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Heterometallic Bismuth–Platinum complex has strong Bi–Pt bond and ionic cage surrounding Bi ion and exhibits electrocatalytic CO₂ reduction.

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Ionic-Caged Heterometallic Bismuth–Platinum Complex Exhibiting Electrocatalytic CO₂ ReductionReceived 00th January 20xx,
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An air-stable heterometallic Bi–Pt complex with the formula [BiPt(SAC)₅]_n (**1**; SAC = thioacetate) was synthesized. The crystal structure, natural bond orbital (NBO) and local orbital locator (LOL) analyses, localized orbital bonding analysis (LOBA), and X-ray absorption fine structure (XAFS) measurements were used to confirm the existence of Bi–Pt bonding and an ionic cage of O atoms surrounding the Bi ion. From the cyclic voltammetry (CV) and controlled potential electrolysis (CPE) experiments, **1** in tetrahydrofuran reduced CO₂ to CO, with a faradaic efficiency (FE) of 92% and a turnover frequency (TOF) of 8 s^{−1} after 30 min of CPE at −0.79 V vs. NHE. The proposed mechanism includes an energetically favored pathway via the ionic cage, which is supported by the results of DFT calculations and reflectance infrared spectroelectrochemistry data.

Introduction

Donor-acceptor heteroatomic systems, such as M–E¹ and Ln/An–M complexes² and M–M' complexes/clusters³ (M: metal, E: main group element, Ln: lanthanoid, An: actinoid) have been studied in the fields of catalysis,^{1a,2a,3a,3f} magnetism,^{2f,2i} and luminescence.^{2g,3g,3h} These compounds show unique properties not expected from the individual types of atoms they contain. The heteroatomic bond/interactions can be used to tune the electron density of the donor and acceptor ions/atoms. Thus, scientists have designed heteroatomic compounds by changing the combination of atoms and ligands.

Bismuth (Bi) complexes have been used as catalysts because of their Lewis acidities and low toxicity.⁴ Rosenthal *et al.* developed Bi-based cathodes with active sites for CO₂

reduction.⁵ They reported that CO₂ was reduced to CO with high faradaic efficiency (FE) at a low applied overpotential. As mentioned above, the Bi ion has a strong impact on the electrocatalytic reduction of CO₂.

Donor-acceptor complexes with heterometallic Bi–M bond are potentially good catalysts,⁶ because the Bi–M interactions can be used to adjust the Lewis acidity of the Bi ion or the Lewis basicity of the M ion by changing the bond distance. Recently, Fürstner *et al.* reported that a Rh–Bi complex with weak Rh–Bi π -interactions catalyzes the conversion of small molecules.^{6a} Furthermore, Limberg *et al.*^{6b} and Braunschweig *et al.*^{6c} have reported Bi–Pt complexes with Bi–Pt bonds. Limberg *et al.* also indicated that their complexes have potential applications as catalysts, due to the Lewis basicity of the Pt ion and the Lewis acidity of the Bi ion. Their characterization of the Bi(6p_z)–Pt(5d_{z²}) bonds revealed that there is a Pt→Bi donative bond for the Bi^{III} ion, where the Pt^{II} ion has a square pyramidal geometry and the Bi ion forms Bi–Cl bond along the axial site (Fig. 1a).^{6o} In another Bi–Pt complex, the Pt⁰ atom has Pt–Bi covalent bond and a square planar geometry, and the Bi ion has no axial ligand (Fig. 1b).^{6o}

In this work, we synthesized an air-stable heterometallic Bi–Pt complex [BiPt(SAC)₅]_n (**1**) to explore the new electronic state, Bi–Pt bonding feature, and catalytic property. The existence of heterometallic Bi–Pt covalent bond was confirmed, where the Pt ion forms a Pt(BiS₅) octahedral geometry and the Bi ion has a Bi(PtO₅) pentagonal pyramidal geometry. Meanwhile, the Bi ion and O atoms form ionic bonds (we call this surrounding structure an “ionic cage”) according to the crystal structure analysis, theoretical calculations, and spectroscopic measurements. This characteristic structure is also supported by the donation of S atoms in the ligand to the Pt atom. DFT calculations provided further evidence for the structure of **1**,

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† Electronic supplementary information (ESI) available: X-ray crystallographic data for **1**. CCDC. For ESI and crystallographic data in CIF or other electronic format see DOI:

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while the mass spectrometry results indicated that it is stable in solution. In catalysis experiments, **1** demonstrated the ability to reduce CO₂ with a high FE.

