Synthesis and Structure of *s-cis-* and *s-trans-*μ-Butadiene-2,3-diyldiplatinum Complexes by the Reaction of μ-Ethynediyldiplatinum Complexes with Tetracyanoethylene

Kiyotaka Onitsuka and Shigetoshi Takahashi*

The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan

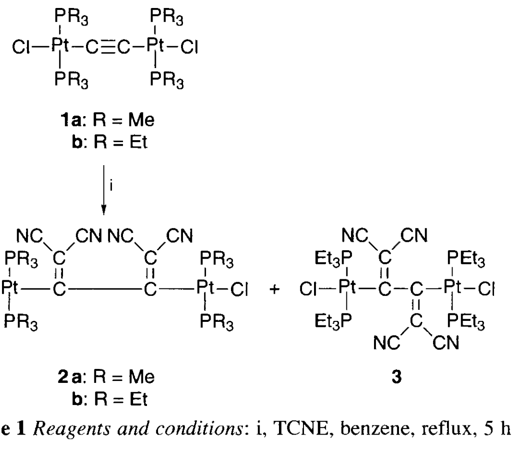
Reactions of μ-ethynediyldiplatinum complexes with tetracyanoethylene in refluxing benzene result in the formation of *s-cis* and *s-trans*-μ-butadiene-2,3-diyldiplatinum complexes, of which structures are established by X-ray crystallographic analysis.

It is well known that the acetylenic group of a transition metal acetylide is electron rich and susceptible to electrophilic attack at the β-position.[1] Thus, the attack of a proton electrophile converts an acetylide to a vinylidene complex. On the other hand, the attack of an electron-poor olefin causes cycloaddition to the C≡C bond.[2,3] For example, tungsten and ruthenium acetylide complexes react with tetracyanoethylene (TCNE) to give σ-cyclobutenyl complexes, which isomerize to σ-butadienyl complexes and further to π-allyl complexes, through the formation of green charge-transfer (CT) complexes. Previously, we reported the synthesis of the first μ-ethynediyl ditransition metal complexes, in which two metal atoms are linked by just one acetylene unit.[4] Because the moiety $M(PR_3)_2X$ in the complexes is known to act as a good electron donor,[5] the reactivity of the μ-ethynediyl complexes toward electron-poor olefins may be of much interest. Thus, we have investigated the reaction of μ-ethynediyldiplatinum complexes with TCNE and found the formation of *s-cis-* and *s-trans-*μ-butadiene-2,3-diyldiplatinum complexes, which may provide the first examples of butadiene-2,3-diyl dinuclear complexes, though a large number of studies have been made on the chemistry of hydrocarbon-bridged multinuclear complexes[6] including μ-butadienediyl complexes.[7]

Treatment of μ-ethynediyldiplatinum complex **1a** with TCNE (Scheme 1) in refluxing benzene gave a green solution, suggesting the formation of a charge-transfer (CT) complex.[3] Then, the reaction mixture changed to orange with the progress of the reaction. After 5 h a yellow compound **2a**, which is stable in air even in solution, was isolated as crystals in 56% yield. In the FAB MS the molecular ion (m/z = 916) was observed, indicating that the product **2a** must be derived from one molecule of **1a** and one molecule of TCNE, and the result of elemental analyses also supported the composition of **2a**. The ^{31}P NMR spectrum of **2a** revealed AB quartet signals at δ −5.64 ($^1J_{Pt-P}$ 2607 Hz) and −7.35 ($^1J_{Pt-P}$ 2616, $^4J_{Pt-P}$ 38 Hz), and the coupling constant of $^2J_{P-P}$ 423 Hz indicates a *trans* conformation around the Pt atom. In order to establish the structure of **2a**, we have carried out an X-ray diffraction analysis.†

As shown in Fig. 1, two platinum atoms having a square-planar geometry are linked by an *s-cis*-butadiene-2,3-diyl bridge, which was made from the μ-ethynediyl group and TCNE. Two Pt–C bond distances are 2.00(1) and 2.005(10) Å, which agree with those of vinylplatinum[8] and butadienylplatinum complexes.[9] The bond lengths of the butadienediyl bridge are 1.37(1) for C(1)–C(2), 1.47(1) for C(1)–C(5) and 1.36(1) Å for C(5)–C(6), respectively. These values are comparable with those of the μ-butadiene-1,4-diyldiiron complex.[7] The torsion angle of C(2)–C(1)–C(5)–C(6) is 55(1)°, which is slightly smaller than those of the reaction products of mononuclear acetylide complexes with TCNE.[3] The dihedral angles between the Pt coordination plane and the $C{=}C(CN)_2$ plane are 91.0 and 91.5°, respectively. The slightly small bond angles of P(1)–Pt(1)–P(2) [158.1(1)°] and P(3)–Pt(2)–P(4) [162.0(1)°] may be due to the steric repulsion between two bulky platinum moieties, and the two coordination planes around Pt atom make a dihedral angle of 45.4°.

