ORGANOMETALLICS

Volume 20, Number 5, March 5, 2001

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American Chemical Society

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Published on February 3, 2001 on http://pubs.acs.org | doi: 10.1021/om001027u

Communications

Bis Deprotonation of a Platinum(II)-Bonded Propene Affords an Unprecedented η^1,η^3-Allyl Moiety Bridging Two Metal Centers

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Received December 4, 2000

*Summary: The conversion of a η^2-bonded propene (complex **1**) into a bridging η^1,η^3-allyl moiety (complex **4**) is reported. The formation of **4** occurs through the following sequence of reactions: deprotonation of the methyl group of the coordinated propene in **1** and formation of the η^1-allyl complex **2**, displacement of the η^2-olefin of a second molecule of **1** by the η^1-allyl moiety of **2** and formation of the η^1,η^2-allyl-bridged dinuclear complex **3**, and finally further deprotonation of the η^1-bonded methylene group of **3** and simultaneous release of a chloride ion by one platinum unit leading to formation of the η^1,η^3-allyl-bridged platinum dimer **4**.*

There is great interest in η^2-alkene complexes of a platinum triad, especially those carrying a positive charge. Cationic η^2-olefin complexes of nickel and palladium are active, although often elusive, chemical species that are key intermediates in several catalytic processes.[1] Several cationic η^2-alkene complexes have been reported also for Pt(II),[2−4] in most of them the unsaturated ligand easily undergoes exchange processes,[3a,b,4] and only in the presence of bulky substituents on the ancillary ligands is the exchange process hampered.[3c] However in a recent theoretical investigation Strømberg and Svensson came to the conclusion that the cationic *cis*-$Pt(NH_3)_2Cl^+$ fragment should form with olefins a more stable η^2-complex than those formed by neutral $Pt(NH_3)Cl_2$ or anionic $PtCl_3^-$ moieties.[5]

Cationic platinum species that meet both the requirement of Strømberg and Svensson and that of bulky substituents on the ancillary ligands are the complexes [Pt(η^2-alkene)Cl(tmeda)]$^+$ (tmeda = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine) reported by some of us some years ago.[2] In these complexes the olefin is tightly bound to the metal and has a highly electrophilic character.[2c,6]

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10.1021/om001027u CCC: $20.00 © 2001 American Chemical Society
Publication on Web 02/03/2001

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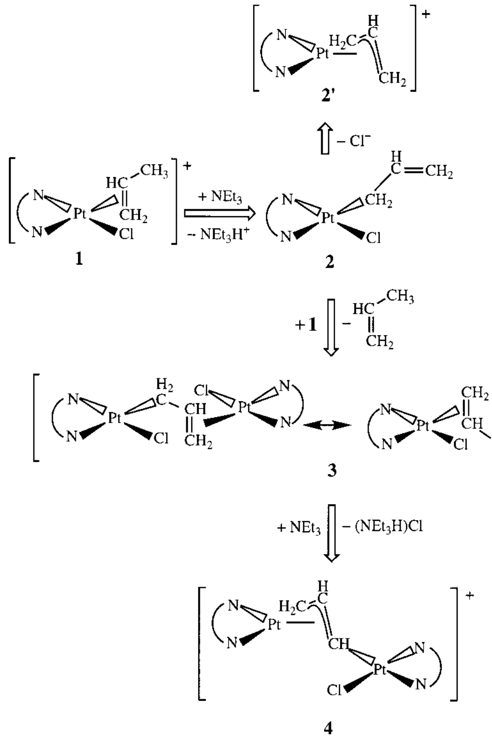
Scheme 1



In particular, the ethene derivative reacts with almost any type of nucleophile to give the corresponding addition products, and in the case of noncoordinating bases such as 1,8-bisdimethylaminonaphthalene (proton sponge) a *para*-carbon of the naphthalene ring adds to the olefin, while the removed proton is taken up by the two NMe_2 groups in *peri* positions.[6e]