Results and discussion

An ORTEP diagram of **1** is shown in Fig. 1c. The Pt ion is hexacoordinated, whereas the Bi ion is in a pentagonal pyramidal environment. Since this structure is different from the reported Bi–Pt complexes,^{6b,6c,6o} we expect **1** to have a unique electronic state (Fig. 1). Four SAC[−] ligands are coordinated to the Pt ion through the S donor atoms (the PtS₄ plane) and to the Bi ion via the O donor atom (the BiO₄ plane), forming a paddlewheel-like moiety ([BiPt(SAC)₄]⁺). These moieties are bridged by another SAC[−] ligand, so that the S atom is coordinated to the axial site of Pt ion, and the O atom is coordinated to the in-plane site (equatorial plane) of the Bi atom. The coordination distance between the Pt ion and axial S atom was determined to be 2.489 Å, which is close to the Pt^{III}-to-axial ligand distance.⁷ The distance between the Pt and Bi ions was 2.653 Å. This value is around 6.6% shorter than the sum of the calculated covalent radii⁸ (cf. Rh–Bi complex:^{3m} 13% shorter) and the same as the Bi–Pt covalent bond (cf. 2.664 Å).^{6o} In addition, this value is shorter than that of Bi(1,2)–Pt(1) covalent bond of a metal cluster (Bi₁₆Pt₁₁I₆.^{3p} cf. 2.666 Å), where Bi(1) forms the [Bi^{III}I₄]^{2−} unit and the Bi(2) metal only has strong interaction with Pt(1) metal. The S_{axis}–Pt–Bi angle in **1** was 173.72°. These results indicate that there should be strong interactions between the Bi and Pt ions.

Fig. 1. Reported structures with (a) donative and (b) covalent Pt–Bi bond, and the associated coordination.^{6o} (c) ORTEP diagram of [BiPt(SAC)₅] (**1**) with thermal ellipsoids at 60% at room temperature and (d) structure of **1** (red: O atoms, yellow: S atoms, white: C atoms, orange: P atoms). All H atoms were omitted for clarity.

An energy diagram for **1** from density functional theory (DFT) calculations is shown in Fig. 2a. The highest occupied

Fig. 2. (a) Energy diagram of **1**. The free S atom of the ligand is actually coordinated to the Pt ion in the solid state. However, we omitted the chain structure to simplify the calculation. (b) Contour maps of the local orbital locator (LOL) for **1** in the Bi–Pt plane. (c) LOL isosurface showing the degree of the polarizing power and the polarizability of the Bi and Pt ions, respectively. The C and H atoms and one of the O atoms were omitted for clarity.

molecular orbital (HOMO) is a filled antibonding orbital ((Pt(d_{z^2}) + L_{axial}) + Bi($6p_z$) + L^*). (Two occupied orbitals that come from the free S atom are higher in energy than this HOMO. However, those orbitals are much more stable due to their coordination to the Pt ion in the solid state.) The solid-state UV/vis spectrum of **1** showed peaks at around 3.0, 3.6, and 4.5 eV (Fig. S1). The results of time-dependent DFT (TDDFT) calculations matched the experimental spectra, and we assigned each of the peaks as a transition from the Pt ion to the Bi ion. The results of natural bonding orbital (NBO) analysis, shown in Fig. S2, indicate that there are several interactions between the Bi and Pt ions. The energy of the interaction between Pt(d_{z^2}) and Bi($6p_z$) orbitals was calculated to be 179.12 kcal/mol, which is similar to that for a covalent bond. The interaction energies from Pt–S σ orbitals to the Bi($6p_z$) orbital were calculated to be ~12 kcal/mol for the equatorial Pt–S σ orbitals and 15.31 kcal/mol for the axial Pt–S σ orbital. Furthermore, there are interactions between the Bi($6s$) and Pt–S σ^* orbitals (~6 kcal/mol for the equatorial Pt–S σ^* orbitals and 26.64 kcal/mol for the axial Pt–S σ^* orbital). These interactions are much stronger than those of other

reported Bi–Pt complexes,^{6b} strongly supporting the presence of Pt–Bi bond.