Similar treatment of **1b** bearing triethylphosphine ligands afforded orange crystals in 65% yield, and the FAB MS and the result of elemental analysis indicates that the product of the above reaction is also made from one molecule of **1b** and one molecule of TCNE. In the ^{31}P NMR spectrum, however, not only AB quartet signals at δ 13.06 ($^1J_{Pt-P}$ 2495, $^2J_{P-P}$ 423 Hz) and 7.68 ($^1J_{Pt-P}$ 2616, $^2J_{P-P}$ 423, $^4J_{Pt-P}$ 38 Hz) but also a singlet signal at δ 8.00 ($^1J_{Pt-P}$ 2612 Hz) were observed in a 1 : 1 : 2 integral ratio, suggesting that the product is a 1 : 1 mixture of μ-*s-cis*-butadiene-2,3-diyldiplatinum complex **2b** and another complex **3**, which has the same composition as that of **2b**, possessing four magnetically equivalent phosphine ligands. Fortunately, we were able to obtain a single crystal of **3** by



Scheme 1 *Reagents and conditions*: i, TCNE, benzene, reflux, 5 h

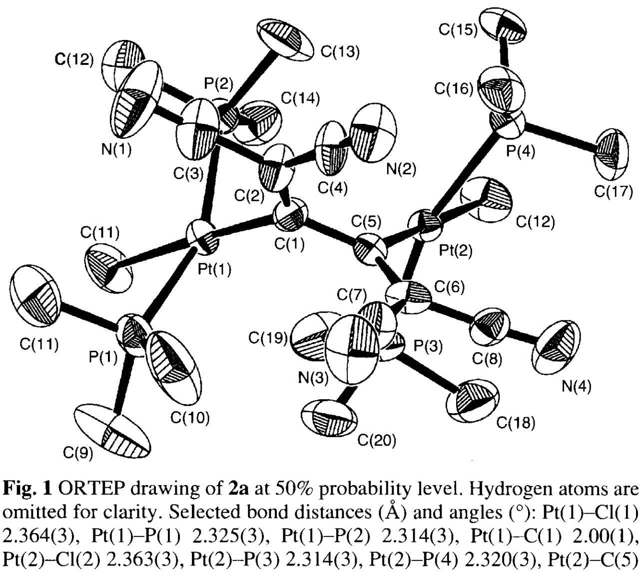


Fig. 1 ORTEP drawing of **2a** at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pt(1)–Cl(1) 2.364(3), Pt(1)–P(1) 2.325(3), Pt(1)–P(2) 2.314(3), Pt(1)–C(1) 2.00(1), Pt(2)–Cl(2) 2.363(3), Pt(2)–P(3) 2.314(3), Pt(2)–P(4) 2.320(3), Pt(2)–C(5) 2.005(10), C(1)–C(2) 1.377(1), C(1)–C(5) 1.47(1), C(5)–C(6) 1.36(1), Cl(1)–Pt(1)–P(1) 86.0(1), Cl(1)–Pt(1)–P(2) 85.4(1), P(1)–Pt(1)–P(2) 158.1(1), P(1)–Pt(1)–C(1) 96.9(3), P(2)–Pt(1)–C(1) 93.7(3), Cl(2)–Pt(2)–P(3) 84.6(1), Cl(2)–Pt(2)–P(4) 84.6(1), P(3)–Pt(2)–P(4) 162.0(1), P(3)–Pt(2)–C(5) 93.8(3), P(4)–Pt(2)–C(5) 97.3(3), Pt(1)–C(1)–C(2) 121.8(8), Pt(1)–C(1)–C(5) 118.8(7), Pt(2)–C(5)–C(1) 118.1(7), Pt(2)–C(5)–C(6) 119.2(8), C(2)–C(1)–C(5) 119.4(10), C(1)–C(5)–C(6) 122.7(10).

