

Fixation of Both O₂ and CO₂ from Air by a Crystalline Palladium Complex Bearing *N*-Heterocyclic Carbene Ligands

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Supporting Information

Synthetic Procedures

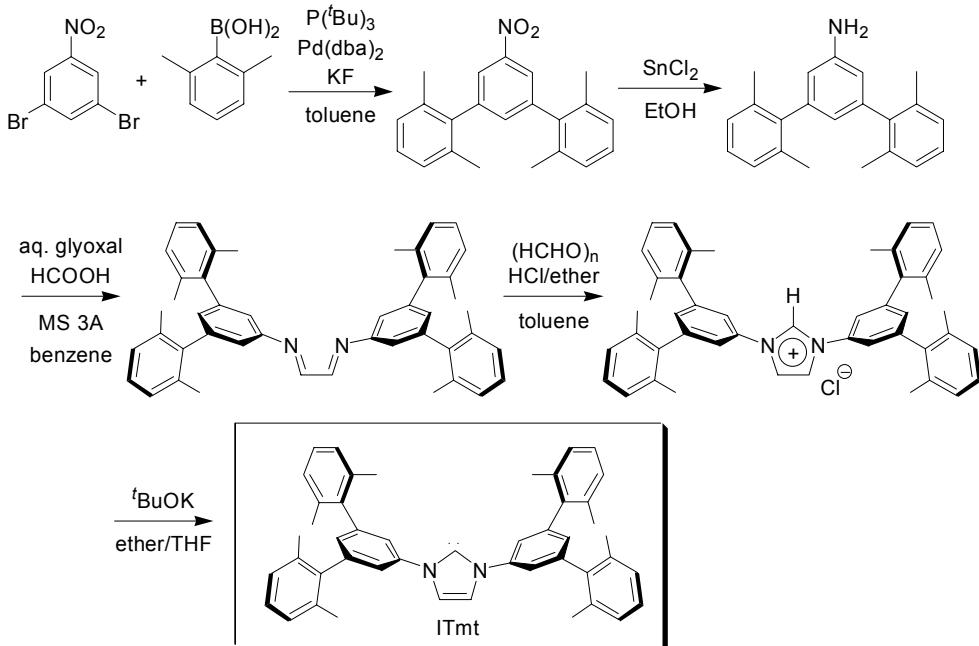
General Methods. ¹H, ¹³C{¹H}, ¹⁹F{¹H}, and ³¹P{¹H} NMR spectra were recorded on 400 or 500 MHz spectrometers with residual protiated solvent, deuterated solvent, C₆F₆, or 85% H₃PO₄ used as reference. Infrared spectra were obtained with a JASCO FT-IR420. For measurements of reflectance IR microspectra, an infrared microscope attachment, JASCO IRT-30, was used. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo. Melting points were determined by differential scanning calorimetry. Ether, toluene, tetrahydrofuran, and pentane were distilled from sodium/benzophenone. The other chemicals were used as received from chemical company. Pd(dba)₂,¹ 2,6-dimethylphenylboronic acid,² 3,5-dibromonitrobenzene,³ Pd(IPr)₂,⁴ and Pd(IMes)₂,⁵ Pd(IMes)₂O₂⁶ were synthesized according to literature procedures.

dba = 1,5-diphenyl-1,4-pentadien-3-one

IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene

IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene

Scheme S1. Synthetic pathway for the new carbene ligand, ITmt.



Synthesis of 3,5-bis(2,6-dimethylphenyl)nitrobenzene. A 500 mL 3-neck round bottom flask containing 3,5-dinitrobromobenzene (18.3 g, 65.0 mmol), 2,6-dimethylphenylboronic acid (20.0 g, 133 mmol), and potassium fluoride (24.9 g, 429 mmol) was brought into a drybox. Into the flask, Pd(dba)₂ (748 mg, 1.30 mmol) and 'Bu₃P (316 mg, 1.56 mmol) were weighed. After bringing the flask out of the drybox, THF (100 mL) was added to the mixture, and the resulting mixture was stirred at 80 °C for 6 h. After cooling the mixture to room temperature, the reaction mixture was filtered through the short plug of Celite and silica gel. After absorption of the filtrate to silica gel by evaporation, the product was purified by column chromatography with CHCl₃/hexane (10%) eluent to give **1** as a pale yellow solid (20.2 g, 93.8%). ¹H NMR (CDCl₃, 400 MHz) δ 2.08 (s, 12H), 7.15 (d, *J* = 7.2 Hz, 4H), 7.22 (dd, *J* = 6.4 Hz, 8.0 Hz, 2H), 7.32 (t, *J* = 1.6 Hz, 1H), 8.06 (d, *J* = 1.6 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 20.7 (Me), 122.3 (CH), 127.4 (CH), 127.7 (CH), 135.3 (4°), 136.2 (CH), 139.0 (4°), 142.8 (4°), 148.5 (4°); mp 151.5–153.4 °C; Anal. Calcd. for C₂₂H₂₁NO₂: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.69; H, 6.56; N, 3.97.