To further understand the nature of bonding between the Bi and Pt ions, localized orbital locator (LOL, v_o) analysis was carried out (Fig. 2b,c).⁹ v_o was scaled by using the Kohn-Sham kinetic energy density ratio between the instantiated molecular system and a homogeneous electron gas. A region with a high v_o value indicates high electron localization at the atomic shells, covalent bonds, and lone pairs. A local maximum (3, –3) critical point ($v_o = 0.525$) was observed between the Bi and Pt ions (Fig. 2b). A large independent domain was found between the two atoms in the $v_o = 0.35$ isosurface plot (Fig. 2c). These results suggest that there is strong bonding between the two atoms, because the electrons surrounding the attractor ($v_o > 0.5$) have lower kinetic energy. The other two peaks on the left and right of Fig. 2b were assigned to the sub-valence shells of the Bi and Pt ions. The v_o dropped down to zero near the core region because the pseudopotential was applied. These results are also strong evidence for the presence of Bi–Pt covalent bond.

The Raman spectrum of **1** is shown in Fig. S3. Peaks at 124, 151, 217, 235, and 271 cm^{-1} (optical window of setup $> 110 \text{ cm}^{-1}$) were assigned to the ^{194,195,196}Pt–Bi stretching mode and its overtone, on the basis of reported values for M–M stretching modes.^{6a,10} The peaks at 388 and 531 cm^{-1} were assigned to the M–ligand stretching modes. These results also indicate the presence of the Pt–Bi bond.

Fig. 3. XANES of **1** (red) and two standard samples (black: Bi_2O_5 , blue: BiCl_3) at the Bi- L_3 -edge.

Further evidence for the Bi–Pt bond came from the X-ray absorption fine structure (XAFS) measured for **1** at room temperature. The X-ray absorption near edge structures (XANES) at the Bi L_3 -edge and Pt L_3 -edge are shown in Fig. 3 and S4. The white line (peak) around the Bi L_3 -edge of **1** was shifted from 13430 and 13433 eV (the respective energies at 0.5 normalized absorption for the standard samples $\text{Bi}^{\text{III}}\text{Cl}_3$ and $\text{Bi}^{\text{V}}_2\text{O}_5$) to 13428 eV. In addition, the white line (peak) around the Pt L_3 -edge of **1** was shifted from 11563 eV (the position of white line is the same as that for PtCl_2) to 11565 eV. Although the apparent oxidation states of the ions in **1** are $[\text{Bi}^{\text{III}}\text{Pt}^{\text{II}}(\text{SAC}^-)_5]_n$, the results above indicate that the oxidation state of Bi ion here is lower than trivalent (probably between monovalent and trivalent),^{5e,11} and that of the Pt ion is higher than divalent. In other words, the electrons of the Pt ion are donated to the Bi

ion, leading to a fractional decrease in the oxidation state of the latter. These results agree with the crystal structure analyses and theoretical calculations discussed earlier.

To determine the exact oxidation states and the extent of Bi–Pt bonding interaction in **1**, localized orbital bonding analysis (LOBA)¹² was employed and implemented in Q-Chem software package.¹³ Table S3 shows the LOBA for all atoms in **1**. Here, we expect to see contributions for Bi–O dative bonding, in which some of the participating electrons should be localized on both Bi and O. Surprisingly, we did not observe any Bi–O bonding localization. The implication is that the Bi is not datively linked to O as expected from the bonding molecular orbital (MO). Rather, the Bi–O interaction is predominantly non-bonding, causing the Bi to sit in an ionic cage surrounded by negatively charged oxygen. This arrangement also has implication for the redox activity of **1**, as will be discussed below.

