ELSEVIER

Inorganica Chimica Acta 223 (1994) 1–4

Inorganica Chimica Acta

Preliminary Communication

Chemistry of π-complexes derived from $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2CCPh)](O_3SCF_3)$. Interconversion between η^3-alkoxoallyl and η^3-oxoallyl complexes and between η^3-aminoallyl and η^3-iminoallyl complexes

Mark W. Baize, Joan L. Furilla, Andrew Wojcicki*

Department of Chemistry, The Ohio State University, Columbus, OH 43210, USA

Received by Editor 25 February 1994; received by Publisher 29 March 1994

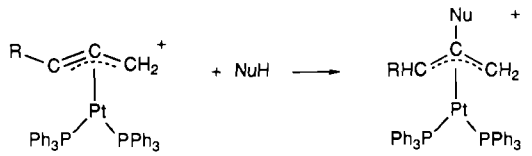
Abstract

The η^3-alkoxoallyl complexes of platinum (**2a–c**: R = Me (**a**), Et (**b**), i-Pr (**c**)) derived from $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ (**1**) and ROH are dealkylated by OMe^- to form the η^3-oxoallyl complex $(Ph_3P)_2Pt(\eta^3\text{-}CH_2C(O)CHPh)$ (**3**). Reactions of **3** with Et_3O^+ and $(MeO)_2SO_2$ regenerate the η^3-alkoxoallyl complexes **2a,b**. Treatment of **1** with H_2O affords binuclear $[((Ph_3P)_2Pt(\eta^3\text{-}(CH_2)(CHPh)C))_2O]^{2+}$ (**4**), which is converted to **3** upon treatment with two equivalents of OMe^-. The η^3-aminoallyl complexes $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2C(NHR)CHPh)]^+$ (**6**), obtained from **1** and RNH_2 (R = *p*-$MeC_6H_4NH_2$, *p*-$O_2NC_6H_4NH_2$), react with LiPh to afford the η^3-iminoallyl complexes $(Ph_3P)_2Pt(\eta^3\text{-}CH_2C(NR)CHPh)$ (**7**). Complexes **7** are protonated by HBF_4 and alkylated by $(MeO)_2SO_2$ to yield **6** and $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2C(NRMe)CHPh)]^+$ (**8**), respectively. The complex $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2C(NMe_2)\text{-}CHPh)]^+$ (**5**) undergoes fluxional behavior at ambient temperatures in solution, and this behavior is ascribed to rotation about the C=NMe_2 bond. The reported chemistry is rationalized by η^3-allyl and metallacyclic resonance hybrid properties of **2–8**.

Keywords: Platinum complexes; Alkoxoallyl complexes; Aminoallyl complexes

Transition-metal η^3-propargyl/allenyl compounds represent a new and growing class of organometallic π-complexes [1,2]. They have been the subject of a recent review [1], which emphasizes approaches to synthesis, structural properties and reaction chemistry.

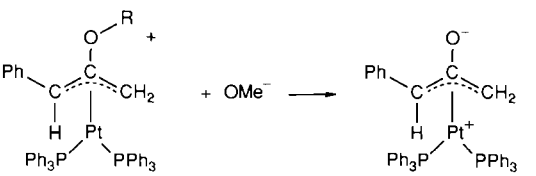
With respect to reaction chemistry, the platinum complexes $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2CCR)]^+$ (R = H, Ph (**1**)) show an unusual variety of behavior and most promising applications to synthesis [3,4]. Particularly intriguing are reactions with nucleophiles (NuH), which may be viewed as additions of NuH to the orthogonal, uncoordinated C=C bond of η^3-CH_2CCR, with the Nu fragment adding to the central carbon atom (Eq. (1):



(1)

Nu = OR, NR_2, SR among others). In this communication, we report further results on the reaction of **1** with hydroxo compounds and organic amines, as well as some chemistry of the resulting products. The chemistry of these products may be rationalized by their behavior as resonance hybrids of metal η^3-allyl and four-membered metallacyclic structures.

Treatment of **1**(OTf) with ROH under various conditions leads to the formation of the appropriate η^3-alkoxoallyl products **2** (R = Me (**a**), Et (**b**), i-Pr (**c**))



2a-b **3**

(2)

*Corresponding author.

