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Markovnikov versus anti-Markovnikov selectivity in the amination of terminal olefins coordinated to platinum(II)

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Abstract

The products of addition of secondary amines to platinum(II)-coordinated terminal olefins undergo a fast Markovnikov (M)–anti-Markovnikov (anti-M) isomerization process, leading to an equilibrium composition different from that obtained under kinetic control; in basic medium, the amination products undergo intramolecular ring closing reaction which is faster for the anti-M isomers, so decreasing the M/anti-M ratio in the final complexes.

Keywords: Amination; Platinum(II) coordinated olefins; Markovnikov/anti-Markovnikov

The addition of nucleophiles to olefins coordinated to late transition metals is a key step in many organometallic reactions [1]. In this context, particular attention has been devoted to the amination of terminal olefins, the interest being focused on catalytic pathways able to enhance the regioselectivity of the nucleophilic attack (M versus anti-M) [2,3].

Selectivity aspects, concerned with the formation of M and anti-M addition products and subsequent ring closing reactions with formation of azametallacyclobutane species, have been widely investigated in the case of platinum(II) [4–6]; however, differences between kinetically and thermodynamically controlled compositions of the isomeric mixtures have never been reported or discussed.

We have investigated the reaction of the cationic complexes $[PtCl(\eta^2\text{-olefin})(tmeda)]^+$ (olefin = propene, **1a**, and styrene, **1b**; tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) [7] with dialkylamines ($NHMe_2$, **m**, and $NHEt_2$, **n**) (Scheme 1) in $CDCl_3$ and over the temperature range 243–303 K. The addition reaction was fast in the whole range of temperatures (occurring within the mixing time of the reagents) and showed a net kinetic preference for the M isomer (M/anti-M ratio ~80:20). With time, and at a rate that increased as the temperature was raised [8], the solution reached an equilibrium composition which was in favour of the M isomer in the case of **2an** (M/anti-M ratio ⩾95:5, Fig. 1) and in favour of the anti-M isomer in the case of **2bm** and **2bn** (M/anti-M ratio ~30:70 and 10:90, respectively; Fig. 2). In the examined systems, the equilibration between the two forms (M and anti-M) was a rapid process at temperatures above 263 K, as witnessed by the fast equilibration of solutions having initially the kinetically controlled composition.

Under basic conditions (addition of a slight excess of aqueous KOH to a dichloromethane solution of the platinum substrate at ambient temperature), the deprotonated amination products (**2** in Scheme 1) undergo a further transformation in which the aminic nitrogen displaces the *cis* chloride forming azaplatinacyclobutane species (**3** in Scheme 1) [4a,4b]. We have found that the M/anti-M ratio decreases in the conversion of the linear addition product into the ring closed species. The linear addition product **2an**, containing at equilibrium only 5% of anti-M isomer, yields, upon ring closing reaction, compound **3an** for which the anti-M isomer raises to 25%. Similarly, the linear

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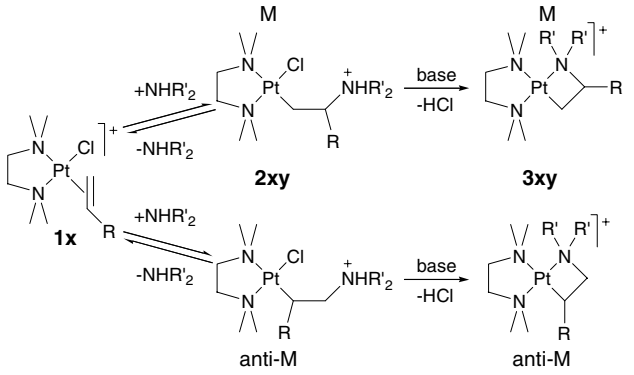

Scheme 1. Summary of the amine addition reaction leading to **2** and of the following ring closing reaction leading to **3**.

addition product **2bm**, for which at equilibrium the anti-M isomer is already prevalent (70%), gives, after ring closing process, compound **3bm** for which the anti-M isomer is the exclusive form. The behaviour of **2an** and **2bm** can be explained by assuming a greater propensity of the linear anti-M addition products to undergo ring closing reaction.

The first outcome of this investigation is a net kinetic preference for the M addition product that does not appear to depend very much upon the type of olefin substituent (methyl or phenyl). A slipping of the olefin in the π-bonded precursor, which brings the more substituted carbon atom farther from the metal centre and more exposed to the solvent, can account for such a kinetic preference [5].