Synthesis of 3,5-bis(2,6-dimethylphenyl)aniline. To a mixture of 3,5-bis(2,6-dimethylphenyl)nitrobenzene (17.0 g, 51.3 mmol) and SnCl₂ (85.3 g, 450 mmol), EtOH (700 mL) was added at room temperature. The mixture was refluxed for 2 h, and cooled to room temperature. The reaction mixture was poured into water (800 mL) to give a white suspension. Aqueous NaOH (3 M, 700 mL) was added to the white suspension to basify the mixture. The white suspension was extracted with CH₂Cl₂, and the combined organic layer was dried over MgSO₄. After evaporation of the solvent, the residual colorless oily product was dissolved in CH₂Cl₂. After addition of hexane (150 mL) and a solution of HCl in ether (1.0M, 100 mL, 100 mmol) to the solution, reducing the volume of the solvents by evaporation gave a white crystalline solid. The white solid of anilinium chloride was isolated by filtration followed by washing with hexane. The white solid was dissolved in CH₂Cl₂, and resulting solution was washed with aqueous NaOH. After drying organic phase with MgSO₄, evaporation of the solvent gave the product as a white solid (14.2 g, 91.9%). ¹H NMR (CDCl₃, 400 MHz) δ 2.16 (s, 12H), 3.74 (s, 2H), 6.37 (t, *J* = 1.6 Hz, 1H), 6.50 (d, *J* = 1.6 Hz, 2H), 7.10–7.14 (m, 4H), 7.18 (dd, *J* = 8.8 Hz, 5.6 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 20.8 (Me), 114.0 (CH), 120.2 (CH), 126.7 (CH), 127.0 (CH), 135.7 (4°), 141.8 (4°), 142.2 (4°), 146.3 (4°); mp 116.2–123.8 °C (dec.); Anal. Calcd. for C₂₂H₂₃N: C, 87.66; H, 7.69; N, 4.65. Found: C, 87.40; H, 7.71; N, 4.50.

Synthesis of 1,3-bis(3,5-bis(2,6-dimethylphenyl)phenyl)imidazolium chloride. Benzene (20 mL), aqueous glyoxal (40%, 2.18 mL, 19.0 mmol), and formic acid (10 drops) were subsequently added to 3,5-bis(2,6-dimethylphenyl)aniline (11.5 g, 38.1 mmol) at room temperature. After the mixture was stirred at room temperature for 5 min, molecular cieves 3A (ca. 35 g, activated by microwave oven) was added to the mixture with argon gas flowing. The resulting mixture was stirred at 80 °C for 16 h to form a yellow-green solution. Molecular sieves was filtered off and washed with CH₂Cl₂. Evaporation of the solvent gave the diazabutadiene product as a yellow solid (11.4 g, 95.9%) with a small amount of impurities. This material was used for next step without further purification. A suspension of paraformaldehyde (210 mg, 7.00 mmol) in toluene (15 mL) was stirred at 120 °C until the suspension became homogeneous. After cooling to room temperature, a solution of crude 1,3-bis(3,5-bis(2,6-dimethylphenyl)phenyl)diazabuta-1,3-diene (4.37 g, 7.00 mmol) in toluene (15 mL) was added to the solution. A ethereal solution of HCl (2.0 M, 3.50 mL, 7.00 mmol) was added dropwise to the mixture. The resulting dark brown solution was stirred at 120 °C for 1 h, and cooled to room temperature. The reaction mixture was filtered and the residue was washed with toluene, then hexane to give the product as a pale pink-white solid (1.91 g, 40.6%). ¹H NMR (DMSO-*d*₆, 400 MHz) δ 2.08 (s, 24H), 7.10 (t, *J* = 1.2 Hz, 2H), 7.13–7.18 (m, 8H), 7.21 (dd, *J* = 8.8 Hz, 5.6 Hz, 4H), 8.75 (t, *J* = 1.2 Hz, 2H), 10.49 (s, 1H); ¹³C{¹H} NMR (DMSO-*d*₆, 100 MHz) δ 20.5 (Me), 119.9 (CH), 121.4 (CH), 127.3 (CH), 127.6 (CH), 130.5 (CH), 134.1 (CH), 134.9 (4°), 135.1 (4°), 139.5 (4°), 142.7 (4°); mp 364.7–365.3 °C; Anal. Calcd. for C₄₇H₄₅ClN₂: C, 83.84; H, 6.74; N, 4.16. Found: C, 83.63; H, 6.83; N, 3.96.