SSDI 0020-1693(94)03983-U

[3,5]. However, attempts at introduction of another alkoxide group, at one of the terminal carbon atoms, by reaction of **2a–c** with one equivalent of NaOMe in MeOH resulted instead in dealkylation of the OR group to afford the η^3-oxoallyl complex **3**[1] (Eq. (2)).

^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic properties of **3** show similarities to those of its precursor complexes [3], except for the absence of the appropriate signals of O*R*. The appearance of three proton resonances for the C*H*$_2$C(O)C*H*Ph hydrogens, two with relatively large *J*(Pt–H) coupling constants (80,36 Hz), indicates that the Ph group is *syn* [6], as for **2a–c** [3,5]. In general, NMR spectroscopic data of **3** compare well with those of a series of complexes $L_2Pt(\eta^3$-CH(R)C(O)CHR) (L = AsPh$_3$, PPh$_3$, other phosphines, ½ bipy; R = H, Ph, C(O)Me, CO_2Me), obtained via synthetic routes very different from that in Eq. (2) [7]. However, $(Ph_3P)_2Pt(\eta^3$-CH$_2$C(O)CH$_2$) was recently prepared by base induced cleavage of the corresponding η^3-acetalallyl platinum complex [8].

The bonding in these η^3-oxoallyl [7] as well as in the corresponding η^3-alkoxoallyl platinum complexes is best described as a hybrid of slipped metal η^3-allyl (**A**) and puckered metallacyclic (**B**) resonance structures (Fig. 1). This conclusion is derived from X-ray structural [7] and NMR spectroscopic evidence [3, 7], e.g. a relatively large ^2J(H–H) (up to 6.6 Hz) for the CH$_2$ protons [3]. Resonance structure **B** of **2a,b**, incorporating an alkyloxonium ion feature, likely accounts for the dealkylation of these complexes by NaOMe. Interestingly, whereas **2a–c** [3, 5], **3** and *syn,syn*-$(Ph_3P)_2Pt(\eta^3$-CH(Ph)C(O)CHPh) [7c] show no fluxional behavior at ambient temperatures, other platinum η^3-oxoallyl complexes undergo scrambling of the *syn* and *anti* groups of CHR. The observed fluxionality has been attributed to inversion of the puckered metallacyclic ring (cf. **B**) [7].

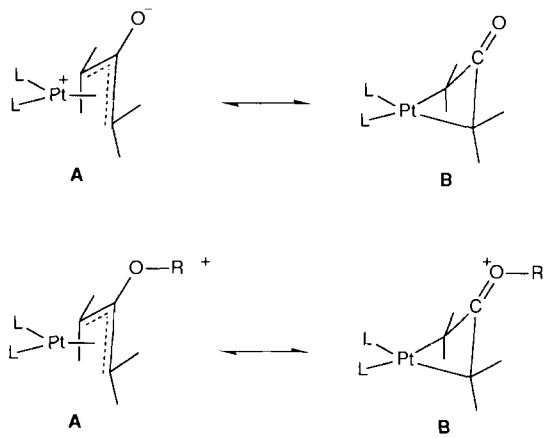
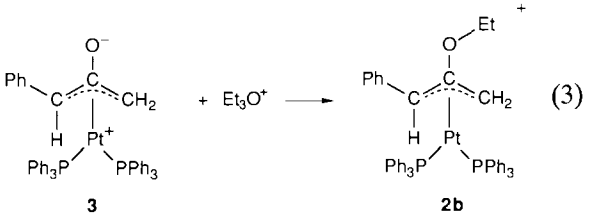


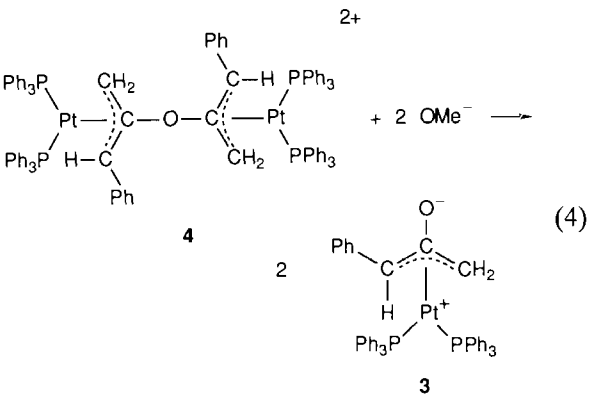
Fig. 1. η^3-Allyl (**A**) and metallacyclic (**B**) resonance structures of **3** (top) and **2** (bottom).

