in toluene at reflux.



6a-b

a R = 4-$NO_2C_6H_4$

b R = 4-MeC_6H_4



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We are investigating the scope of cycloaddition reactions of **1**.

Supplementary material

Tables of crystal data and data collection and refinement details, positional parameters, anisotropic thermal parameters, and bond distances and angles for complex **1a** are available from the authors on request prior to the publication of a full paper.

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[3] **6a**: yield 86%. Selected NMR data ($CDCl_3$): ^1H NMR δ: 8.3–7.1 (m, 13H, C_6H_4, Ph), 5.90 (dd, J = 2.0, 1.7 Hz, 1H, C*H*Ph), 4.42 (dd, J = 3.2, 2.0 Hz, 1H, $=CH_2$), 4.16 (dd, J = 3.2, 1.7 Hz, 1H, $=CH_2$), 2.37 (s, 3H, Me); $^{13}C\{^1H\}$ NMR δ: 151.2, 145.3, 143.6, 139.7, 138.6, 135.7, 129.6, 129.4, 129.3, 128.5, 127.7, 127.6, 125.1, 88.0, 63.0, 21.9. MS (EI): m/z 449.1046 (M^+; calc. for $C_{23}H_{19}N_3O_5S^+$ 449.1046).

[4] **6b**: yield 80%. Selected NMR data: ^1H NMR (C_6D_6) δ: 7.9–6.0 (m, 13H, C_6H_4, Ph), 5.80 (m, 1H, C*H*Ph), 4.05 (m, 1H, $=CH_2$), 3.69 (m, 1H, $=CH_2$). 1.96 (s, 3H, Me), 1.77 (s, 3H, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 151.5, 144.8, 144.5, 138.9, 138.4, 135.8, 130.6, 130.0, 129.1, 128.8, 128.7, 128.1, 127.3, 127.0, 86.2, 62.5, 21.5, 21.1, MS (EI): m/z 418.134 (M^+; calc. for $C_{24}H_{22}N_2O_3S^+$ 418.135).

[5] **7**: Selected NMR data ($CDCl_3$): ^1H NMR δ: 7.9–7.0 (m, 13H, C_6H_4, Ph), 2.42 (s, 3H, Me), 2.38 (s, 3H, Me), 1.75 (s, 3H, Me); $^{13}C\{^1H\}$ NMR δ: 150.9, 144.9, 138.4, 135.1, 130.9, 130.6, 129.8, 129.4, 128.4, 128.3, 127.8, 127.0, 121.0, 118.4, 109.1, 21.6, 21.0, 10.2.