

**(Electronic Supplementary Information)**

**Vinylidene rutheniums with an electrostructurally flexible NO ligand and their  
ruthenacyclobutene formation**

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## Experimental Procedures

**General Procedures.** Reactions were carried out under an atmosphere of dry dinitrogen, whereas subsequent workup was performed in air. Commercially available reagent grade chemicals were used without any further purification, including 54%  $\text{HBF}_4$  solution of diethyl ether (Fluka). The starting materials  $\text{RuCl}_3(\text{PAr}_3)_2(\text{NO})$  ( $\text{Ar} = \text{Ph}$  (**1a**), *p*- $\text{MeC}_6\text{H}_4$  (**1b**)) were prepared by previously reported methods.<sup>1</sup>  $^1\text{H}$ ,  $^{13}\text{C}$   $\{^1\text{H}\}$ , and  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectra were recorded in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  using a Varian Gemini-300 and a JEOL JNM-AL-400 spectrometer, referenced to the signals of TMS, solvents employed, or 85 %  $\text{H}_3\text{PO}_4$  as standards, respectively. Infrared spectra (KBr pellets) were run on a JASCO FT/IR-420 spectrometer. Fast atom bombardment mass spectra (FAB-MS) were obtained on a JEOL JMS-SX102A or a JEOL JMS-700N spectrometers. Elemental analyses were performed using a PERKIN ELMER 2400II elemental analyzer.

**Preparations of  $\text{RuCl}(\text{NO})(\text{PAr}_3)_2\{\text{=C=CH}(\text{C}_6\text{H}_4\text{Me})\}$  ( $\text{Ar} = \text{Ph}$  (**2a**), *p*- $\text{MeC}_6\text{H}_4$  (**2b**)):**  $\text{HC}\equiv\text{CC}_6\text{H}_4\text{Me}$  (0.18 g, 1.55 mmol),  $\text{Et}_3\text{N}$  (0.15 g, 1.48 mmol), and  $(\text{CuOTf})_2(\text{C}_6\text{H}_6)$  (5.4 mg, 11  $\mu\text{mol}$ ) were added to a  $\text{C}_6\text{H}_6$  (10 mL) solution of  $\text{RuCl}_3(\text{PPh}_3)_2(\text{NO})$  (**1a**) (0.11 g, 0.14 mmol). The mixture was refluxed for 1h and evaporated to dryness. The residue was separated by chromatography on a silica gel using a toluene eluent. From the second red band,  $\text{RuCl}(\text{NO})(\text{PPh}_3)_2\{\text{=C=CH}(\text{C}_6\text{H}_4\text{Me})\}$  (**2a**) was isolated as a red solid (86 mg, 76%). From the first band, the collected fraction was further chromatographed on a silica gel column using hexane as an eluent. After additional preparative TLC purification with hexane, the diyne compound  $(\text{MeC}_6\text{H}_4)\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{C}_6\text{H}_4\text{Me})$  was isolated (ca. 12 mg, ca. 37% based on **1a**), which was characterized by NMR, IR, and EI-HR-MS spectra. Similarly to the **2a** formation from **1a** under the support by the Cu(I) catalyst, the complex  $\text{RuCl}_3\{\text{P}(\text{C}_6\text{H}_4\text{Me})_3\}_2(\text{NO})$  (**1b**) gave  $\text{RuCl}(\text{NO})\{\text{P}(\text{C}_6\text{H}_4\text{Me})_3\}_2\{\text{=C=CH}$ -

(C<sub>6</sub>H<sub>4</sub>Me)} (**2b**) in a 47% yield.

When the similar reaction was carried out for **1a** in the absence of the Cu(I) catalyst, the mono(alkynyl) complex RuCl<sub>2</sub>{C≡C(C<sub>6</sub>H<sub>4</sub>Me)}(PPh<sub>3</sub>)<sub>2</sub>(NO) (**3a**) was obtained (29%) as a major product, besides **2a** in a decreased yield, 24%. Furthermore the complex **3a** was treated with HC≡CPh in the presence of the Cu(I) catalyst and Et<sub>3</sub>N in refluxing C<sub>6</sub>H<sub>6</sub>, and the formation of diyne compounds, PhC≡C-C≡C(C<sub>6</sub>H<sub>4</sub>Me) and PhC≡C-C≡CPh, along with a HC≡CPh dimerization, probably enyne product, was observed in hexane-extracted material.