The LOBA results show a strong interaction between Bi and Pt (MO 105 in Tables S2 and S3). This interaction is composed of the d-orbitals (61%, essentially d_{z^2}) of platinum and the p-orbitals (35%, essentially p_z) of bismuth. The electron density of the Bi–Pt bond pair is localized on Bi (0.71 electrons) and Pt (1.2 electrons). This further justifies the percentage contribution above, suggesting an MO that is predominantly of Pt character. In the typical M–M bonding, each participating metal contributes a single electron.¹⁴ However, LOBA shows that the bond pair here is contributed by Pt d_{z^2} on the z-axis (Bi–Pt bond axis). This interaction is compensated by a strong and concerted Pt–S interaction, leading to more electron density being transferred from S atoms to Pt, as indicated by the almost 25% share of the Pt–S bond pairs on Pt (Tables S2 and S3). The exact oxidation state (Ox. St) of the corresponding metal ions is calculated using the effective core potential (ECP) as modified in formula 1.¹²

Ox. St = total electron excluding ECP cores – (sum of a and b electrons over 60% threshold) (1)

The oxidation state of Bi is clearly computed as +2.6, which agrees with the experimental results from XANES. The oxidation state of Pt was determined in the same way while considering the average equatorial sulfur donation (0.5555 electrons) and the axial sulfur donation (0.312 electrons), giving an oxidation state of +2.4.

The electrocatalytic activity of **1** towards the reduction of CO_2 in tetrahydrofuran (THF) containing 0.10 M tetrabutylammonium hexafluorophosphate (TBAF_6) as a supporting electrolyte was investigated by using cyclic voltammetry (CV) and controlled potential electrolysis (CPE) with glassy carbon working electrode. The CV curves of **1** under an N_2 atmosphere and CO_2 -saturation conditions without proton source are shown in Fig. S8. There are peaks at –0.20, –0.62, and –1.15 V vs. NHE with 47, 63, 94 μA under N_2 . After saturating the solution with CO_2 , the currents of the reduction processes at –0.22, –0.65, and –1.13 V vs. NHE increased, and the broad oxidation processes were at 0.2, –0.05, and –0.91 V vs. NHE. Complex **1** under CO_2 -saturation conditions exhibited the largest increase in the current for CO_2 reduction as

compared to the results under N_2 . However, there is an irreversible signal at around -1.25 V vs. NHE, because the reduced CO_2 needs to take proton from somewhere. Thus, trifluoroethanol (TFE) was used as a proton source.

Fig. 4. CV curves of 5 mM **1**. Black: under N_2 , red: under CO_2 . Reactions were carried out in THF with 0.1 M TBAPF₆ supporting electrolyte at a scan rate of 0.1 V/s using glassy carbon working electrode.

The CV curves of **1** with proton source under an N_2 atmosphere and CO_2 -saturation conditions are shown in Fig. S8a. There are peaks at -0.35 , -0.67 , and -0.80 V vs. NHE with 37, 47, and 52 μA under N_2 . The peak at -1.15 V vs. NHE without proton source was dramatically shifted to -0.80 V vs. NHE with proton source, because the reduced species was stabilized by the proton. In addition, the difference between $E(\text{reduction})$ and $E(\text{oxidation})$ decreased with a proton source. After saturating the solution with CO_2 , the currents of the reduction processes at -0.33 , -0.61 , and -0.79 V vs. NHE increased, and there was a broad oxidation process in the E range of -0.4 to -0.9 V vs. NHE because two oxidation processes overlapped. Complex **1** under CO_2 -saturation conditions exhibited the largest increase in CO_2 reduction current as compared to the results under N_2 . From the CV curves with various scan rates (Figs. S8, S9), the diffusion coefficient (D) of **1** in THF was calculated as 3.3×10^{-5} cm²/s by the Randles-Sevcik equation (Equation S1 in Electronic Supporting Information).¹⁵

To confirm the stability of the reduced species, we measured the XAFS spectra of **1** in the solid state, the solution of **1**, and the solution of reduced **1** (produced with an excess amount of CoCp₂ and proton source). We used CoCp₂ for the chemical reduction. Without proton source, **1** was decomposed by CoCp₂ after several minutes in solution, forming an insoluble red precipitate (probably Pt salt). On the other hand, with proton source, **1** was stable in solution without producing any precipitate. These phenomena were similar to the situation of electrochemical reduction. The Pt L₃-edge spectrum is shown in Fig. S4. The Fourier transforms of extended X-ray absorption fine structure (EXAFS) of **1** in the solid state, the solution of **1**, and the solution of reduced **1** are almost identical, indicating that all of them have similar coordination environments around

the Pt ion (Fig. S4). These results suggest that the Bi–Pt bond and the structure were maintained during redox reaction.