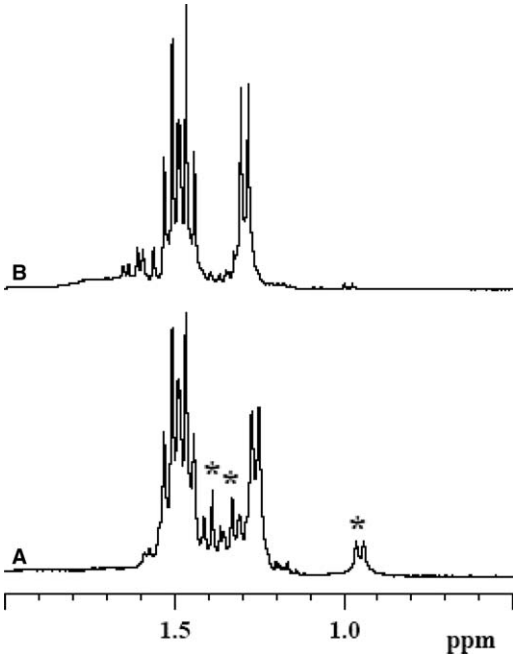

Fig. 1. Region of the NMR spectrum of compound **2an** showing the resonance peaks of the CH_3 protons of propene and diethylamine for the anti-M (doublet at 0.95 ppm for propene and triplets at 1.34 and 1.39 ppm for diethylamine: peaks labelled with an asterisk) and M (doublet at 1.26 ppm for propene and triplets at 1.43 and 1.49 ppm for diethylamine) isomers. The signals of the anti-M isomer practically disappear as the temperature is raised from 243 K (kinetically controlled composition, spectrum A) to 293 K (equilibrium composition, spectrum B; the multiplet centred at 1.59 ppm belongs to one of the two Pt–CH_2– protons).

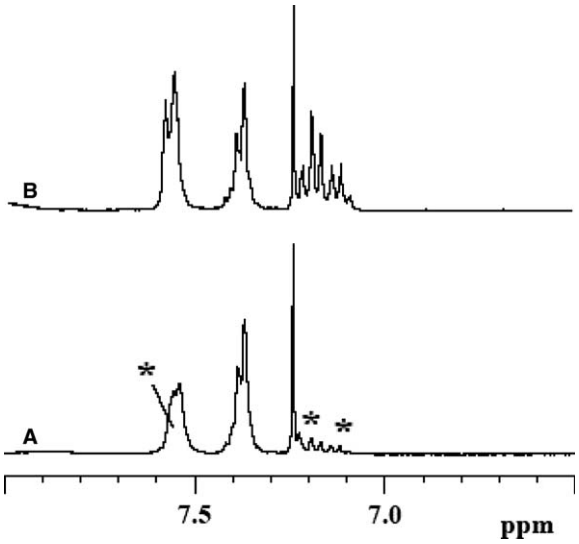

Fig. 2. Region of the NMR spectrum of compound **2bm** showing the resonance peaks of the phenyl protons of styrene for the anti-M (7.12, 7.19, and 7.58 ppm for p, m, and o protons, respectively; peaks labelled with an asterisk) and M isomers (7.40 for o and p protons and 7.57 for m protons). The signals of the anti-M isomer increase considerably as the temperature is raised from 243 K (kinetically controlled composition, spectrum A) to 293 K (thermodynamically controlled composition, spectrum B).

In contrast, the thermodynamic stabilities of the M and anti-M addition products appear to depend very much upon the nature of the substituents. A methyl group favours the M isomer, whereas a phenyl group favours the anti-M form. This could be attributed to a phenyl stabilization and a methyl destabilization of the high electron charge localized on the metal-bound carbon atom.

The new finding of a ready M/anti-M isomerization appears to contradict a recent paper by Pryadun et al. [9] reporting a very slow isomerization (months at room temperature) for the transformation of an initially formed anti-M addition product (*cis*-[$PtCl_2\{\eta^1$–$CH(Me)CH_2NHEt_2\}(PPh_3)$]) into the M isomer (*cis*-[$PtCl_2\{\eta^1$–$CH_2CH(Me)NHEt_2\}(PPh_3)$]). The Pryadun data, however, are susceptible to a different interpretation. The presence of a strong labilizing ligand (PPh_3) *trans* to the leaving chloride and of excess diethylamine able to deprotonate the ammonium group could have induced a fast ring closing reaction with the consequence that the reported isomerization process does not concern the linear ammonium ethanide species (analogous to compounds **2** in Scheme 1) but the ring closed product (analogous to compounds **3** in Scheme 1) [10].

