Synthesis, Characterization, and Properties of Ethylene-Coordinated Complexes of β-Platinum(II) Ketones

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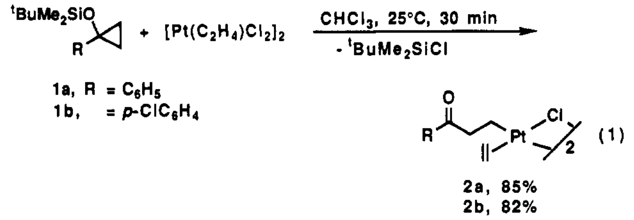
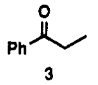
Summary: The reaction of siloxycyclopropanes **1a,b** with Zeise's dimer ($[Pt(C_2H_4)Cl_2]_2$) in $CHCl_3$ yields ethylene-coordinated β-platinum ketones **2a,b** in high yields, respectively. The structure of **2b** has been determined by X-ray diffraction methods, showing a chloride-bridged dimeric structure. Treatment of **2a** with carbon monoxide gives the monomeric CO complex **3a**, which has intramolecular coordination of the carbonyl group.

Metal-induced ring opening of cyclopropanes is of considerable interest in terms of an easy access to metal–carbon σ bonds.[1] Above all, siloxycyclopropanes 1 are noteworthy because of their marked reactivity toward a wide range of metal salts as well as synthetic utility.[2] We have previously revealed that the ring opening of 1 with metal salts occurred between siloxy and adjacent carbons and usually brought about the desilylation to form stable or intermediary β-metallo ketones.[3,4] In this context we were particularly intrigued by the possibility of the formation of stable β-platinum ketones by the ring opening of 1 with Zeise's dimer,[5] although unfunctionalized cyclopropanes are known to react with this platinum complex to give platinacyclobutanes.[6] Very recently Jennings et al. have reported their work on the reaction of a tetrasubstituted cyclopropane, a methoxy group being one of the substituents, with Zeise's dimer.[7] This has prompted us to present our results, and we report here the first isolation and characterization of the ethylene complexes of β-platinum ketones 2, which were quite smoothly allowed by this reaction.

The reaction of the (1-phenyl)siloxycyclopropane compound **1a** with $[Pt(C_2H_4)Cl_2]_2$ in $CHCl_3$ took place readily with liberation of a chlorosilane to give an orange solution of β-platinum ketone **2a**. Dropping the solution into pentane, followed by recrystallizing from toluene, allowed the isolation of **2a** as white microcrystals (mp 102–104.5 °C dec).[8] The ^{1}H NMR measurement suggested the formation of an ethylene complex of β-platinum ketone **2a**, giving a singlet at δ 3.85 ($^2J_{Pt-H}$ = 79 Hz, 4 H) for ethylene protons, a triplet at δ 1.55 ($^2J_{Pt-H}$ = 72 Hz, 2 H) for methylene protons on the carbon at the α-position from platinum, and a triplet at δ 2.98 ($^3J_{Pt-H}$ = 29 Hz, 2 H) for methylene protons on the β-carbon. In the IR spectrum a normal C–O stretching frequency was observed at 1684 cm^{-1}. To define the geometry at the Pt atom, an X-ray structure analysis of **2b**,[9] which was prepared from the (*p*-chloro-1-phenyl)siloxycyclopropane compound **1b** in the same way, was carried out (Figure 1).[10] The strikingly simple structure of this complex features the chloride-bridged dimer and the expected square-planar geometry of the Pt(II) atoms, in which the ethylenes are almost perpendicular.[11]



The β-platinum ketones are air-stable for several days but are quite labile to acids. For example, the reaction of **2a** with HCl (from $Me_3SiCl + H_2O$) gave propiophenone (3) quantitatively with the regeneration of Zeise's dimer.



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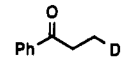

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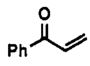

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Reductive Pt–C cleavage of **2a** with Me_3SiD also took place readily to give β-deuteriopropiophenone (4) in high yield together with unidentified black precipitates. β-Elimination of **2a** occurred instantly on addition of 1 equiv of

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(1) For reviews, see: (a) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461. (b) Crabtree, R. H. *Ibid.* **1985**, *85*, 245. (c) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C. *Ibid.* **1989**, *89*, 165.