recrystallization from dichloromethane–toluene and found **3** to be a μ-*s*-*trans*-2,3-butadienediyldiplatinum complex by an X-ray crystallography.†

The molecule of **3** (Fig. 2) sits on a crystallographic centre of symmetry lying at the mid-point between C(1) and C(1′). Therefore, the *s*-*trans*-butadiene-2,3-diyl group has a planar structure and the two Pt coordination planes are parallel. The C(1)–C(2) and C(1)–C(1′) bond lengths are 1.35(2) and 1.54(3) Å, respectively. The former is slightly shorter and the latter is longer than those of μ-*s*-*cis*-butadienediyl complex **2a**, indicating that π-conjugation of the μ-*s*-butadiene-2,3-diyl group in **3** is smaller than that in **2a** though **3** has a structural advantage for the conjugation. The dihedral angle between the Pt coordination plane and the PtC=C(CN)$_2$ plane is 91.9°.

It should be noted that the isomerization between **2b** and **3** was not observed even at 120 °C in tetrachloroethane. This suggests that the bulky metal moieties and dicyanomethylene groups restrict the rotation around the C–C single bond of the butadiene-2,3-diyl-bridge. It is proposed that complex **2** may be produced by the cycloaddition of TCNE to the C≡C triple bond of **1** followed by the cleavage of the C–C single bond of cyclobutene-1,2-diyl complex, and the mechanism concerning the formation of **3** is now under investigation.

This work was supported by Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236104 from Ministry of Education, Science and Culture. We are grateful to the Materials Analysis Center, ISIR, Osaka University for the support of spectral measurements, X-ray crystallography and microanalyses.

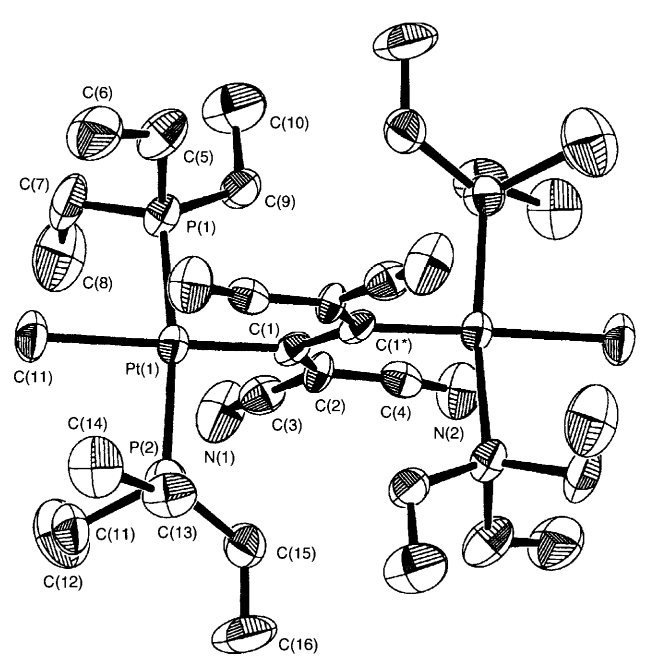


Fig. 2 ORTEP drawing of **3**·2C$_7$H$_8$ at 50% probability level. Hydrogen atoms and the solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Pt(1)–Cl(1) 2.367(4), Pt(1)–P(1) 2.328(4), Pt(1)–P(2) 2.331(4), Pt(1)–C(1) 2.00(1), C(1)–C(1*) 1.54(3), C(1)–C(2) 1.35(2), Cl(1)–Pt(1)–P(1) 86.6(1), Cl(1)–Pt(1)–P(2) 87.2(1), P(1)–Pt(1)–C(1) 92.6(4), P(2)–Pt(1)–C(1) 93.8(4), Pt(1)–C(1)–C(1*) 123(1), Pt(1)–C(1)–C(2) 118.6(10), C(2)–C(1)–C(1*) 117(1).