In the presently investigated systems, the intramolecular cyclization, via displacement of the *cis* chloride by the N

atom of the 2-aminoethanide chain, has been clearly established (see also Supplementary Information). Generally, either the presence of a labilizing ligand *trans* to the leaving chloride [4], and/or of a significant steric bulk on the ethanide chain was required (such a steric bulk promoting the ring closing reaction by Thorpe–Ingold effect [11]) [6]. However, notwithstanding the fact that our addition products lack a labilizing ligand *trans* to the leaving chloride, a ready ring closing reaction is observed with propene and styrene. Furthermore, we could prove that it is possible to completely remove the substituents from the ethanide chain and still have the ring closing reaction.

Hence, the ethene derivative [PtCl(η^1–$CH_2CH_2NHEt_2$)(tmeda)](ClO_4), **2cn**, was treated with a slight excess of $NHEt_2$. Under such weakly basic conditions, partial conversion of the linear compound **2cn** into the cyclic compound **3cn** took place (Figure S1, Tables S1 and S2). Therefore, we can conclude that in the systems here considered neither the *trans* labilization of the leaving chloride nor the presence of substituents on the ethanide chain is necessary for the ring closing reaction to take place. The main difference between our substrates and those previously investigated [4,6] is the absence of a formal negative charge on the aminoethanide compound (deprotonated compound **2**) undergoing cyclization. A greater electrophilicity of the metal centre could therefore be an important aiding factor for the ready occurrence of the ring-closing process.

Another outcome of the present investigation is the greater propensity for the linear anti-M isomer, as compared to the M one, to undergo ring closing reaction. The anti-M addition product differs from the M isomer for having the alkyl substituent (methyl or phenyl in the present investigation) and the amine group on different carbons of the ethanide chain. Steric repulsion between the two groups would set them in an antiperiplanar conformation. As a consequence, the amine group should be brought in a synclinal conformation with respect to platinum and therefore in a suitable position to give chloride substitution and ring closing reaction. This cooperative effect cannot be present in the M isomer having the alkyl substituent and the amine group on the same carbon atom of the ethanide chain.

The X-ray structure of the species **3bn** [12] is reported in Fig. 3 [13–19]. The cyclobutane metallacycle is rather strained and ''quasi planar''; as a consequence, the substituents on adjacent atoms of the aminoethanide chain are placed in eclipsed positions. Notwithstanding the large deviation from theoretical values of bond angles, the cyclobutane-metallacycle bond distances are rather normal and in accord with values found in the analogous [Pt($CH_2CH_2NMe_2$–κC,κN)Cl(PPh_3)] complex in which, however, the ethanide chain had no substituents and the Pt–N bond was ca. 0.04 Å longer because of the phosphine *trans* influence [4b]. The accumulation of electron charge on the platinum-bound carbon atom (C8) is revealed by the narrowing of the corresponding angle in the phenyl ring

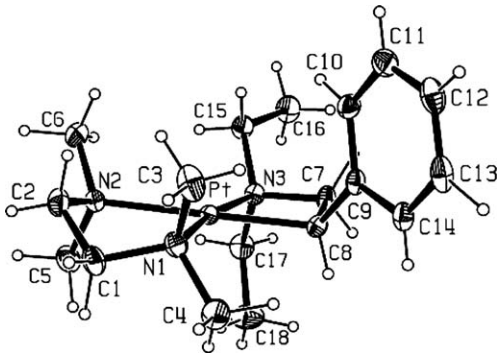

Fig. 3. ORTEP drawing of the complex cation [Pt{CH(Ph)CH_2NEt_2–κC,κN}(tmeda)]$^+$ (**3bn**), the ellipsoids enclose 20% probability. Selected bond distances [Å] and angles [°]: Pt–N1 2.084(3), Pt–N2 2.209(3), Pt–N3 2.085(3), Pt–C8 2.053(4), C8–C7 1.522(6), C7–N3 1.516(5), C8–Pt–N1 100.3(1), N1–Pt–N2 83.3(1), N2–Pt–N3 106.0(1), C8–Pt–N3 70.4(1), Pt–N3–C7 92.0(2), N3–C7–C8 103.5(3), C7–C8–Pt 93.1(2), N1–Pt–N3 170.5(1), C8–Pt–N2 176.4(1).

[C10–C9–C14 = 117.3(4)°] [20,21] and the lengthening of the *trans* Pt–N2 bond, which is 0.12 Å longer than the other two Pt–N bonds (the latter Pt–N distances are practically coincident, no matter if one belongs to a four-member and the other to a five-member chelate ring). The stabilization of such an electron charge by the phenyl ring has been invoked to explain the thermodynamic preference for the anti-M addition product in the styrene derivatives. The steric interaction between substituents on *cis* ligands [particularly C9···C3 = 3.426(8) and C6···C15 = 3.548(8) Å] can fully explain the pyramidal distortion of the platinum coordination centre.