**RuCl(NO)(PPh<sub>3</sub>)<sub>2</sub>{=C=CH(C<sub>6</sub>H<sub>4</sub>Me)}** (**2a**): IR (KBr, pellet): ν(C=C, N=O) 1651 (s) 1624 (s) 1604 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, -40 °C): δ 7.59–7.31 (m, 30H, PPh<sub>3</sub>), 6.77 (d, *J* = 8.1 Hz, 1.2H, C<sub>6</sub>H<sub>4</sub>Me), 6.52 (d, *J* = 8.1 Hz, 0.8H, C<sub>6</sub>H<sub>4</sub>Me), 6.30 (d, *J* = 8.1 Hz, 1.2H, C<sub>6</sub>H<sub>4</sub>Me), 5.79 (d, *J* = 8.1 Hz, 0.8H, C<sub>6</sub>H<sub>4</sub>Me), 5.12 (t, *J* = 4.9 Hz, 0.4H, =C=CH(C<sub>6</sub>H<sub>4</sub>Me)), 4.91 (t, *J* = 5.5 Hz, 0.6H, =C=CH(C<sub>6</sub>H<sub>4</sub>Me)), 2.21 (s, 1.8H, C<sub>6</sub>H<sub>4</sub>Me), 2.10 (s, 1.2H, C<sub>6</sub>H<sub>4</sub>Me). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, -40 °C): δ 30.8 (s, 0.6P, PPh<sub>3</sub>), 29.1 (s, 0.4P, PPh<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, -40 °C): δ 324.9 (t, *J* = 20 Hz, Ru=C<sub>α</sub>), 324.4 (t, *J* = 20 Hz, Ru=C<sub>ω</sub>), 116.3 (brs, =C=C<sub>β</sub>). FAB-MS (*m/z*): 776.8 ([M-(NO)]<sup>+</sup>), 690.7 ([RuCl(NO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>), 655.9 ([Ru(NO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>). Anal. Calcd for C<sub>45</sub>H<sub>38</sub>NClO<sub>2</sub>Ru: C, 66.95; H, 4.74; N, 1.74. Found: C, 67.28; H, 4.91; N, 1.63.

**RuCl(NO){P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>}<sub>2</sub>{=C=CH(C<sub>6</sub>H<sub>4</sub>Me)}** (**2b**): IR (KBr, pellet): ν(C=C, N=O) 1650 (s) 1620 (s) 1598 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, -40 °C): δ 7.33 (brs, 12H, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 7.09 (brs, 12H, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 6.72 (d, *J* = 7.7 Hz, 1.2H, CH(C<sub>6</sub>H<sub>4</sub>Me)), 6.46 (d, *J* = 8.1 Hz, 0.8H, CH(C<sub>6</sub>H<sub>4</sub>Me)), 6.22 (d, *J* = 7.7 Hz, 1.2H, CH(C<sub>6</sub>H<sub>4</sub>Me)), 5.72 (d, *J* = 8.1 Hz, 0.8H, CH(C<sub>6</sub>H<sub>4</sub>Me)), 5.11 (t, *J* = 4.8 Hz, 0.4H, =C=CH(C<sub>6</sub>H<sub>4</sub>Me)), 4.88 (t, *J* = 5.5 Hz, 0.6H, =C=CH(C<sub>6</sub>H<sub>4</sub>Me)), 2.26 (brs, 18H, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 2.09 (brs, 3H, CH(C<sub>6</sub>H<sub>4</sub>Me)). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, -40 °C): δ 28.2 (s, 0.6P, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 26.6 (s,

0.4P, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, -40 °C): δ 325.5 (t, *J* = 21 Hz, Ru=C<sub>α</sub>), 325.3 (t, *J* = 20 Hz, Ru=C<sub>β</sub>), 116.4 – 115.8 (m, =C=C<sub>β</sub>). FAB-MS (*m/z*): 860.7 ([M-NO]<sup>+</sup>), 774.6 ([RuCl(NO)(P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>), 739.7 ([Ru(NO)(P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>). Anal. Calcd for C<sub>51</sub>H<sub>50</sub>NClOP<sub>2</sub>Ru: C, 68.72; H, 5.65; N, 1.57. Found: C, 69.01; H, 5.68; N, 1.44.