Complex **3** can be alkylated to regenerate **2**. Thus, it reacts with $Et_3O^+PF_6^-$ in CH_2Cl_2 at room temperature to give essentially a quantitative yield of **2b** (Eq. (3)). Methylation of **3** with an excess of $(MeO)_2SO_2$ in $CDCl_3$ under comparable conditions proceeds similarly to **2a**.



(3)

Stirring a solution of **1**(OTf) (0.18 g, 0.18 mmol) and a large excess (0.1 ml) of H_2O in 10 ml of CH_2Cl_2 for four days, followed by removal of all volatiles and recrystallization from benzene/pentane, afforded **4**$(OTf)_2$[2] as a white–beige powder. This sparingly soluble product exhibits ^1H and $^{31}P\{^1H\}$ NMR spectroscopic properties very similar to those of **2a–c** [3] and **3**, and shows notable absence of an IR ν(OH) band. The assigned structure is supported by reaction of **4** with two equivalents of NaOMe, which affords **3** as the only platinum complex (Eq. (4)).



(4)

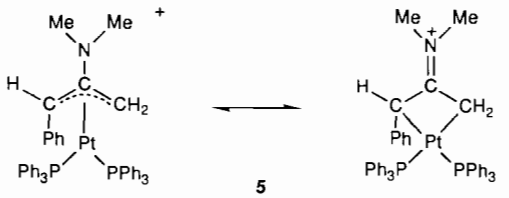
Reactions of **1**(OTf) with H_2O under other conditions, e.g. with one equivalent of H_2O in CH_2Cl_2/THF, also afforded **4** rather than an η^3-hydroxoallyl complex, $[(Ph_3P)_2Pt(\eta^3$-CH$_2$C(OH)CHPh)]$^+$. It is possible that

[1] **3**: yield 73%, m.p. 208 °C (dec.). Selected NMR data ($CDCl_3$): ^1H NMR δ: 3.94 (d, *J*(P–H) = 11.6, *J*(Pt–H) = 80 Hz, C*H*Ph), 2.53 (m, *syn* H of CH$_2$), 2.33 (m, *J*(Pt–H) = 36 Hz, *anti* H of CH$_2$); $^{13}C\{^1H\}$ NMR δ: 177.9 (t, *J*(P–C) = 4.9, *J*(Pt–C) = 151 Hz, *C*CC), 66.7 (dd, *J*(P–C) = 57, 3.6, *J*(Pt–C) = 305 Hz, *C*HPh), 49.9 (dd, *J*(P–C) = 52, 4.6, *J*(Pt–C) = 305 Hz, CH$_2$); $^{31}P\{^1H\}$ NMR δ: 21.3 (d, *J*(P–P) = 5.1, *J*(Pt–P) = 3107 Hz), 19.9 (d, *J*(P–P) = 2964 Hz). *Anal.* Found: C, 63.3; H, 4.60. Calc. for $C_{45}H_{38}OP_2Pt$: C, 63.4; H, 4.50%.

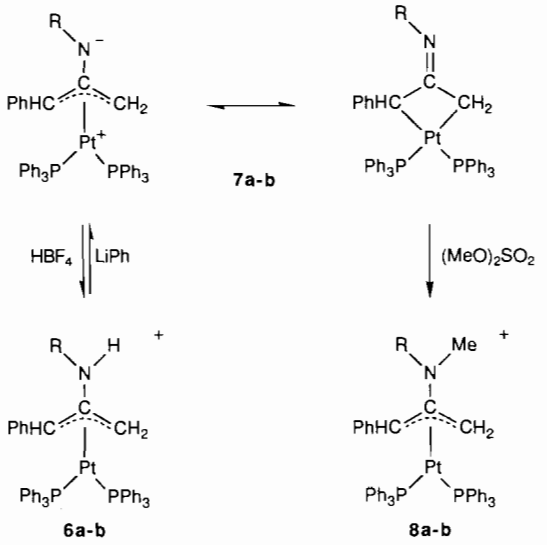
[2] **4**(OTf)$_2$: yield 80%. Selected NMR data (CD_2Cl_2): ^1H NMR δ: 4.0 (d, *J*(P–H) = 11, *J*(Pt–H) = 47 Hz, C*H*Ph), 3.3 (m, *syn* H of CH$_2$), 2.4 (m, *J*(Pt–H) = 55 Hz, *anti* H of CH$_2$); $^{31}P\{^1H\}$ NMR δ: 19.6 (d, *J*(P–P) = 10, *J*(Pt–P) = 3652 Hz), 15.7 (d, *J*(Pt–P) = 3861 Hz). *Anal.* Found: C, 55.4; H, 4.10. Calc. for $C_{92}H_{76}F_6O_7P_4Pt_2S_2$: C, 55.6; H, 3.97%.

such an η^3-hydroxoallyl complex forms from **1** and H_2O, but rapidly reacts with available **1** to yield **4**.