Synthesis of 1,3-bis(3,5-bis(2,6-dimethylphenyl)phenyl)imidazolidene (ITmt). In a drybox, THF (15 mL) was added to a mixture of 1,3-bis(3,5-bis(2,6-dimethylphenyl)phenyl)imidazolium chloride

(1.01 g, 1.50 mmol) and $^t\text{BuOK}$ (174 mg, 1.55 mmol) at room temperature. The resulting red-orange suspension was stirred at room temperature for 1.5 h. After evaporation of the solvent, the residue was dissolved in toluene to give a yellow suspension. The suspension was filtered through Celite, and the residue was washed with toluene. Evaporation of the solvent from filtrate gave the product as an orange solid (640 mg, 67.0%). ^1H NMR (THF- d_8 , 400 MHz) δ 2.14 (s, 24H), 6.83 (t, J = 1.6 Hz, 2H), 7.07-7.14 (m, 12H), 7.84 (d, J = 1.6 Hz, 4H), 7.89 (s, 4H); $^{13}\text{C}\{\text{H}\}$ NMR (THF- d_8 , 100 MHz) δ 21.4 (Me), 119.2 (CH), 120.1 (CH), 128.0 (CH), 128.1 (CH), 128.3 (CH), 136.5 (4°), 142.3 (4°), 143.5 (4°), 143.7 (4°), 217.7 (4°, carbene).

Synthesis of two-coordinate bis(carbene) complex 1. A mixture of $\text{Pd}[\text{P}(o\text{-tol})_3]_2$ (179 mg, 0.250 mmol), 1,3-bis(3,5-bis(2,6-dimethylphenyl)phenyl)imidazolidene (350 mg, 0.550 mmol), and toluene (20 mL) was stirred at room temperature for 30 min. Solvents were evaporated from the reaction mixture, then hexane (15 mL) was added to the residue. After stirring the mixture at room temperature for 5 min, the resulting suspension was filtered off to give the product as a red solid (257 mg, 74.5%). Recrystallization of the product by diffusion of hexane to toluene solution at -30 °C gave colorless crystals suitable for X-ray analysis. ^1H NMR (THF- d_8 , 400 MHz) δ 1.90 (s, 48H), 6.50 (s, 4H), 6.82 (d, J = 8.0 Hz, 16H), 6.87 (dd, J = 6.4 Hz, 8.0 Hz, 8H), 7.52 (s, 4H), 7.99 (s, 8H); $^{13}\text{C}\{\text{H}\}$ NMR (THF- d_8 , 100 MHz) δ 21.8 (Me), 119.9 (CH), 123.6 (CH), 127.5 (CH), 127.7 (CH), 128.2 (CH), 136.6 (4°), 141.5 (4°), 142.3 (4°), 143.8 (4°), 195.7 (4°, carbene).

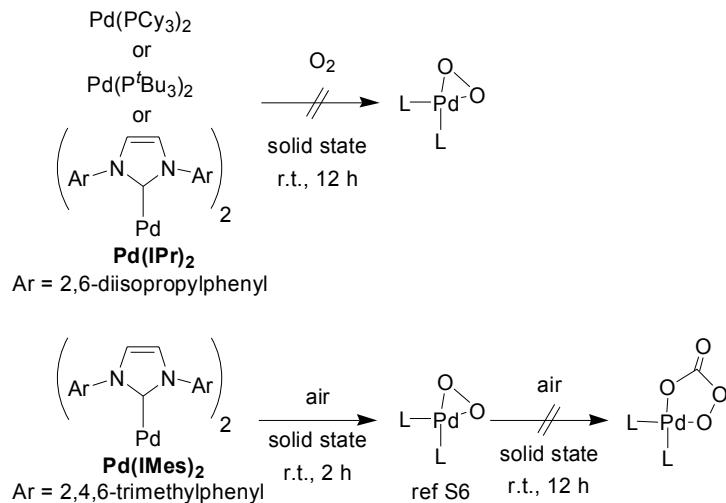
Solid-state reaction of bis(carbene) complex 1 in the air to produce peroxocarbonate complex 2. In a drybox, a deep red powder of **1** (48.6 mg, 35.2 μmol) was homogenized with mortar. Immediately after the material on the mortar was brought out of the drybox, the color started to change from deep red to pale yellow. After exposure to air for 3 h at room temperature, the resulting pale yellow solid was brought into drybox again to prepare NMR samples. Characterization of the resulting solid by ^1H NMR (C_6D_6 , CD_2Cl_2), ^{13}C NMR (CD_2Cl_2), and IR spectroscopy indicated that the solid is spectroscopically pure peroxocarbonate complex **2**. Recrystallization of the product by diffusion of cyclohexane to CD_2Cl_2 solution at -30 °C gave colorless crystals suitable for X-ray analysis. ^1H NMR (C_6D_6 , 400 MHz) δ 2.04 (s, 24H), 2.07 (s, 24H), 6.14 (s, 1H), 6.21 (s, 1H), 6.41 (t, J = 2 Hz, 1H), 6.43 (t, J = 2 Hz, 1H), 6.65 (d, J = 2 Hz, 2H), 6.82 (d, J = 2 Hz, 2H), 6.92-6.96 (br, 8H), 7.01-7.13 (m, 4H); ^1H NMR (CD_2Cl_2 , 400 MHz) δ 2.00 (s, 48H), 6.60 (s, 2H), 6.72 (s, 2H), 6.92 (d, J = 1.2 Hz, 4H), 6.99-7.07 (m, 24H), 7.11-7.17 (m, 8H); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz) δ 21.4 (Me), 21.5 (Me), 125.17 (CH), 125.19 (CH), 125.6 (CH), 127.9 (CH), 128.0 (CH), 132.5 (CH), 136.29 (4°), 136.33 (4°), 140.08 (4°), 140.12 (4°), 140.5 (4°), 140.7 (4°), 142.6 (4°), 142.8 (4°), 161.8 (4°, carbene), 164.8 (4°, carbene), 167.0 (4°, carbonyl); IR (KBr): 1637, 1673 cm^{-1} (C=O); Anal. calcd. for $\text{C}_{96}\text{H}_{88}\text{N}_4\text{O}_4\text{Pd}\cdot\text{CD}_2\text{Cl}_2$: C, 74.72; H, 6.01; N, 3.63. Found: C, 74.46; H, 6.24; N, 3.52.