The propene derivative **1** has revealed a very unusual and unprecedented reactivity, displaying a cascade of three subsequent reaction steps (see Scheme), the first of which is deprotonation of the propene methyl and formation of the neutral η^1-allyl complex **2**. A similar reaction was reported by Rosenblum and co-workers for the cationic alkene complexes of iron.[7] Complex **2**, which contains a reactive terminal olefin function, can displace the propene from another molecule of **1** to form the monocationic complex **3**, in which the allyl group is η^1-bound to one platinum atom and η^2-bound to the second platinum atom. **3** can undergo further deprotonation of the bridging allyl moiety, converting the η^1,η^2-species into a η^1,η^3-species. The last transformation, which also requires the simultaneous loss of a chloride ion from one of the two platinum units, completes the reaction sequence leading to **4** (Scheme 1). Although **2** was not directly detected in the reaction mixture (in this reaction sequence it is only a reactive intermediate), compound **3** (together with free propene) could be fully characterized by ^1H NMR (it was sufficient to perform the reaction in the absence of triethylamine to prevent its further transformation into **4**).[8] At room temperature, the two metal units of **3** are equivalent in the NMR time scale and the protons of the bridging allyl group exhibit an AX_4 pattern in accord with rapid interchange of the η^1- and η^2-bonding modes.[9] Under the conditions of a substoichiometric amount of NEt_3 used to increase the concentration of **3**, a monomeric allyl complex (**2′**), which most likely derives from **2** by dissociation of a Cl⁻ ion and simultaneous $\eta^1 \rightarrow \eta^3$ rearrangement of the allyl ligand, was also detected in solution.[10]

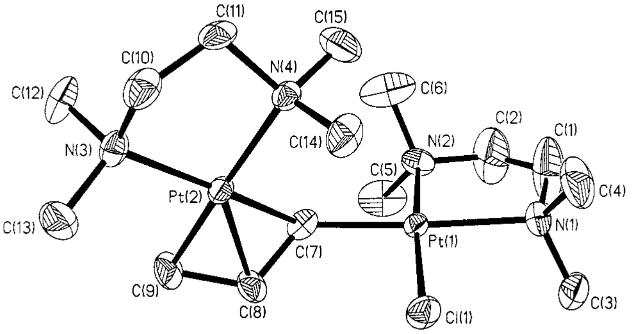


Figure 1. View of the molecular structure of the complex cation **4**.

Complex **4**[11] was characterized by ^1H, ^{195}Pt, and $^1H/^{13}C$ (normal and long-range correlation) NMR spectra,[12] and its structure was also confirmed by an X-ray analysis performed on its perchlorate salt (Figure 1).[13] The two platinum units are nearly perpendicular (dihedral angle between the two PtN_2 planes of 77.0°) in order to reduce steric interactions between the two coordination shells (nonbonding distances between donor atoms Cl(1) and N(2) of Pt(1) and donor atom N(4) of Pt(2) of 4.39 and 4.21 Å, respectively). The allyl plane [C(7)C(8)C(9)] forms a dihedral angle of 60.6° with the coordination plane of the η^3-bonded platinum [Pt(2)N(3)N(4)]. The shortest Pt−C distance is that of the allyl with the η^1-bound platinum [Pt(1)−C(7), 2.00(1) Å], and those with the η^3-bound platinum [Pt(2)−C(7), Pt(2)−C(8), and Pt(2)−C(9)] are in the range 2.07−2.24 Å. The Pt(2)−C(7) distance involving the carbon atom already involved in the η^1-bond with Pt(1) is very long and gives

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[8] NMR in $CDCl_3$ of **3**: $\delta(^1H)$ 2.85 [s, 12H, CH_3N], 2.88 [s, 12H, CH_3N], 2.78 [m, 4H, $-CH_2N$], 3.00 [m, 4H, $-CH_2N$], 3.56 [d, 4H, $^3J(H-H) = 10$ Hz, $^2J(Pt-H) = 85$ Hz, C(allyl-terminal)H], 6.45 [q, 1H, C(allyl-central)H].