We reported earlier [3] that **1** reacts with Et_2NH to afford the η^3-aminoallyl complex $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2C(NEt_2)CHPh)]^+$, which shows only one set of signals for the two Et groups in the ambient temperature ^1H and $^{13}C\{^1H\}$ NMR spectra. To investigate possible fluxional behavior of such η^3-aminoallyl complexes, we have synthesized the analogous dimethylamino derivative **5**[3] by a similar reaction of **1** with Me_2NH. Its ^1H NMR spectrum in $CDCl_3$ at 45 °C shows one sharp triplet (J(P–H) = 10.0 Hz) at δ 2.99 for the Me groups. As the temperature is lowered this signal broadens, and coalescence occurs at 5 °C (250 MHz). At −50 °C, two sharp triplets are observed at δ 3.15 and 2.85. Throughout these measurements, the three signals of the η^3-allyl protons (*syn*,*anti*-CH_2, *syn*-*CH*Ph) remain essentially unchanged in position and appearance to demonstrate that PtC_3 ring inversion, reported for $[(Ph_3P)_2Pt(\eta^3\text{-}CH_2C(NMe_2)CH_2)]^+$ [9], is not occurring. The observed fluxionality of **5** is best attributed to rotation about the C=NMe_2 bond. A free energy of activation, $\Delta G^{\ddagger} = 13.5$ kcal/mol, was calculated from the coalescence temperature [10] for this process.



The primary amines p-$MeC_6H_4NH_2$ and p-$O_2NC_6H_4NH_2$ also readily react with **1** to afford, respectively, the η^3-aminoallyl complexes **6a** and **6b**[4], analogous to **5**, as *syn* (minor)–*anti* (major) mixtures. **6a,b** undergo quantitative deprotonation by LiPh in THF to give the corresponding η^3-iminoallyl complexes, which were isolated as beige (**7a**) and orange (**7b**) solids[5] (Scheme 1).



Scheme 1.

The preparation of **7a,b** completes a series of platinum complexes with the isoelectronic ligands η^3-oxoallyl, η^3-iminoallyl and η^3-alkylideneallyl (or η^3-trialkylidenemethane [3]). Complexes **7a,b** are protonated by HBF_4 to regeneratc **6a,b**, and methylated by $(MeO)_2SO_2$ to yield **8a,b**[6]. Other reactions of **7**, including those with metal complexes, are under investigation.

In conclusion, we have shown that platinum η^3-alkoxoallyl and η^3-aminoallyl complexes can be dealkylated and deprotonated, respectively, to the corresponding η^3-oxoallyl and η^3-iminoallyl complexes and that such reactions can be reversed. The four classes of compounds are best described as resonance hybrids of η^3-allyl and metallacyclic structures, and these representations are useful in rationalizing and exploring their chemistry.

Supplementary material

Complete spectroscopic data for complexes **3–8** are available from the authors on request.

Acknowledgements

This research has been supported by The Ohio State University. J.L.F. is a National Needs Fellow in a program funded by the US Department of Education.

[3] **5**(OTf): yield 91%. Selected NMR data ($CDCl_3$): ^1H NMR δ: 4.41 (m, *syn* *CH*Ph), 2.72 (m, *syn* H of CH_2), 2.29 (dd, J(P–H) = 10.6, J(H–H) = 7.9, J(Pt–H) = 54 Hz, *anti* H of CH_2); $^{13}C\{^1H\}$ NMR δ: 153.5 (t, J(P–C) = 4.4, J(Pt–C) = 120 Hz, *CC*C), 61.4 (d, J(P–C) = 50, J(Pt–C) = 219 Hz, *C*HPh), 38.0 (d, J(P–C) = 45, J(Pt–C) = 182 Hz, CH_2). MS (FAB): m/z 879.50 (M^+; calc. for $C_{47}H_{44}NP_2Pt^+$ 879.50).

