Unprecedented Higher Stability of *E*- than *Z*-Olefin Complexes of Platinum(II). Molecular Structures of the η³-Methallyl(triphenylphosphine)(*Z*- and *E*-but-2-ene)-platinum(II) Cation

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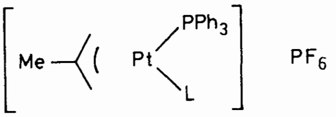
The C=C bond of *Z*-but-2-ene in one of the title complexes lies almost in the co-ordination plane, while that of the corresponding *E*-but-2-ene complex, which unprecedentedly is more stable in solution than the former, forms an angle of 67° with the plane.

Transition metal complexes are generally believed to possess higher stability for *Z*- than *E*-olefin co-ordination,[1] and available stability data[1—3] support this notion. We describe here the first example of a reversal of this stability order and unique structural features in *Z*- and *E*-olefin complexes of platinum(II) containing the η³-methallyl ligand which exercises extremely small steric effects on the co-ordinated olefin.[4,5]



(**1**); L = MeCH=CHMe
(**2**); L = MeCH=CHEt
(**3**); L = MeCH=CHPh
(**4**); L = CH_2=CHPh
(**5**); L = PhCN

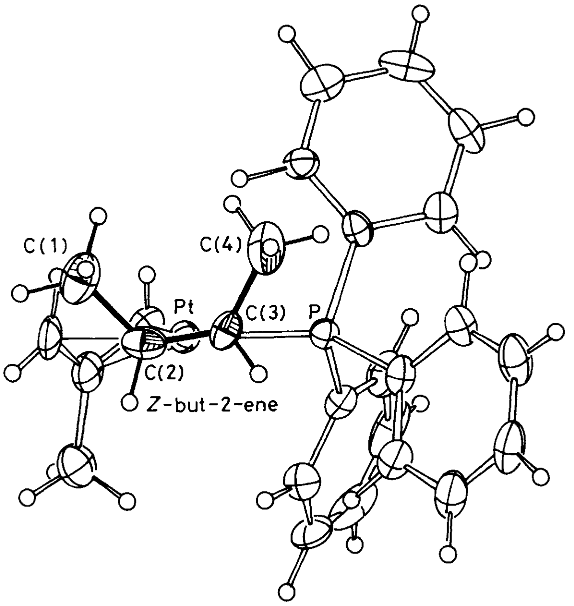


Figure 1. The molecular structure of Z-(**1**).

The relative stability of a pair of the Z- and E-olefin complexes (**1**)—(**3**),† as expressed by the K value for reaction (1), was determined by separately measuring the equilibria between (**4**) or (**5**)[4] and the corresponding Z- or E-olefin complex by ^1H and ^{13}C n.m.r. spectroscopy. The observed K values ($CDCl_3$; 23 °C), 0.45 ± 0.10 for (**1**), 0.48 ± 0.10 for (**2**), and 0.25 ± 0.10 for (**3**) indicate that the E-olefin complexes are more stable than the Z. The corresponding K values for the known Pt^{II}, Pd^{II}, and Rh^{I} complexes are greater than 2.[1—3]

$$\{Pt\}(E\text{-olefin}) + Z\text{-olefin} \overset{K}{\rightleftharpoons} \{Pt\}(Z\text{-olefin}) + E\text{-olefin} \quad (1)$$

$$\{Pt\} = Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)^+ \ PF_6^-$$

The solid state structures of the complexes Z- and E-(**1**) were determined by X-ray crystallography. *Crystal data:* $C_{26}H_{30}PPtPF_6$, $M = 713.6$, Z-(**1**), monoclinic, space group $P2_1/c$, $a = 11.149(2)$, $b = 15.460(3)$, $c = 15.701(2)$ Å, $\beta = 90.21(2)°$, $Z = 4$, $D_c = 1.752$, $D_m = 1.72$ g cm^{-3}, E-(**1**), monoclinic, space group $P2_1/c$, $a = 13.886(2)$, $b = 11.872(4)$, $c = 16.740(2)$ Å, $\beta = 91.17(1)°$, $Z = 4$, $D_c = 1.718$, $D_m = 1.71$ g cm^{-3}. Intensity data were collected by the θ–2θ scan technique with $\sin\theta/\lambda \leqslant 0.64$ on a Rigaku automated four-circle diffractometer using Zr-filtered Mo-K_α radiation. Both structures were solved by the heavy-atom method, and refined including all hydrogen atoms by the block-diagonal least-squares method. The final R factors for Z- and E-(**1**) are 0.069 and 0.068 for 4064 and 4814 $[|F_o| > 3\sigma(|F_o|)]$ reflexions, respectively.‡