**RuCl<sub>2</sub>{C≡C(C<sub>6</sub>H<sub>4</sub>Me)}(PPh<sub>3</sub>)<sub>2</sub>(NO) (3a):** IR (KBr, pellet): ν(C≡C) 2124 (w), ν(N=O) 1866 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.00 – 7.95 (m, 12H, PPh<sub>3</sub>), 7.41 – 7.33 (m, 18H, PPh<sub>3</sub>), 6.87 (d, *J* = 7.9 Hz, 2H, C<sub>6</sub>H<sub>4</sub>Me), 6.47 (d, *J* = 7.9 Hz, 2H, C<sub>6</sub>H<sub>4</sub>Me), 2.27 (s, 3H, C<sub>6</sub>H<sub>4</sub>Me). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 14.7 (s, PPh<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 135.5 (s, C<sub>6</sub>H<sub>4</sub>Me), 134.7 (t, *J* = 5.3 Hz, PPh<sub>3</sub>), 130.7 (s, C<sub>6</sub>H<sub>4</sub>Me), 130.5 (s, PPh<sub>3</sub>), 129.7 (t, *J* = 25 Hz, PPh<sub>3</sub>), 128.2 (s, C<sub>6</sub>H<sub>4</sub>Me), 127.9 (t, *J* = 5.3 Hz, PPh<sub>3</sub>), 123.8 (s, C<sub>6</sub>H<sub>4</sub>Me), 114.9 (t, *J* = 1.4 Hz, Ru-C≡C), 98.0 (s, Ru-C≡C), 21.3 (s, C<sub>6</sub>H<sub>4</sub>Me). FAB-MS (*m/z*): 806 ([M-Cl]<sup>+</sup>), 776 ([M-Cl-(NO)]<sup>+</sup>), 691 ([RuCl(NO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>). Anal. Calcd for C<sub>45</sub>H<sub>37</sub>NCl<sub>2</sub>OP<sub>2</sub>Ru: C, 64.21; H, 4.43; N, 1.66. Found: C, 64.09; H, 4.42; N, 1.69.

**Preparation of RuCl[C(COOMe)=CHC{=CH(C<sub>6</sub>H<sub>4</sub>Me)}]{P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>}<sub>2</sub>(NO) (4b and 4b’):** Methyl propiolate (HC≡CCOOMe) (34 μL, 0.38 mmol) and tetrafluoroboric acid, HBF<sub>4</sub> (4.5 μL, 0.033 mmol, 54% in diethyl ether) were added to a CH<sub>2</sub>Cl<sub>2</sub> solution (5.0 mL) of RuCl(NO){P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>}<sub>2</sub>{=C=CH(C<sub>6</sub>H<sub>4</sub>Me)} (2b) (0.17 g, 0.19 mmol). After the mixture was concentrated to ca. 1.0 mL, the residue was separated by chromatography on a silica gel using a CH<sub>2</sub>Cl<sub>2</sub> eluent to give RuCl[C(COOMe)=CHC{=CH(C<sub>6</sub>H<sub>4</sub>Me)}]{P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>}<sub>2</sub>(NO) (4b (53 mg, 29%) and 4b’ (86 mg, 46%)).

**RuCl[C(COOMe)=CHC{=CH(C<sub>6</sub>H<sub>4</sub>Me)}]{P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>}<sub>2</sub>(NO) (4b):** IR (KBr, pellet): ν(N=O) 1768 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.94 (s, 1H, C(COOMe)=CH), 7.54 – 7.50

(m, 12H, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 7.04 (d, *J* = 7.8 Hz, 12H, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 6.91 (d, *J* = 8.0 Hz, 2H, CH(C<sub>6</sub>H<sub>4</sub>Me)), 6.58 (d, *J* = 8.0 Hz, 2H, CH(C<sub>6</sub>H<sub>4</sub>Me)), 5.55 (s, 1H, CH(C<sub>6</sub>H<sub>4</sub>Me)), 3.28 (s, 3H, COOMe), 2.27 (s, 21H, CH(C<sub>6</sub>H<sub>4</sub>Me) and P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>, overlapping). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 23.6 (s, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 167.8 (s, COOMe), 151.6 (t, *J* = 11 Hz, Ru–C<sub>α</sub>), 150.0 (t, *J* = 5.3 Hz, C(COOMe)=CH), 139.7 (s, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 135.7 (s, CH(C<sub>6</sub>H<sub>4</sub>Me)), 135.2 (t, *J* = 9.6 Hz, Ru–C<sub>α</sub>), 134.8 (s, CH(C<sub>6</sub>H<sub>4</sub>Me)), 134.5 (t, *J* = 5.4 Hz, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 130.4 (t, *J* = 2.3 Hz, CH(C<sub>6</sub>H<sub>4</sub>Me)), 128.3 (t, *J* = 5.0 Hz, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 128.2 (t, *J* = 24 Hz, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 128.1 (s, CH(C<sub>6</sub>H<sub>4</sub>Me)), 127.9 (s, CH(C<sub>6</sub>H<sub>4</sub>Me)), 50.5 (s, COOMe), 21.4 (s, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 21.2 (s, CH(C<sub>6</sub>H<sub>4</sub>Me)). FAB-MS (*m/z*): 975.3 ([M]<sup>+</sup>), 940.4 ([M-Cl]<sup>+</sup>), 775.2 ([RuCl{P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>}<sub>2</sub>(NO)]<sup>+</sup>), 671.2 ([M-P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>]<sup>+</sup>). Anal. Calcd for C<sub>55</sub>H<sub>54</sub>NClO<sub>3</sub>P<sub>2</sub>Ru: C, 67.72; H, 5.58; N, 1.44. Found: C, 67.96; H, 5.85; N, 1.19.