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[10] NMR in $CDCl_3$ of **2′**: $\delta(^1H)$ 3.01 [s, 6H, $^3J(Pt-H)$ 37 Hz, CH_3N], 3.26 [s, 6H, $^3J(Pt-H)$ 35 Hz, CH_3N], 3.07 [m, 2H, $-CH_2N$], 3.19 [m, 2H, $-CH_2N$], 2.42 [dd, 2H, $^2J(H-H) = 1.5$, $^3J(H-H) = 11.5$, $^2J(Pt-H) = 76$ Hz, C(allyl-terminal)H], 3.59 [dd, 2H, $^3J(H-H) = 8$ Hz, $^2J(Pt-H) = 24$ Hz, C(allyl-terminal)H], 4.72 [m, 1H, C(allyl-central)H]; $\delta(^{13}C)$ 54.3 [CH_3N], 54.7 [CH_3N], 63.1 [$-CH_2N$], 44.3 [C(allyl-terminal)], 105.9 [C(allyl-central)]. It is to be noted that **2′** is the only reaction end product when higher terminal olefins (e.g., 1-hexene) are considered. In these cases **2** is detectable in solution in the early stage of the reaction (^1H NMR), but because of the alkyl substituent on the terminal carbon of the η^1-allyl moiety, the reaction of substitution of the alkene of a second molecule of **1** by the allyl group of **2** is inhibited, precluding the formation of **3**. Therefore the evolution toward **2′** becomes the only possible path.

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an indication of the steric repulsion between the two coordination centers. The overall molecular structure is nonsymmetrical and rather rigid and causes a diastereotopic splitting of all NMe_2 groups. The splitting is particularly large for $Pt(1)-N(2)Me_2$, for which one Me is shifted at 3.8 ppm (all the other Me resonances are in the range 2.7−3.0 ppm).

In the case of platinum, a η^2-olefin derivative is generally considered an end product.[14] However at high temperature the $[Pt_2Cl_4(\eta^2\text{-alkene})_2]$ complexes were reported to lose an HCl molecule and give a small yield of the corresponding allyl species $[Pt_2Cl_2(\eta^3\text{-allyl})_2]$. The alkene needed to have two alkyl substituents on the same olefinic carbon in order to be able to lose an alkyl proton, and therefore in that series the propene analogue (having only one alkyl substituent) did not give this type of reaction.[15] In compound **1**, the $[PtCl(tmeda)]^+$ fragment attached to the alkene is capable of greatly enhancing the Brønsted acidity of the α-alkyl protons of the alkene so that deprotonation takes place under mild conditions. Furthermore, while the tmeda ligand remains firmly bis-coodinated to platinum because of the Thorpe−Ingold effect of the methyl substituents, the chloride can easily dissociate, allowing the $\eta^1 \rightarrow \eta^3$ rearrangement of the allyl moiety (in other platinum complexes the presence of a precipitating agent for chloride was required in order to promote the complete $\eta^1 \rightarrow \eta^3$ rearrangement of an allyl moiety[16]). The combination of these two factors has led to the unprecedented reaction sequence described above and has provided new stereochemical and reactivity information on allyl platinum complexes which are often involved in catalytic processes.[17]

Acknowledgment. This work was supported by the University of Bari and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), Cofin. 1998 (No. 9803026360).