Independent synthesis of 2 by the reaction of 1 with CO_2 and O_2 in solution. In a drybox, deep red powders of **1** (14.5 mg, 10.5 μmol) and THF (1.0 mL) were put into a Schlenk flask. After bringing the tube out of the drybox, a piece of dry ice was thrown into the Schlenk flask with argon flowing. Consumption of all the dry ice in 10 min led no color change. After freezing the solution with cooling by liquid nitrogen, the Schlenk flask was evacuated, purged with pure O_2 gas, and warmed to room temperature. Immediately the red color of the solution disappeared. The solution was stirred at room temperature for 2 min, and the solvents were removed under reduced pressure to form white solid. The Schlenk flask was brought into drybox again. The white solid was dissolved in CD_2Cl_2 . The NMR spectra of the resulting white solid were identical with those of **2** obtained by the solid-state reaction.

Independent synthesis of palladium peroxy complex 3. In a drybox, deep red powders of **1** (19.6 mg, 14.2 μmol) and C_6D_6 (0.60 mL) were put into a screw-cap NMR tube. After bringing the tube out of the drybox, the solution was frozen and purged with O_2 . The color of the solution immediately changed from red to pale yellow. Evacuation of the solvent and O_2 afforded a pale yellow solid (20.1 mg, quant.). Recrystallization of the product by diffusion of hexane to THF solution at -30 °C gave colorless crystals

suitable for X-ray analysis. ^1H NMR (C_6D_6 , 400 MHz) δ 2.04 (s, 4H), 6.40 (s, 4H), 6.43 (s, 4H), 6.92 (d, $J = 7.2$ Hz, 16H), 7.03 (t, $J = 7.2$ Hz, 8H), 7.39 (s, 8H); $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6 , 100 MHz) δ 21.8 (Me), 122.9 (CH), 124.6 (CH), 128.0 (CH), 128.7 (CH), 130.9 (CH), 136.5 (CH), 141.1 (4°), 141.5 (4°), 142.5 (4°), 180.7 (4°, carbene).

Control experiments for reactions of two-coordinate palladium(0) species with O_2 or CO_2 .
Scheme S2. Reaction of PdL_2 ($\text{L} = \text{PCy}_3$, $\text{P}'\text{Bu}_3$, IPr , IMes) with O_2 or the air.



(1) Reactions of PdL_2 ($\text{L} = \text{PCy}_3$, $\text{P}'\text{Bu}_3$, IPr) with gaseous O_2 . In a drybox, powdered PdL_2 ($\text{L} = \text{PCy}_3$, $\text{P}'\text{Bu}_3$, or IPr) was placed into a 20 mL Schlenk flask. After bringing the flask out of the drybox, the Schlenk flask was evacuated and purged with O_2 , and the valve of the flask was closed. After being left at room temperature for 12 h, the flask was evacuated again and was brought into the drybox. In the drybox, the resulting solid was mixed with KBr to make a KBr pellet for IR spectroscopy. There was no change in all IR spectra from the starting materials.

(2) Reaction of $\text{Pd}(\text{IMes})_2$ with O_2 or the air in the solid state. In a drybox, powdered $\text{Pd}(\text{IMes})_2$ was placed into two 20 mL Schlenk flasks. After bringing the flask out of the drybox, the first Schlenk flask was evacuated and purged with O_2 , and the valve of the flask was closed. The second Schlenk flask was evacuated and purged with air, and the valve of the flask was closed. After leaving the two flasks at room temperature for 12 h, the flasks were evacuated again and were brought into the drybox. ^1H NMR spectra of these two samples were identical to the recently reported $(\text{IMes})_2\text{PdO}_2$.⁶

Monitoring of the solid-state reaction of 1 with air by microscopic IR spectroscopy. In the drybox, several pieces of red microcrystals of **1** were placed into a 4 mL vial and the vial was capped. After bringing the vial out of the drybox, the vial was moved to the reflectance IR microspectrometer. A few pieces of the microcrystals were placed on the mirror plate. Immediately, a set of sequential measurement of reflectance microscopic IR spectra of the microcrystals of **1** was started. First seven spectra were collected in every 5 min (0, 5, 10, 15, 20, 25, and 30 min) followed by additional four measurements at 40, 50, 60, and 90 min with taking photographs (Figure S1) by a CCD camera attached to the spectrometer. The time course of the spectral change is shown in Figure S3 along with the spectra of the independently synthesized complexes **1-3** (Figure S2). One can see disappearance of an absorption at 1284 cm^{-1} of **1** and appearance of a peak at 1260 cm^{-1} of **3** at the early stage of the reaction. New peaks of $\text{C}=\text{O}$ vibration at 1637 and 1673 cm^{-1} and a medium peak at 1272 cm^{-1} of **2**, which were assignable to the peroxocarbonate complex **2**, grew up simultaneously. The deep red color of **1** disappeared from the surface of the crystal as **1** was consumed (see the main text). Finally, the resulting spectrum became identical with that of the independently synthesized **2**.