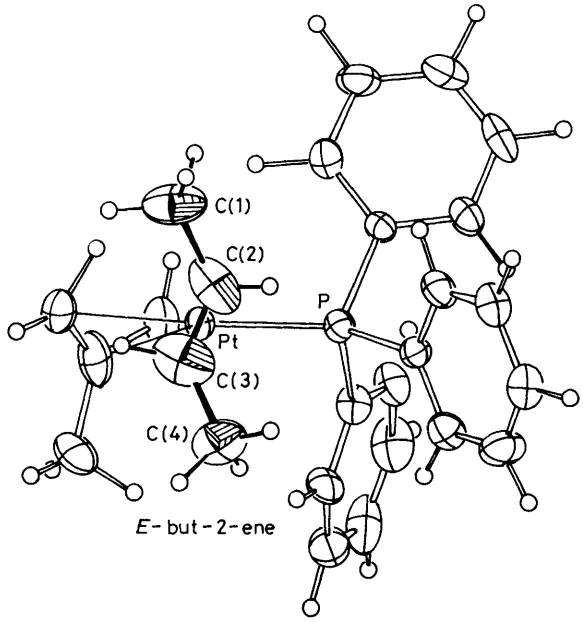


Figure 2. The molecular structure of E-(**1**).

The structure of Z-(**1**) (Figure 1) reveals that the olefinic C=C bond lies almost in the co-ordination plane,§ as in the styrene analogue (**4**),[5] with the two Pt–C(olefin) bond lengths being quite different (2.256 and 2.185 Å). In contrast, the C=C bond in E-(**1**) (Figure 2) is neither parallel nor perpendicular to the plane, but rotationally distorted, making an angle of 67.1° with the plane [Pt–C(olefin) = 2.235 and 2.229 Å].

There appears to be no significant difference in intramolecular van der Waals contacts between the two complexes. However, in Z-(**1**) the C(1)–C(2)–C(3)–C(4) plane (maximum deviation from the best plane 0.004 Å) makes an angle of 109° with the Pt–C(2)–C(3) plane, thus possibly reducing the orbital overlap in the Pt–olefin bond to some extent.[6] Molecular models suggest that another configuration of Z-(**1**) in which the C=C bond is perpendicular to the co-ordination plane with the two methyl groups on the allyl side¶ contains steric constraints similar to those in Figure 1, but the displacement of the methyl groups away from Pt remains still significant.

The degree of bending back of the olefin–methyl substituents and possibly also of the hydrogen atoms in E-(**1**) is somewhat smaller than those in other E-olefin complexes of Pt^{II},[3,7,8] as indicated by the olefinic torsion angles C(1)–C(2)–C(3)–C(4) [153.8° in E-(**1**) and 143—150° in the other complexes].

We believe that the present complex system is the least amenable of known systems to electronic control over the relative stability of Z- and E-olefin complexes;[6] this electronic control originates from the varying extent of metal to olefin π electron back donation, and is affected by rotational distortion. For square-planar complexes the π interaction energy

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† Complexes (**1**)—(**3**) were prepared by a method similar to that for (**4**),[4a] and characterised by elemental analyses, and their ^1H and/or ^{13}C n.m.r. spectra.

‡ Computations were carried out on an ACOS 900S computer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ The angle between the C=C bond and the pseudo-co-ordination plane defined by Pt, P, and the centre of gravity of the allyl triangle is 7.4°.

¶ The ^1H n.m.r. ($CDCl_3$) chemical shifts of the olefinic hydrogen atoms (overlapping at δ *ca.* 5.0) and methyl groups (δ 1.95, 1.96) of Z-(**1**) are consistent with, if not indicative of, this configuration, rather than the in-plane one, in solution. The n.m.r. data of E-(**1**)[4b] in solution are in agreement with the structure in Figure 2.

would be comparable for the in-plane and out-of-plane orientation of the C=C bond,[9] and would be very small for cationic η^3-allylplatinum(II) complexes.[4]

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