The cyclic species (**3**) of this work are closely related to the metallacycles recently proposed by Hartwig for the rhodium-catalyzed anti-M amination of vinylarenes [3]. Our findings prove that the formation of such intermediates is very likely, and the greater propensity of the anti-M isomer to undergo ring closing reaction may be the reason for the anti-M selectivity of the Hartwig reaction.

In conclusion, the present investigation has demonstrated the following aspects: (i) the kinetic preference for the Markovnikov isomer in the amination of platinum-coordinated olefins; (ii) the ready isomerization between Markovnikov and anti-Markovnikov addition products taking place at room temperature; (iii) the ease of the ring closing reaction in systems that lack a formal negative charge on the metal core; (iv) the faster ring closure of the linear anti-Markovnikov amination product (as compared to the Markovnikov one) contributing to the increase of this form in the ring closed products.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.01.014.

References

[1] (a) J. Haggin, Chem. Eng. News 71 (1993) 23;
(b) F.A. Cotton, G. Wilkinson, in: Advanced Inorganic Chemistry, sixth ed., Wiley, New York, 1999;
(c) M. Beller, J. Seayed, A. Tillack, H. Jiao, Angew. Chem., Int. Ed. 45 (2004) 3368–3398.

[2] (a) T.E. Müller, M. Beller, Chem. Rev. 98 (1998) 675–703;
(b) H.M. Senn, P.E. Blöchl, A. Togni, J. Am. Chem. Soc. 122 (2000) 4098–4410;
(c) U. Nettekoven, J.F. Hartwig, J. Am. Chem. Soc. 124 (2002) 1166–1167;
(d) M. Kawatsura, J.F. Hartwig, J. Am. Chem. Soc. 122 (2000) 9546–9547;
(e) M. Utsonomiya, J.F. Hartwig, J. Am. Chem. Soc. 125 (2003) 14286–14287.

[3] (a) M. Utsonomiya, R. Kuwano, M. Kawatsura, J.F. Hartwig, J. Am. Chem. Soc. 125 (2003) 5608–5609;
(b) M. Utsonomiya, J.F. Hartwig, J. Am. Chem. Soc. 126 (2004) 2702–2703;
(c) J. Takaya, J.F. Hartwig, J. Am. Chem. Soc. 127 (2005) 5756–5757.

[4] (a) A. De Renzi, A. Panunzi, A. Vitagliano, Gazz. Chim. Ital. 108 (1978) 45–50;
(b) A. De Renzi, B. Di Biasio, G. Morelli, A. Vitagliano, Inorg. Chim. Acta 63 (1982) 233–241;
(c) A. Panunzi, A. De Renzi, R. Palumbo, G. Paiaro, J. Am. Chem. Soc. 91 (1969) 3879–3883;
(d) E. Benedetti, A. De Renzi, G. Paiaro, A. Panunzi, C. Pedone, Gazz. Chim. Ital. 102 (1972) 744–754;
(e) A. De Renzi, G. Paiaro, A. Panunzi, V. Romano, Chim. Ind. (Milan) 55 (1973) 248–251.

[5] (a) O. Eisenstein, R. Hoffmann, J. Am. Chem. Soc. 103 (1981) 4308–4320;
(b) C. Hahn, Chem. Eur. J. 10 (2004) 5888–5899.

[6] (a) M. Green, J.K.K. Sahran, I.M. Al-Najjar, Organometallics 3 (1984) 520–524;
(b) J.K.K. Sahran, M. Green, I.M. Al-Najjar, J. Chem. Soc., Dalton Trans. 5 (1984) 771–777;
(c) M. Green, J.K.K. Sahran, I.M. Al-Najjar, J. Chem. Soc., Dalton Trans. 7 (1981) 1565–1571.

[7] (a) G. Gervasio, S.A. Mason, L. Maresca, G. Natile, Inorg. Chem. 27 (1986) 2207–2211;
(b) L. Maresca, G. Natile, Comments Inorg Chem. 16 (1994) 95–112, and quoted references;
(c) F.P. Fanizzi, L. Maresca, G. Natile, C. Pacifico, Gazz. Chim. Ital. 124 (1994) 184;
(d) G. Bandoli, A. Dolmella, F.P. Fanizzi, N.G. Di Masi, L. Maresca, G. Natile, Organometallics 21 (2002) 4595–4603;
(e) G. Lorusso, G. Boccaletti, N.G. Di Masi, F.P. Fanizzi, L. Maresca, G. Natile, Eur. J. Inorg. Chem. 24 (2004) 4751–4754.