The mass spectrum (Fig. S5) shows that **1** is stable in solution. We optimized the [BiPt(SAc)₄]⁺ paddle-wheel structure (Fig. S6) and performed TDDFT calculations (Fig. S7) to confirm the molecular structure in solution, using a model including CH₂Cl₂ because of the relatively large optical window and the similar spectra of **1** in CH₂Cl₂ and THF. The results of the TDDFT calculations supported that **1** has a paddle-wheel structure in solution.

To understand the electrochemical process, we assigned each CV peak. The first redox pair centered at ca. -0.28 and -0.64 V vs. NHE come from the dissociation of the solvent molecule from the Pt ion and the dimerization process, respectively.¹⁶ The pair centered at ca. -0.80 V vs. NHE were assigned to the redox reactions of [BiPt(SAc)₄]⁺ $\leftrightarrow$ [BiPt(SAc)₄][−] on the basis of the theoretical value of -0.78 V vs. NHE as determined using the model shown in Figure S9.¹⁷ The current of the reduction peak at -0.79 V vs. NHE was increased dramatically by the CO_2 reduction process. The cathodic current of **1** is comparable with those of Bi-based cathode system^{5a} and Pt(II) complexes.¹⁸

A proposed mechanism of CO_2 reduction is shown in Figure 5, together with the results of DFT calculations focusing on the axial [Bi(p_z) + Pt(d_{z²)] orbital (AO) and differences in the Gibbs free energy. Here, we initially considered Pt ion as a possible reaction site, but excluded it for the following reasons. (i) The orbital of the Bi ion in the reduced species extends out from the O₄ plane, whereas that of the Pt ion does not. (ii) A part of the electron density of the Pt(d_{z²) orbital is donated to the Bi ion. (iii) The Pt ion undergoes an energetically less favored pathway (which will be further discussed in the Electronic Supporting Information).}}

After the solvent molecule dissociates from the Pt ions, there is no electron at the AO in the solution because there is no axial ligand. At -0.79 V, the reduced species is formed ([BiPt(SAc)₄]⁺ $\rightarrow$ [BiPt(SAc)₄][−]) and AO becomes occupied by electrons (step A). Here, the Bi ion changes from electrophilic to nucleophilic. The C atom of the CO_2 molecule approaches the Bi ion and stabilizes the AO (step B). This pathway is energetically disfavored by a small amount of 4 kcal/mol. Then, two H⁺ approach the O atom of CO_2 stepwise, and the protonation dramatically stabilizes the AO (step C). The second protonation induces the H₂O and CO ligands to withdraw electrons from the AO (step D). Step C and step D occur with energies of 29 and 44 kcal/mol, respectively, both on the same order as that for molecule-based reaction.¹⁹ Then, two additional electrons are provided to the AO by the electrode. The Bi ion can subsequently release H₂O and CO, and the reduced species are re-produced ((D) $\rightarrow$ (A): 59 kcal/mol). However, **1** can undergo an energetically more favored pathway via the ionic cage. In this pathway, CO moves to an equatorial site, where its p_z orbital is stabilized by back donation from AO (step E). These processes occur with an energy change of -168 kcal/mol (-0.80 V vs. NHE)¹⁷. One SAc moves to the axial site of the Pt ion (the axial orbitals are stabilized by the S atom), and the coordinated H₂O

Fig. 5. Proposed mechanism and results of DFT calculation, with special focus on the axial $[\text{Bi}(p_2) + \text{Pt}(d_2^2)]$ orbital (AO) and the differences of Gibbs free energy.

moves to an equatorial site (step F). Then, the coordination geometry of the Bi ion becomes pentagonal pyramidal or the ionic cage, like that in the solid state (Pt ion forming a $\text{PtS}_3\text{Bi}\cdots\text{S}$ square pyramidal structure). This process occurs spontaneously with an energy change of -20 kcal/mol. Finally, the Bi ion releases CO with an energy increase of 37 kcal/mol, because there is no donative bond between the Bi ion and CO. This mechanism proposed for the catalyst suggests not only its further potential for CO_2 reduction but also various other catalytic reactions.²⁰