(2) For reviews, see: (a) Ryu, I.; Sonoda, N. *J. Synth. Org. Chem., Jpn.* **1985**, *43*, 112. (b) Nakamura, E. *Ibid.* **1989**, *47*, 931.

(3) (a) Ryu, I.; Murai, S.; Matsumoto, K.; Ando, M.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283. (b) Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7192. (c) Ryu, I.; Ogawa, A.; Sonoda, N. *Nippon Kagaku Kaishi* **1985**, 442; *Chem. Abstr.* **1985**, *103*, 214888q. (d) Ryu, I.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1986**, *51*, 2389. (e) Ryu, I.; Suzuki, H.; Ogawa, A.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1988**, *29*, 6137. (f) Nakahira, H.; Ryu, I.; Han, L.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1991**, *32*, 229. Cf.: (g) Aoki, S.; Fujikura, T.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1988**, *110*, 3296. (h) Ito, Y.; Inoue, M.; Suginome, M.; Murakami, M. *J. Organomet. Chem.* **1988**, *342*, C41.

(4) Some metal salts, such as ZnI_2 and $[Rh(CO)_2Cl]_2$, induced isomerization of 1 to allyl silyl ethers and/or enol silyl ethers; see: (a) Ryu, I.; Aya, T.; Otani, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* **1987**, *321*, 279. (b) Ikura, K.; Ryu, I.; Ogawa, A.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1989**, *30*, 6887.

(5) Taken in part from: Ikura, K. B.S. Thesis, Osaka University, Suita, Osaka, Japan, 1988.

(6) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, p 573.

(7) Hoberg, J. O.; Larsen, R. D.; Jennings, P. W. *Organometallics* **1990**, *9*, 1334.

(8) Spectroscopic and analytical data for complex **2a**: mp 102–104.5 °C dec; IR (KBr) 3060, 2919, 1684, 1609, 1448, 1358, 1214, 757, 689 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.01 (d, 2 H, J_{H-H} = 7.3 Hz), 7.59 (t, 1 H, J_{H-H} = 7.3 Hz), 7.46 (t, 2 H, J_{H-H} = 7.3 Hz), 3.80 (s, 4 H, $^2J_{Pt-H}$ = 81 Hz), 2.99 (t, 2 H, $^3J_{Pt-H}$ = 27 Hz, J_{H-H} = 7.3 Hz), 1.49 (t, 2 H, $^2J_{Pt-H}$ = 67 Hz, J_{H-H} = 7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 202.4, 136.2, 133.4, 128.6, 40.4 ($^2J_{Pt-C}$ = 27 Hz), 6.3 ($^1J_{Pt-C}$ = 700 Hz). Anal. Calcd for $C_{22}H_{26}O_2Cl_2Pt_2$: C, 33.73; H, 3.34. Found: C, 33.89; H, 3.27.

(9) Spectroscopic and analytical data for complex **2b**: mp 127–127.5 °C dec; IR (KBr) 3074, 2936, 2879, 1683, 1589, 1487, 1395, 1352, 1211, 1092, 1013, 964, 520, 421 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.92 (d, 2 H, J_{H-H} = 8.8 Hz), 7.43 (d, 2 H, J_{H-H} = 8.8 Hz), 3.80 (s, 4 H), 2.93 (t, 2 H, $^3J_{Pt-H}$ = 25 Hz, J_{H-H} = 7.3 Hz), 1.47 (t, 2 H, $^2J_{Pt-H}$ = 74 Hz, J_{H-H} = 7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 201.7, 139.9, 134.4, 130,0, 129.0, 40.4 ($^2J_{Pt-C}$ = 29 Hz), 6.0 ($^1J_{Pt-C}$ = 702 Hz). Anal. Calcd for $C_{22}H_{24}O_2Cl_4Pt_2$: C, 31.00; H, 2.84. Found: C, 30.85; H, 2.81.

(10) Crystals of **2b** were grown from chloroform/cyclohexane. Crystal data: $C_{22}H_{24}O_2Cl_4Pt_2$, M_r = 852.40, triclinic, space group $P\bar{1}$, a = 4.986 (3) Å, b = 6.587 (3) Å, c = 18.790 (17) Å, α = 91.32 (7)°, β = 91.32 (7)°, γ = 81.21 (8)°, V = 603.3 (7) Å^3, Z = 1, D_c = 2.346 g cm^{-3}, λ(Mo Kα) = 0.7107 Å, μ = 126.4 cm^{-1}, $F(000)$ = 396, θ–2θ scan method. The structure was solved by the heavy-atom method and refined anisotropically by a block-diagonal least-squares procedure. R = 0.069 for 1579 unique observed reflections ($|F_o| \geq 2\sigma(F_o)$, $2\theta \leq 50°$).