[4] **6b**(OTf): yield 96% (*c.* 90% *anti*, 10% *syn*), pale yellow solid. Selected NMR data ($CDCl_3$), *anti* isomer: ^1H NMR δ: 9.69 (t, J(P–H) = 4.1 Hz, NH), 5.1 (m, *CH*Ph), 3.6 (m, *anti* H of CH_2), 2.7 (m, *syn* H of CH_2); $^{31}P\{^1H\}$ NMR δ: 15.0 (d, J(P–P) = 8.9, J(Pt–P) = 3620 Hz), 13.9 (d, J(Pt–P) = 3365 Hz). MS (FAB): m/z 972.25 (M^+; calc. for $C_{51}H_{43}N_2O_2P_2Pt^+$ 972.24).

[5] **7b**: 90% yield. Selected NMR data (CD_2Cl_2): ^1H NMR δ: 3.82 (m, J(Pt–H) = 73 Hz, *CH*Ph), 2.31 (m, *syn* H of CH_2), 2.22 (m, J(Pt–H) = 66 Hz, *anti* H of CH_2); $^{31}P\{^1H\}$ NMR δ 20.6 (d, J(P–P) = 3.9, J(Pt–P) = 2960 Hz), 18.2 (d, J(Pt–P) = 2782 Hz). MS (FAB): m/z 972.43 ($M^+ + H$).

[6] **8b**(OSO_3Me) (*anti* isomer). Selected NMR data ($CDCl_3$): ^1H NMR δ: 4.45 (m, *CH*Ph), 3.40 (t, NMe), 2.94 (m, *syn* H of CH_2), 2.63 (m, *anti* H of CH_2); $^{13}C\{^1H\}$ NMR δ: 147.6 (t, J(P–C) = 4.2, J(Pt–C) = 84 Hz, *CC*C), 68.9 (d, J(P–C) = 45 Hz, *C*HPh), 42.5 (d, J(P–C) = 41.2, J(Pt–C) = 145 Hz, CH_2). MS (FAB): m/z 986.28 (M^+; calc. for $C_{52}H_{45}N_2O_2P_2Pt^+$ 986.26).

References

[1] A. Wojcicki, *New J. Chem., 18* (1994) 61.

[2] P.J. Stang, C.M. Crittell and A.M. Arif, *Organometallics, 12* (1993) 4799.

[3] P.W. Blosser, D.G. Schimpff, J.C. Gallucci and A. Wojcicki, *Organometallics, 12* (1993) 1993.

[4] T.-M. Huang, J.-T. Chen, G.-H. Lee and Y. Wang, *J. Am. Chem. Soc., 115* (1993) 1170.

[5] K. Daniel and A. Wojcicki, unpublished results.

[6] (a) D.J. Mabbott, B.E. Mann and P.M. Maitlis, *J. Chem. Soc., Dalton Trans.,* (1977) 294; (b) N.M. Boag, M. Green, J.L. Spencer and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.,* (1980) 1200.

[7] (a) D.A. Clarke, R.D.W. Kemmitt, M.A. Mazid, P. McKenna, D.R. Russell, M.D. Schilling and L.J.S. Sherry, *J. Chem. Soc., Dalton Trans.*, (1984) 1993; (b) A. Imran, R.D.W. Kemmitt, A.J.W. Markwick, P. McKenna, D.R. Russell and L.J.S. Sherry, *J. Chem. Soc., Dalton Trans.,* (1985) 549; (c) K.W. Chiu, W. Henderson, R.D.W. Kemmitt, L.J.S. Prouse and D.R. Russell, *J. Chem. Soc., Dalton Trans.,* (1988) 427; (d) J. Fawcett, W. Henderson, M.D. Jones, R.D.W. Kemmitt, D.R. Russell, B. Lam, S.K. Kang and T.A. Albright, *Organometallics, 8* (1989) 1991.

[8] A. Ohsuka, T. Fujimori, T. Hirao, H. Kurosawa and I. Ikeda, *J. Chem. Soc., Chem. Commun.,* (1993) 1039.

[9] J.-T. Chen, T.-M. Huang, M.-C. Cheng, Y.-C. Liu and Y. Wang, *Organometallics, 11* (1992) 1761.

[10] H.S. Gutowsky and C.H. Holm, *J. Chem. Phys., 25* (1956) 1228.