As additional evidence for the proposed mechanism, we measured the reflectance infrared spectra during electrolysis (Fig. 6). (We avoid discussing the peaks around $2300\text{--}2400\text{ cm}^{-1}$, because they could not be distinguished from those of free CO_2 and other species.) The peak at 1720 cm^{-1} is assigned to the C=O stretching mode of SAc ligands, being shifted from that of **1** with N_2 (1563 cm^{-1}) by coordinating the CO_2 . We observed sharp peaks at 1640 and 1960 cm^{-1} . These peaks are within the region of C=O stretching mode of the CO_2 adduct, in which the C atom interacts with a metal ion.²¹ However, we cannot determine which metal this is, because the peak positions are similar for both metals.²¹ In addition, the intensity of these peaks decreased, and a broad peak corresponding to water stretching mode appeared around $1600\text{--}1700\text{ cm}^{-1}$. These results show that the reduction ($\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$) indeed happened. Remarkably, we did not observe any additional peak corresponding to the C≡O stretching mode (e.g. Pt-C≡O and Bi-C≡O stretching modes at 2150 and $1550\text{--}1680$

cm^{-1} , respectively).²² This result means that CO is released in the gas state as soon as it is produced from CO_2 , or that the CO does not interact with the metal ions. These results support the proposed mechanism.

Fig. 6. Reflectance infrared spectra data during several minutes of electrolysis of 1 mM **1**. Blue: under N_2 , red: under CO_2 , black: under CO_2 . The experiments were carried out at -0.6 or -0.8 V vs. NHE in THF with 0.1 M TBAPF₆ supporting electrolyte.

Figure S12 plots the current density vs. time in the CPE of a CO₂-saturated THF solution of **1** in a gas-tight electrochemical cell at -0.79 V vs. NHE. The headspace gas was periodically sampled and analyzed by gas chromatography. The analysis confirmed that there was no CO₂ reduction product (CO) at -0.33 V vs. NHE after 30 min of electrolysis. On the other hand, at -0.79 V vs. NHE the CO appeared after 30 min. After 30 min of CPE, the amount of CO in the headspace produced during electrolysis was quantified, and the FE for CO was calculated to be 92%. (After this electrolysis, **1** also shows the same CV). This FE is comparable to that reported for Bi nanoparticles (96.1% at -2.0 V vs. SCE (-1.75 V vs. NHE)),^{5d} but the potential (-0.79 V vs. NHE) is much less negative. In addition, this potential is only 270 mV lower than the standard reduction potential for CO₂ + 2H⁺ + 2e⁻ → CO + H₂O (E_0 : -0.51 V vs. NHE), and ~ 1.1 V less negative than the standard reduction potential for CO₂ + e⁻ → CO₂⁻ (E_1 : -1.9 V vs. NHE).²³ Also, without complex **1**, CO₂ was not reduced after 30 min of electrolysis, indicating that complex **1** is a necessary catalyst. The turnover frequency (TOF) was calculated as 8 s⁻¹ by Equation S2 in the Electronic Supporting Information.²⁴ Although this TOF is still small, it can be improved by tuning the experimental condition^{24a} or better design of the molecule. The energy efficiency (EE) was calculated to be 59.4% for E_0 by Equation S3.^{5a} Therefore, the EE when using **1** is twice of that using Bi nanoparticles (28% for E_0).

Conclusions

In summary, an air-stable heterometallic Bi–Pt complex with the formula [BiPt(SAC)₅]_n (**1**; SAC = thioacetate) was synthesized. The Bi–Pt bond and the ionic cage surrounding the Bi ion were confirmed based on the crystal structure, NBO and LOL analyses, and XAFS measurements. From CV and CPE analyses using **1** as electrocatalyst, CO₂ was reduced to CO with FE = 92% and TOF = 8 s⁻¹ during 30 min of electrolysis at -0.79 V vs. NHE. The performance enhancement is attributed to improved catalytic property of Bi ion in the solution, which is in turn due to the existence of the Bi–Pt bond and ionic cage surrounding the Bi ion. The EE value is calculated as 59.4% for E_0 . These results also prove the potential of the donor-acceptor heteroatomic Bi–Pt system for catalysis.