(11) To our knowledge, such types of platinum complexes having the alkyl-substituted structure of Zeise's dimer have rarely been seen except for the methyl Pt(II) complex $[Pt_2(\mu\text{-}Cl_2)Me_2(C_2H_4)_2]$; see: Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 1253.

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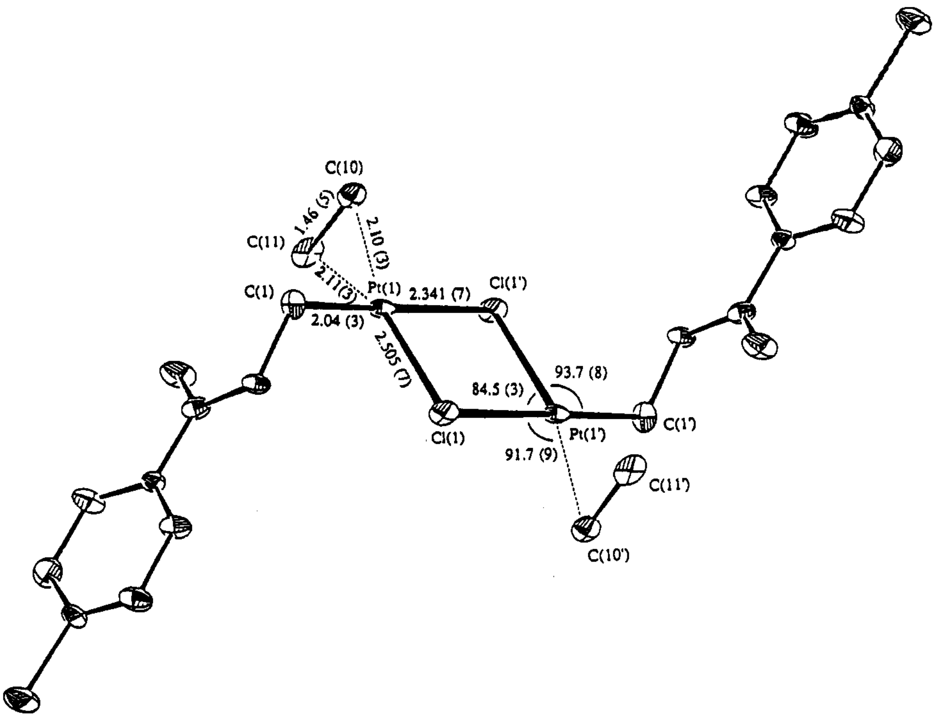
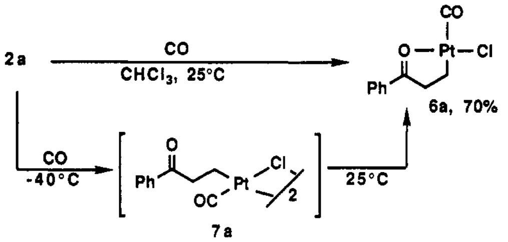


Figure 1. ORTEP drawing of complex **2b**. The molecule lies on the crystallographic center of symmetry. Selected bond distances (Å) and angles (deg) are shown.

Scheme I



diisopropylamine to give the α,β-unsaturated ketone **5** in 88% yield.[12]

The ligand exchange of **2a** with carbon monoxide was quite intriguing since the participation of an internal carbonyl group was also observed (Scheme I). Bubbling of carbon monoxide into a $CHCl_3$ solution of **2a** at 25 °C gave the monomeric CO complex **6a** (70%). The structural and stereochemical formulation was consistent with the spectroscopic data:[13] two C–O stretching frequencies (2071 and 1535 cm^{-1}) showed the coordination of carbon monoxide and an internal carbonyl oxygen to platinum, and the low coupling constant at δ 8.8 ($^1J_{Pt-C}$ = 550 Hz) could be attributed to the alkylplatinum group trans to carbon monoxide rather than trans to Cl.[14] This result is in contrast with the reaction of the methyl(ethylene)platinum analogue with carbon monoxide to form the dimeric CO complex $[Pt_2(\mu\text{-}Cl)_2Me_2(CO)_2]$.[12] However, when this reaction was monitored by low-temperature ^1H NMR spectroscopy (−40 °C, $CDCl_3$), distinct peaks were observed[15] at δ 3.55 (t, 2 H, $^3J_{Pt-H}$ = 26 Hz) and δ 2.26 (t, 2 H, $^2J_{Pt-H}$ = 64 Hz), which might indicate the formation of the dimeric complex **7a**. The complex **7a** was thermally unstable, and an increase of temperature readily allowed the conversion of **7a** into **6a**.