Figure S1. Sequential color change of the crystal during the microscopic IR monitoring of the reaction of **2** with the air.

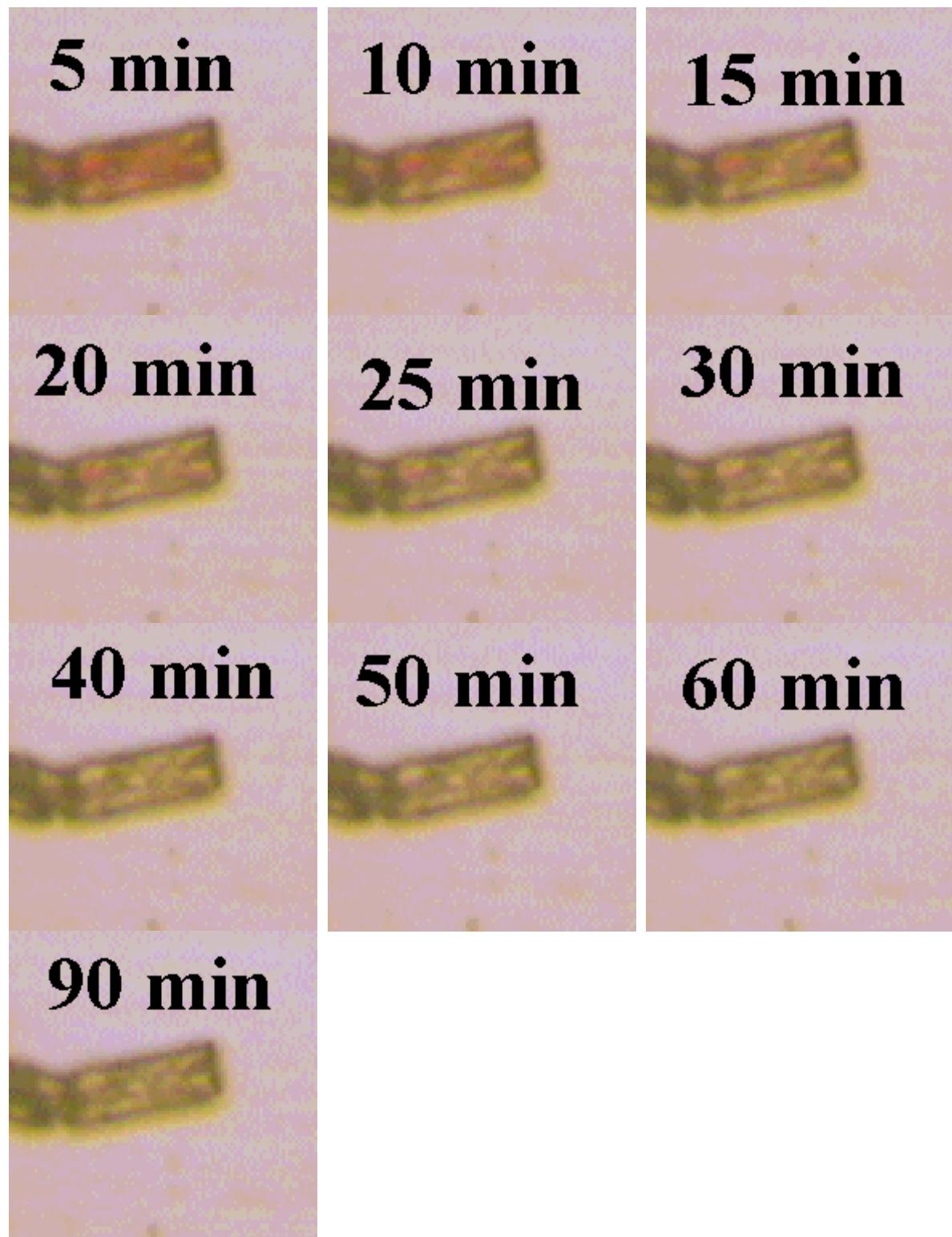


Figure S2. IR spectra of independently synthesized **1**, **3**, and **2**.