Experimental

General information. Bismuth chloride and S-potassium thioacetate were obtained from Tokyo Chemical Industry Co., Ltd. and used as received. All synthetic processes were carried out in air atmosphere.

Synthesis of **1.** An aqueous solution of K₂PtCl₄ (90 mg, 0.22 mmol, 20 ml) and S-potassium thioacetate (100 mg, 0.88 mmol) was added to an aqueous suspension of BiCl₃ (70 mg, 0.22 mmol) and heated at 50 °C. After 10 minutes, the formed yellow precipitate was filtrated to remove water. The precipitate was then dissolved in toluene and filtrated again to remove impurities (120 mg; 68.2% yield). Finally, crystals of **1** were

obtained from the solution by slow evaporation. ¹H NMR (500 MHz, CDCl₃): δ 2.44 (s, 3H), 2.41 (s, 12H). IR (ATR): 1694, 1566, 1412, 1346, 1116, 952, 646 cm⁻¹; ESI-TOF MS (m/z): [BiPt(SAC)₅]⁺ simu. for C₁₀H₁₅O₅S₅PtBi, 818.8602; found, 818.8617, [BiPt(SAC)₄]⁺ simu. for C₈H₁₂O₄S₄PtBi, 703.9070; found, 703.9048; Elemental analysis (calcd., found for C₁₀H₁₅O₅S₅PtBi): C (15.91, 15.69), H (1.94, 1.82), N (0.00, 0.00), S (20.56, 20.54).

Characterization and instrumental procedures. Single-crystal X-ray diffraction data were collected on a Bruker APEX-II diffractometer with a Bruker APEX-II CCD detector and a cryogenic system (DX-CS190LD, Japan Thermal Engineering Co., Ltd.). Details about the data collection are included in each CIF file. The elemental analysis was performed on a JM-11 microanalyzer (J-SCIENCE LAB CO., Ltd.). Raman spectra were acquired on an inVia Raman microscope/WiRe4 system. FT-IR spectra of the single crystal were acquired on a JASCO FT/IR 6700 spectrometer using an ATR method.

Calculation details. The calculations were performed using Gaussian09 program package. The molecular structure measured from the crystal of **1** was simplified in GaussView5.0. Although **1** has a polymeric structure, we used the monomer structure to reduce the calculation cost. The molecular structure of **1** in solution (an optimized [BiPt(SAC)₄]⁺ paddle-wheel structure) was based on the corresponding structure in the crystal with simplification and modification. The TPSSH (for NBO, structure optimization and TDDFT)²⁵ and wB97XD (for LOL)²⁶ functionals were used with LanL2DZ²⁷ (for structure optimization in the proposed mechanism) and Def2-TZVP²⁸ basis sets including the effective core potential. The SCI-PCM model was used for solution modelling. The SCF procedure was performed in very tight condition. An ultrafine grid was used for integration. The molecular structures were visualized using GaussView5.0 and Avogadro.

Optimization for proposed mechanism. An optimized [BiPt(SAC)₄]⁺ paddle-wheel structure (Figure S4 and Table S1) was used for the initial structure. We did not manually change any atomic positions in the [BiPt(SAC)₄] moiety. CO₂, H⁺, and two electrons (change charge) were added manually, and the structure was optimized step by step. For step (F), 2 H⁺ and 2e⁻ (change charge) were added from step (B) at once and optimized to avoid local minimum of step (E). Free CO₂, CO, H₂O, and H⁺ were optimized independently to calculate the difference in Gibbs free energies.