It should be noted that we have encountered the formation of (siloxy)alkenes, ring-opened isomers of **1**, when 2-alkyl-substituted siloxycyclopropanes were employed as the substrates. This might suggest that the ring opening of **1** with Zeise's dimer includes the intermediacy of platinacyclobutanes at the first step.[16,17] Such an additional aspect of the reaction of **1** with Zeise's dimer will be reported in due course.

Acknowledgment. This work was supported by a Grant-in-Aid from the Ministry of Education, Science and Culture of Japan. We thank the Research Center for Protein Engineering, Institute for Protein Research, Osaka University, for the use of their computer. We thank Professors S. Murai and H. Kurosawa for their helpful discussions.

Supplementary Material Available: Listings of atomic positional and thermal parameters, bond lengths, and bond angles (3 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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[12] (12) For β-hydride elimination from β-Pd(II) ketones and β-Cu(II) ketones, see refs 3a,c.

[13] (13) Spectroscopic and analytical data for complex **6a**: mp 138–140 °C dec; IR (KBr) 3051, 2965, 2071, 1598, 1586, 1535, 1449, 1372, 1247, 681, 552 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 8.17 (d, 2 H, J_{H-H} = 7.8 Hz), 7.79 (t, 2 H, J_{H-H} = 7.3 Hz), 7.54 (dd, 2 H, J_{H-H} = 7.8, 7.3 Hz), 3.78 (t, 2 H, $^3J_{Pt-H}$ = 24 Hz, J_{H-H} = 5.9 Hz), 2.56 (t, 2 H, $^2J_{Pt-H}$ = 44 Hz, J_{H-H} = 5.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 214.0, 157.0, 138.0, 131.7, 129.6, 44.7, 8.8 ($^1J_{Pt-C}$ = 550 Hz). Anal. Calcd for $C_{10}H_9O_2ClPt$: C, 30.66; H, 2.32. Found: C, 30.80, H, 2.34.

[14] (14) (a) Chisholm, M. H.; Clark, H. C.; Manzer, L. E.; Stothers, J. B.; Ward, J. E. H. *J. Am. Chem. Soc.* **1973**, *95*, 8574. (b) Browing, J.; Goggin, P. L.; Goodfellow, R. J.; Hurst, N. W.; Mallison, L. G.; Murray, M. *J. Chem. Soc., Dalton Trans.* **1978**, 872. (c) Chinakov, V. D.; Il'inich, G. N.; Zudin, V. N.; Likholobov, V. A.; Nekipelov, V. M. *J. Organomet. Chem.* **1989**, *366*, 421. A reviewer has suggested that observed the low $^2J_{Pt-H}$ value (44 Hz at δ 2.56) in the ^1H NMR spectrum may be due to the metallacycle structure of **6a**.

[15] (15) δ 8.19 (d, 2 H, J_{H-H} = 7.3 Hz), 7.83 (t, 1 H, J_{H-H} = 7.4 Hz), 7.47 (dd, 2 H, J_{H-H} = 7.4, 7.3 Hz), 3.55 (t, 2 H, $^3J_{Pt-H}$ = 26 Hz, J_{H-H} = 5.9 Hz), 2.26 (t, 2 H, $^2J_{Pt-H}$ = 64 Hz, J_{H-H} = 5.9 Hz).

[16] (16) The formation of olefins from platinacyclobutanes (pyridine complexes) has precedents; for example: Johnson, T. H.; Cheng, S.-S. *J. Am. Chem. Soc.* **1979**, *101*, 5277.

[17] (17) To our best of our knowledge, the fate of an ethylene ligand associated with the formation of platinacyclobutanes from Zeise's dimer and cyclopropanes is still ambiguous.[6] In this context, we are attracted by the possibility of *ethylene-coordinated* platinacyclobutanes as the key intermediates leading to ethylene complexes **2**. However, there still remains an alternative mechanism involving the ionic cleavage of **1** followed by desilylation, as in the ring opening of **1** by other metal ions.[3]