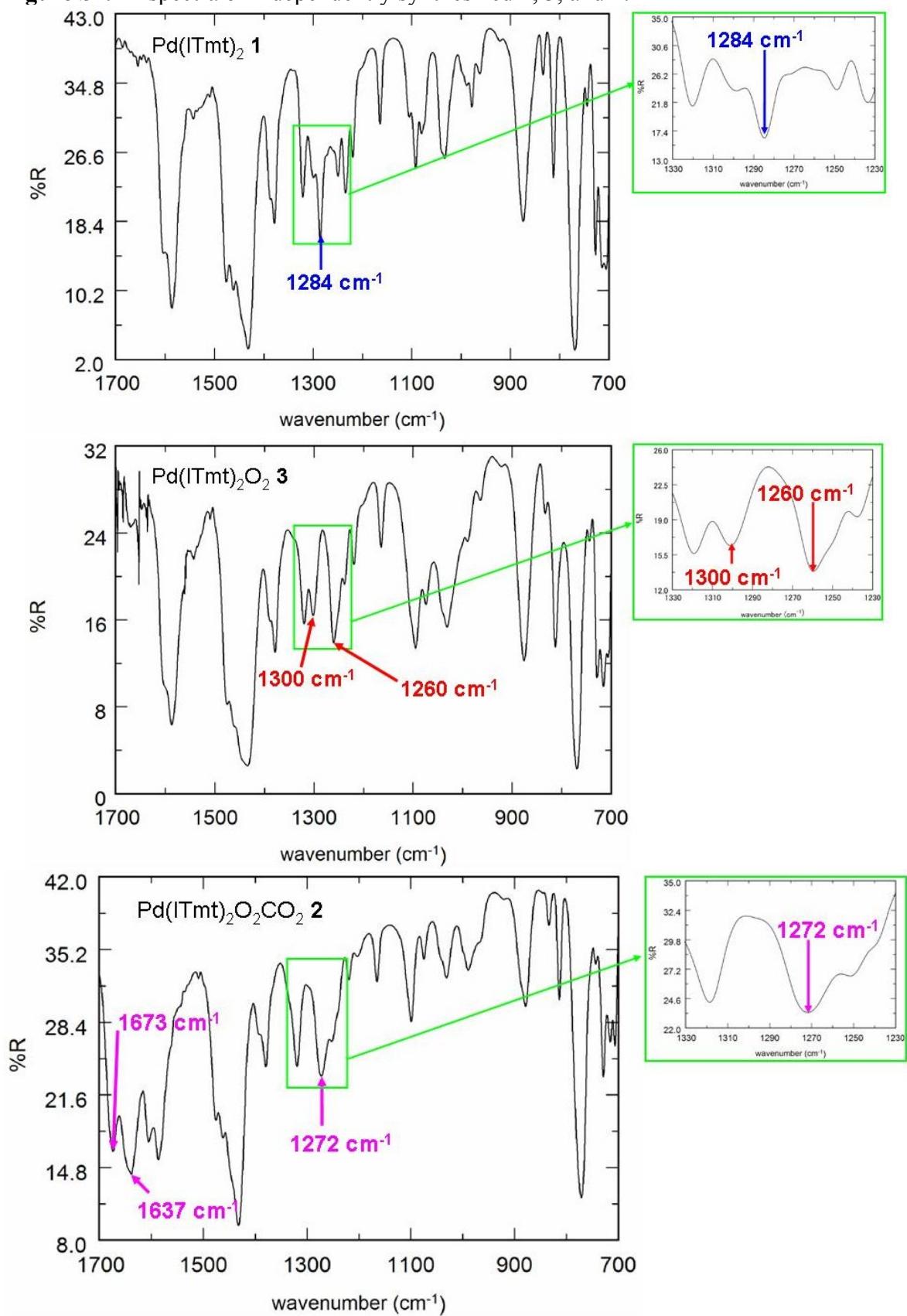


Figure S3. Sequential microscopic IR spectra during the reaction of **1** with the air.