LOBA calculation details. The localized orbital bonding analysis (LOBA)¹² as implemented in Q-Chem software package¹³ was carried out using the DEF2-TZVP²⁸ basis for all atoms (Pt, Bi, S, C, H, and O) at the B3LYP level²⁹ with DEF2-ECP (60 electrons)³⁰ applied to Bi and Pt. For the LOBA,¹² the Pipek-Mezey (PM)³¹ localization procedure and Löwdin³² methods were employed. Since results from methods like Mulliken population analysis³³ and Mayer bonding analysis³⁴ among others are heavily dependent on the basis set choice, we turned to the more

reliable and efficient LOBA method, which has proven to be a simple way to both accurately predict the oxidation state and provide chemically intuitive bonding description in certain transition metal complexes.⁶³ In this case, the crystal structure obtained from single-crystal X-ray diffraction was used without geometry optimization, due to the angular dependency of the charge transfer integral.¹² For C, H, O, and S, only the valence electrons of the neutral atoms were considered for the respective bonding interactions. For Bi and Pt, LOBA used all the electrons left after subtracting the ECP electrons (60) from the number of electrons in neutral Bi and Pt, giving 23 and 18 electrons, respectively. It is expected that all ordinary as well as dative covalent bonds between the bonded atoms should be localized on the participating atoms, with a certain share of electrons localized on each atom. The implication is that for such bonding interactions, LOBA pairs up the atoms and calculates the number of electrons using their respective percentage contributions.

Electrochemistry. The electrochemical experiments were performed using an ALS/HCH Model 620D electrochemical analyzer. A glassy carbon electrode (3 mm in diameter) was used as the working electrode, Pt wire was used as the counter electrode, and Ag wire was used as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in dry THF solution. N₂ and CO₂ gases were bubbled into the solutions for at least 30 min before cyclic voltammetry was performed. All potentials were converted to NHE.

Reflectance infrared spectroelectrochemistry. Changes in the IR spectra accompanying thin-layer bulk electrolysis with CO₂ were measured by using a modified flow-through reflectance spectroelectrochemical cell reported earlier.³⁶ The controlled potentials were measured vs. a modified Ag/AgNO₃ reference electrode (0.42 V vs. NHE). Spectroelectrochemical experiments were carried out using 0.1 M TBAPF₆ in THF with one drop of CF₃OH (~0.04 ml) as electrolyte, which was used for the Fourier Transform IR solvent subtractions. A solution of **1** at 1 mM was prepared using the electrolyte solution, followed by CO₂ bubbling for 10 min. The IR spectra were measured before and after applying -0.8 V (vs. NHE), which is sufficient to induce CO₂ reduction in the CV experiment. After applying this potential, we observed gas (bubble) formation, and so the outlet of the sample solution was not closed. We further confirmed that the potential was not impeded by the bubbles. All the measurements were performed at room temperature. A Hokuto Denko HA-301 potentiostat was used to apply the potential and monitor the thin layer bulk electrolysis.

Controlled potential electrolysis. Controlled potential electrolysis (CPE) experiments were performed by using an ALS/HCH Model 620D electrochemical analyzer. A Gamry five-neck cell was used for all experiments. The cell was equipped with three AceThread ports (one for each electrode) and two joints for gas purging and gas collection after electrolysis. A piece of Pt wire was used for the counter electrode and Ag wire

for the reference electrode. Both are separated from the bulk solution by a porous frit. A glassy carbon working electrode with a surface area of 0.071 cm² was used. The experiment was performed using 0.1 M TBAPF₆ dissolved in dry THF with 1 mM trifluoroethanol as the proton source. The solution was purged with CO₂ gas for 30 min before electrolysis. Gas-phase products were sampled using a gas-tight syringe, and the product of CO₂ reduction was confirmed using a gas chromatograph (Agilent 6890N, 5975C) equipped with Agilent HP-MOLESIEVE columns (length 30 m, ID 0.32 mm, 12 μm film). Helium (99.99%) was used as the carrier gas, and the m/z range was 10–100. The gas chromatography calibration curve was prepared using a known volume of CO gas. CPE measurements were performed at three different times for every sample. The FE was calculated by dividing the actual amount of CO produced by the theoretical amount based on the charge passed during the CPE experiment. The averaged FE values are reported. During electrolysis, the current density decreased at first due to the formation of electrocatalytic species before becoming stable, indicating that the amount of electrogenerated catalytic species remained stable in solution. There was no precipitate, and the color of the solution did not change during electrolysis in the presence of proton source. However, a red precipitate was formed when a proton source was not used. In other words, the solution of **1** is stable for electrolysis.

Conflicts of interest

There are no conflicts to declare.

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