Supporting Information Available: 500 MHz $^1H/^{13}C$ inverse-detected heterocorrelated spectrum for **4** (PDF). An X-ray crystallographic file (CIF) for the crystal structure determination of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) **1** (146 mg, 0.3 mmol) was suspended in dichloromethane (7 mL), then a 3-fold excess of triethylamine was added under stirring; the solid dissolved, and after a few hours, the colorless solution was extracted with small volumes of water (3 × 2.0 mL) to remove the ammonium salt; the mother solution was then filtered, dried over sodium sulfate, and evaporated under vacuum. Trituration with diethyl ether of the sticky solid left a white compound, which was identified as $[\{PtCl(tmeda)\}(\mu\text{-}\eta^1,\eta^3\text{-}CHCHCH_2)\{Pt(tmeda)\}](ClO_4)$ (**4**). The yield, referenced to platinum, was 69%. Compound **4** is partly soluble in water, and colorless crystals of **4** were obtained by concentration of the aqueous extract. Anal. Calcd for $C_{15}H_{36}N_4Cl_2O_4Pt_2$: C, 22.59; H, 4.55; N, 7.02. Found: C, 22.45; H, 4.57; N, 6.99.

(12) NMR in $CDCl_3$ of **4**: numbering of atoms as in Figure 1, listed data are grouped according to subunits in the order Pt(1), Pt(2), and μ-allyl, $\delta(^1H)$ 2.76 [s, 3H, $CH_3N(1)$], 2.81 [s, 3H, $CH_3N(1)$], 2.62 [m, 1H, $-CH_2N(1)$], 2.89 [m, 1H, $-CH_2N(1)$], 3.12 [s, 3H, $^3J(Pt(1)-H) = 30$ Hz, $CH_3N(2)$], 3.82 [s, 3H, $^3J(Pt(1)-H) = 34$ Hz, $CH_3N(2)$], 2.67 [m, 1H, $-CH_2N(2)$], 3.26 [m, 1H, $-CH_2N(2)$], 2.90 [s, 3H, $^3J(Pt(2)-H) = 41$ Hz, CH_3N(3 or 4)], 2.98 [s, 3H, $^3J(Pt(2)-H) = 38$ Hz, CH_3N(3 or 4)], 2.99 [m, 2H, $-CH_2N$(3 or 4)], 3.02 [s, 3H, $^3J(Pt(2)-H) = 41$ Hz, CH_3N(4 or 3)], 3.18 [s, 3H, $^3J(Pt(2)-H) = 34$ Hz, CH_3N(4 or 3)], 2.88 [m, 2H, $-CH_2N$(4 or 3)], 1.84 [dd, 1H, $^2J(H-H) = 1.5$, $^3J(H-H) = 11$, $^2J(Pt(2)-H) = 75$ Hz, C(9)H], 3.12 [dd, 1H, $^3J(H-H) = 5$, C(9)H], 3.12 [d, 1H, $^3J(H-H) = 11$ Hz, C(7)H], 4.75 [m, 1H, $^2J(Pt(2)-H) = 70$ Hz, C(8)H]; $\delta(^{13}C)$ 48.5 [$CH_3N(1)$], 50.2 [$CH_3N(1)$], 61.1 [$-CH_2N(1)$], 51.2 [$CH_3N(2)$], 55.0 [$CH_3N(2)$], 63.4 [$-CH_2N(2)$], 52.0 [CH_3N(3 or 4)], 53.6 [CH_3N(3 or 4)], 66.7 [$-CH_2N$(3 or 4)], 52.8 [CH_3N(4 or 3)], 55.5 [CH_3N(4 or 3)], 62.5 [$-CH_2N$(4 or 3)], 37.0 [$^1J(Pt(2)-C) = 300$ Hz, C(9)], 53.7 [$^1J(Pt(1)-C) = 1060$ Hz, C(7)], 111.1 [$^1J(Pt(2)-C) = 90$ Hz, C(8)]; $\delta(^{195}Pt)$ −4557.3 [Pt(1)], −3231.1 [Pt(2)].

(13) X-ray data: **4**, $C_{15}H_{36}Cl_2N_4O_4Pt_2$, monoclinic, $P2(1)/c$, $a = 13.030(5)$, $b = 13.885(6)$, $c = 13.567(6)$ Å, $\beta = 101.09(3)°$, $V = 2409(2)$ Å^3, $Z = 4$, $d_{calc} = 2.199$ Mg/m^3, $R_1 = 0.0530$, $wR_2 = 0.1425$.

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