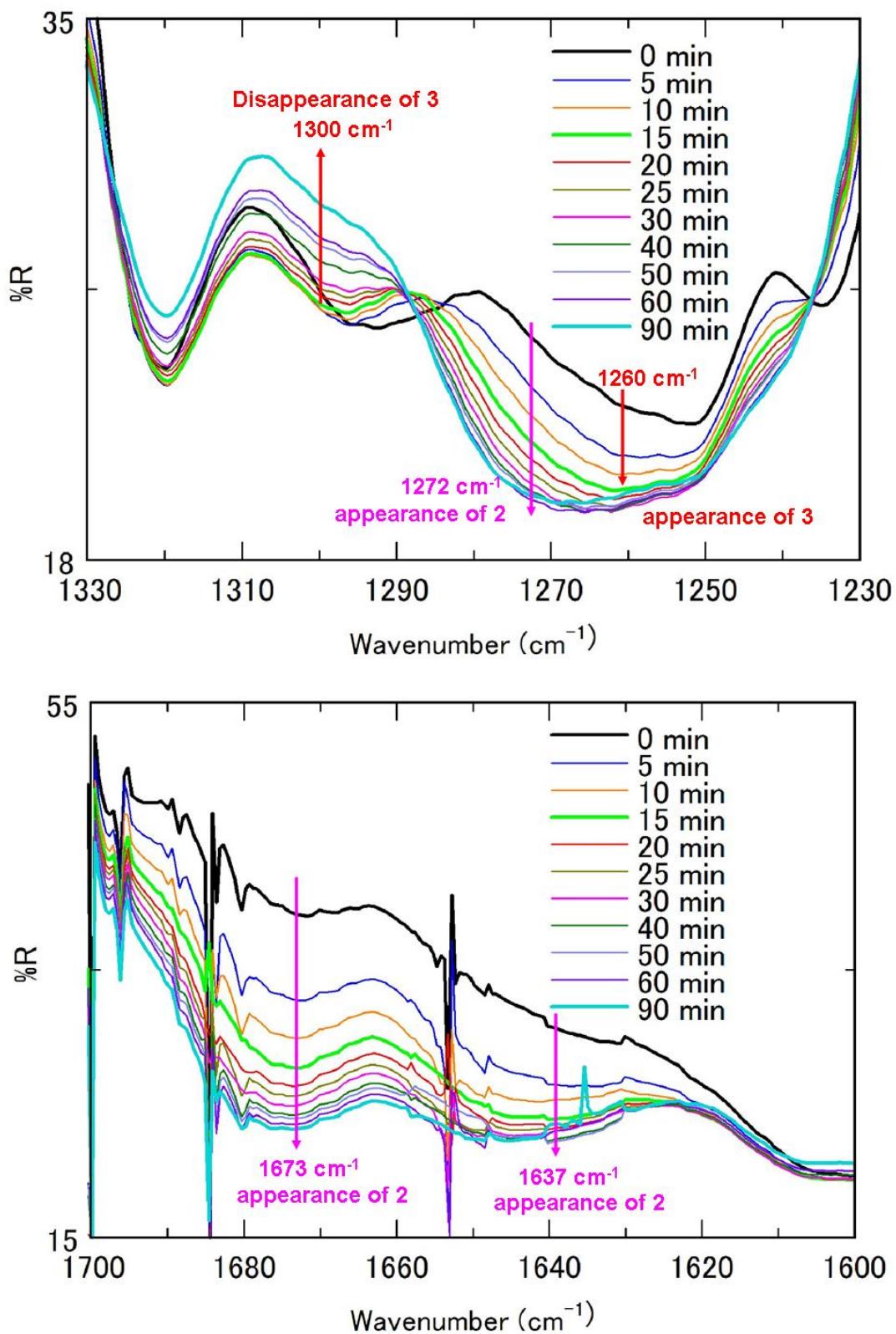
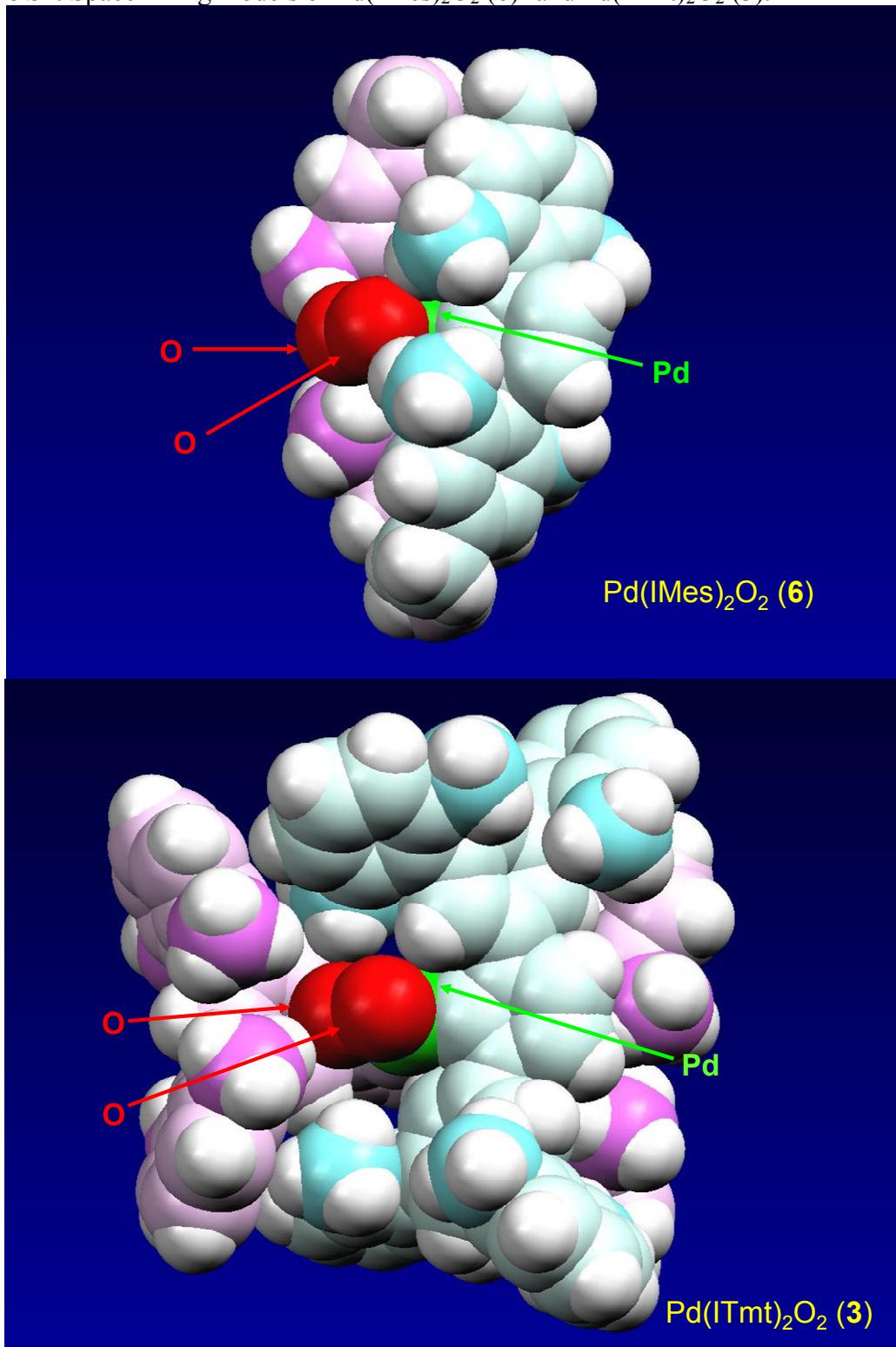