[8] In our experimental conditions (chloroform solution, mM concentrations) the equilibrium was reached in 4 h at 263 K and in almost the mixing time of the reagents at 298 K.

[9] R. Pryadun, D. Sukumaran, R. Bogadi, J.D. Atwood, J. Am. Chem. Soc. 126 (2004) 12414–12420.

[10] Evidences in favour of a ring closed species rather than a linear addition product for the complex formulated as [Pt{$CH_2CH(Me)NHEt_2$}$Cl_2(PPh_3)$] in Ref. [9] are found in the reported NMR parameters for the metallaethanide chain. The values are practically coincident with those reported for the ring closed compound [Pt{$CH_2CH(Me)NMe_2$–κC,κN}$Cl(PPh_3)$] (Ref. [4a,4b]) and very close to those of the M and anti-M isomers of our complex **3an**. Also the reported high value of $^3J_{PtH}$ (up to 70 Hz) is typical of ring-closed species rather than of linear compounds (ca. 40 Hz).

[11] (a) R.M. Beesley, C.K. Ingold, J.F.J. Thorpe, J. Chem. Soc. 107 (1915) 1080–1106;
(b) C.K. Ingold, J. Chem. Soc. 119 (1921) 305;
(c) S.W. Smith, M.S. Newman, J. Am. Chem. Soc. 90 (1968) 1253–1257.

[12] *Crystal data for* [Pt{$(CH_3)_2NCH_2CH_2N(CH_3)_2$}{$CHPhCH_2N(CH_2CH_3)_2$-κC,κN}]$ClO_4$: $C_{18}H_{34}N_3O_4ClPt$, Mw = 587.027, white parallelepiped, monoclinic, space group $P2_1/c$, $a = 10.1870(5)$ Å, $b = 15.6315(7)$ Å, $c = 14.1576(7)$ Å, and $\beta = 95.348(1)°$, $V = 2244.6(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.737$ g cm^{-3}, BrukerAXS X8 APEX CCD system equipped with a four-circle Kappa goniometer and a 4K CCD detector, radiation Mo Kα, $\lambda = 0.71073$ Å, $2\theta_{max} = 80.00°$, temperature of measurement 293 ± 2 K, no. of measured reflections 25,934, no. of independent reflections 12,990, no. of reflections included in the refinement 8248 ($I > 2\sigma(I)$), data reduction and unit cell refinement (package SAINT-IRIX) (Ref. [13]) integrated and corrected for Lorentz, polarization, and absorption effects using the program SADABS (Ref. [14]), $\mu = 6.397$ mm^{-1}, structure solution by direct methods and Fourier methods, SIR2002 (Ref. [15]) and SHELXL97 (Ref. [16]), no. of parameters 380, H atoms were located by Fourier difference and refined with isotropic displacement, $R_1 = 0.0471$ and $wR_2 = 0.0914$ for observed reflections, $R_1 = 0.0888$ and $wR_2 = 0.1080$ for all reflections, refinement residual electron density 3.432 e Å^{-3}, calculations and molecular graphics were carried out using PARST97 (Ref. [17]), WinGX (Ref. [18]) and ORTEP-3 for Windows (Ref. [19]) packages. CCDC – 269917 contains the supplementary crystallographic data for this paper. These data can be obtained on line free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB 2 1 EZ UK; fax +44 1223 336 033; or deposit@ccdc.cam.ac.uk.

[13] Bruker, SAINT-IRIX. Bruker AXS Inc., Madison, Wisconsin, USA, 2003.

[14] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.

[15] M.C. Burla, M. Cavalli, B. Carrozzini, G.L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, Sir2002: the program, J. Appl. Cryst. 36 (2003) 1103.

[16] G.M. Sheldrick, Programs for Crystal Structure Analysis (Release 97-2). Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

[17] (a) M. Nardelli, Comput. Chem. 7 (1983) 95–97;
(b) M. Nardelli, J. Appl. Crystallogr. 28 (1995) 659.

[18] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837–838.

[19] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.

[20] A. Domenicano, P. Mazzeo, A. Vaciago, Tetrahedron Lett. 13 (1976) 1029–1032.

[21] (a) A.R. Campanelli, A. Domenicano, F. Ramondo, J. Phys. Chem. A 107 (2003) 6429–6440;
(b) A.R. Campanelli, A. Domenicano, F. Ramondo, I. Hargittai, J. Phys. Chem. A 108 (2004) 4940–4948.