Received, 19th June 1995; Com. 5/03922C

Footnote

† *Crystal data* for **2a**: $C_{20}H_{36}Cl_2N_4P_4Pt_2$, M_W = 917.51, orthorhombic, space group *Pbca*, a = 18.575(6), b = 21.909(7), c = 15.464(9) Å, V = 6293(3) Å^3, Z = 8, D_c = 1.937 g cm^{-3}, μ(Mo-Kα) = 92.35 cm^{-1}, $6 < 2\theta < 60°$, ω–2θ scan, $R(R_w)$ = 0.039(0.042) for 289 parameters against 4373 reflections [$I > 3\sigma(I)$] out of 9975 unique reflections corrected for absorption using ψ-scan technique, GOF = 1.18. *Crystal data* for **3**·2C$_7$H$_8$: $C_{46}H_{76}Cl_2N_4P_4Pt_2$, M_W = 1270.11, monoclinic, space group $P2_1/c$, a = 13.549(2), b = 14.454(3), c = 13.770(3) Å, β = 90.31(2)°, V = 2697(2) Å^3, Z = 2, D_c = 1.564 g cm^{-3}, μ(Mo-Kα) = 54.85 cm^{-1}, $6 < 2\theta < 50°$, ω–2θ scan, $R(R_w)$ = 0.041(0.046) for 262 parameters against 2370 reflections [$I > 3\sigma(I)$] out of 5002 unique reflections corrected for absorption using ψ-scan technique and decay, GOF = 1.63. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197.

2 H. Masai, K. Sonogashira and N. Hagihara, *J. Organomet. Chem.*, 1971, **34**, 397; K. Onuma, Y. Kai, N. Yasuda and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 1696; A. Davison and J. P. Solar, *J. Organomet. Chem.*, 1979, **166**, C13; P. Hong, K. Sonogashira and N. Hagihara, *J. Organomet. Chem.*, 1981, **219**, 363.

3 M. I. Bruce, J. R. Rogers, M. R. Snow and A. G. Swincer, *J. Chem. Soc., Chem. Commun.*, 1981, 271; M. I. Bruce, T. W. Hambley, M. R. Snow and A. G. Swincer, *Organometallics*, 1985, **4**, 494; M. I. Bruce, T. W. Hambley, M. R. Snow and A. G. Swincer, *Organometallics*, 1985, **4**, 501; M. I. Bruce, T. W. Hambley, M. R. Snow and E. R. T. Tiekink, *J. Organomet. Chem.*, 1986, **303**, 417; M. I. Bruce, D. N. Duffy, M. J. Liddell, M. R. Snow and E. R. T. Tiekink, *J. Organomet. Chem.*, 1987, **335**, 365; M. I. Bruce, D. N. Duffy, M. J. Liddell, M. R. Snow and E. R. T. Tiekink, *Organometallics*, 1988, **7**, 343; M. I. Bruce, T. W. Hambley, M. J. Liddell, M. R. Snow, A. G. Swincer and E. R. T. Tiekink, *Organometallics*, 1990, **9**, 96; M. I. Bruce, D. N. Duffy, M. J. Liddell, E. R. T. Tiekink and B. K. Nicholson, *Organometallics*, 1992, **11**, 1527.

4 H. Ogawa, T. Joh, S. Takahashi and K. Sonogashira, *J. Chem. Soc., Chem. Commun.*, 1985, 1220; H. Ogawa, K. Onitsuka, T. Joh, S. Takahashi, Y. Yamamoto and H. Yamazaki, *Organometallics*, 1988, **7**, 2257; K. Onitsuka, T. Joh and S. Takahashi, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1179.

5 N. Fujita and K. Sonogashira, *J. Polym. Sci., Polym. Chem. Ed.*, 1973, **12**, 1471.

6 J. Halton, M. F. Lappert, R. Pearce and P. I. W. Yarrow, *Chem. Rev.*, 1983, **83**, 135; W. Beck, B. Niemer and M. Wiesser, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 923.

7 M. R. Churchill, J. Wormald, W. P. Giering and G. F. Emerson, *Chem. Commun.*, 1968, 1217; R. E. Davis, *Chem. Commun.*, 1968, 1218; A. Sanders and W. P. Giering, *J. Organomet. Chem.*, 1976, **104**, 67.

8 C. J. Cardin and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1977, 1593.

9 A. Furlani, M. Y. Russo, A. C. Villa, A. G. Manfredotti and C. Gaustini, *J. Chem. Soc., Dalton Trans.*, 1977, 2154; S. A. Benyunes, L. Brandt, A. Fries, M. Green, M. F. Mahon and T. M. T. Papworth, *J. Chem. Soc., Dalton Trans.*, 1993, 3785.