Figure S4. Space filling models of $\text{Pd}(\text{IMes})_2\text{O}_2$ (**6**)⁶ and $\text{Pd}(\text{ITmt})_2\text{O}_2$ (**3**).



Details of X-ray analyses.

Table S1. Crystal data and structure refinement for **1·C₇H₇·C₆H₁₄**, **2·2CD₂Cl₂**, and **3·C₇H₇·H₂O**.

	1·C₇H₇·C₆H₁₄	2·2CD₂Cl₂	3·C₇H₇·H₂O
Empirical formula	C ₁₀₇ H ₁₁₀ N ₄ Pd	C ₉₇ H ₈₈ Cl ₄ D ₄ N ₄ O ₄ Pd	C ₁₀₀ H ₁₀₂ N ₄ O ₃ Pd
Formula weight	1558.39	1626.02	1514.26
Temperature	120(2) K	120(2) K	100(2) K
Wavelength	0.71070 Å	0.71070 Å	0.71070 Å
Crystal system	<i>monoclinic</i>	<i>monoclinic</i>	<i>monoclinic</i>
Space group	<i>P2₁/a</i>	<i>C2/c</i>	<i>C2/c</i>
Unit cell dimensions	<i>a</i> = 15.310(5) Å <i>b</i> = 19.927(6) Å <i>c</i> = 28.867(9) Å α = 90° β = 94.6626(18)° γ = 90°	<i>a</i> = 32.121(15) Å <i>b</i> = 13.230(5) Å <i>c</i> = 25.781(12) Å α = 90° β = 125.4099(17)° γ = 90°	<i>a</i> = 34.854(4) Å <i>b</i> = 17.0305(11) Å <i>c</i> = 30.778(3) Å α = 90° β = 114.6495(11)° γ = 90°
Volume	8778(5) Å ³	8929(7) Å ³	16605(2) Å ³
Z	4	4	8
Density (calculated)	1.179 Mg/m ³	1.209 Mg/m ³	1.211 Mg/m ³
Absorption coefficient	0.261 mm ⁻¹	0.321 mm ⁻¹	0.277 mm ⁻¹
<i>F</i> (000)	3304	3416	6400
Crystal size	0.70 x 0.40 x 0.30 mm ³	0.40 x 0.30 x 0.10 mm ³	0.15 x 0.10 x 0.05 mm ³
Theta range for data collection	1.42 to 25.00°	3.08 to 24.99°	3.10 to 24.99°
Index ranges	-18 ≤ <i>h</i> ≤ 15 23 ≤ <i>k</i> ≤ 23 26 ≤ <i>l</i> ≤ 34	-30 ≤ <i>h</i> ≤ 34 15 ≤ <i>k</i> ≤ 15 28 ≤ <i>l</i> ≤ 21	-40 ≤ <i>h</i> ≤ 39 20 ≤ <i>k</i> ≤ 20 36 ≤ <i>l</i> ≤ 35
Reflections collected	54068	12244	29501
Independent reflections	15293 [R(int) = 0.0274]	3554 [R(int) = 0.0472]	7087 [R(int) = 0.0575]
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	15293/11/1154	3554/7/542	7087/9/875
Goodness-of-fit on <i>F</i> ²	1.190	1.041	1.117
Final <i>R</i> indices [<i>I</i> >2sigma(<i>I</i>)]	<i>R</i> 1 = 0.0802 <i>wR</i> 2 = 0.2259	<i>R</i> 1 = 0.0791 <i>wR</i> 2 = 0.2058	<i>R</i> 1 = 0.0887 <i>wR</i> 2 = 0.2086
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0824 <i>wR</i> 2 = 0.2292	<i>R</i> 1 = 0.0858 <i>wR</i> 2 = 0.2161	<i>R</i> 1 = 0.1025 <i>wR</i> 2 = 0.2176
Largest diff. peak and hole	0.708 and -0.610 e.Å ⁻³	1.842 and -0.728 e.Å ⁻³	0.958 and -0.471 e.Å ⁻³

References and Notes

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