**RuCl[C(COOMe)=CHC{=C(C<sub>6</sub>H<sub>4</sub>Me)(H)}]{P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>}<sub>2</sub>(NO) (4b')**: IR (KBr, pellet): ν(N=O) 1806 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.54 – 7.48 (m, 12H, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 7.18 – 7.12 (m, 3H, C(COOMe)=CH and C(C<sub>6</sub>H<sub>4</sub>Me)(H), overlapping), 6.92 (d, *J* = 8.0 Hz, 12H, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 6.74 (d, *J* = 8.0 Hz, 2H, C(C<sub>6</sub>H<sub>4</sub>Me)(H)), 6.46 (s, 1H, C(C<sub>6</sub>H<sub>4</sub>Me)(H)), 3.29 (s, 3H, COOMe), 2.40 (s, 3H, C(C<sub>6</sub>H<sub>4</sub>Me)(H)), 2.23 (s, 18H, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 24.7 (s, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 167.5 (s, COOMe), 156.6 (t, *J* = 5.3 Hz, C(COOMe)=CH), 148.4 (t, *J* = 13 Hz, Ru–C<sub>α</sub>), 139.8 (s, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 137.8 (s, C(C<sub>6</sub>H<sub>4</sub>Me)(H)), 135.4 (s, C(C<sub>6</sub>H<sub>4</sub>Me)(H)), 134.4 (t, *J* = 5.7 Hz, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 130.3 (s, C(C<sub>6</sub>H<sub>4</sub>Me)(H)), 128.3 (t, *J* = 5.3 Hz, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 127.9 (t, *J* = 24 Hz, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 127.3 (s, C(C<sub>6</sub>H<sub>4</sub>Me)(H)), 50.4 (s, COOMe), 21.3 (s, P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>), 21.3 (s, C(C<sub>6</sub>H<sub>4</sub>Me)(H)) (Two quaternary carbon resonance peaks can't be assigned because of overlapping.). FAB-MS (*m/z*): 975.3 ([M]<sup>+</sup>), 940.4 ([M-Cl]<sup>+</sup>), 775.2 ([RuCl{P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>}<sub>2</sub>(NO)]<sup>+</sup>), 671.2 ([M-P(C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>]<sup>+</sup>). Anal. Calcd for C<sub>55</sub>H<sub>54</sub>NClO<sub>3</sub>P<sub>2</sub>Ru: C, 67.72; H, 5.58; N, 1.44. Found: C, 67.25; H,

5.64; N, 1.37.

**X-ray Crystal Structure Determinations:** Crystallographic data are summarized in Table S1. X-ray quality single crystals were obtained from CH<sub>2</sub>Cl<sub>2</sub> / MeOH (for **2a**•2CH<sub>2</sub>Cl<sub>2</sub> and **4b**•CH<sub>2</sub>Cl<sub>2</sub>) and benzene / hexane (for **4b'**). Diffraction data were collected at room temperature on a Rigaku AFC7 diffractometer equipped with a MSC/ADSC Quantum CCD area detector by using graphite-monochromated Mo K $\alpha$  radiation. Seven preliminary data frames were measured at 0.5° increments of  $\omega$ , in order to assess the crystal quality and preliminary unit cell parameters. The intensity images were obtained with  $\omega$  scans of 0.5° interval per frame for duration of 30 s (**2a**•2CH<sub>2</sub>Cl<sub>2</sub>) and 35 s (**4b**•CH<sub>2</sub>Cl<sub>2</sub> and **4b'**). The frame data were integrated using an MSC d\*TREK program package, and the data set were corrected for absorption using a REQAB program.

The calculations were performed with a TEXSAN program package. Crystal structures were solved by direct methods for **2a**•2CH<sub>2</sub>Cl<sub>2</sub> and **4b**•CH<sub>2</sub>Cl<sub>2</sub> and by Patterson methods for **4b'**, and refined on  $F^2$  by the full-matrix least squares method. In the case of **2a**•2CH<sub>2</sub>Cl<sub>2</sub>, each asymmetric unit contains a half molecule of **2a** and one CH<sub>2</sub>Cl<sub>2</sub> solvent molecule, and one of the chloride atom of the solvent molecule is disordered with occupancy factors of 0.5 / 0.5. Anisotropic refinement was applied to all non-hydrogen atoms except for the solvent molecules of **2a**•2CH<sub>2</sub>Cl<sub>2</sub>, and hydrogen atoms were put at calculated positions with C-H distances of 0.97 Å, while hydrogen atoms of all solvent molecules were not located.

**Table S1.** Crystallographic data for **2a**•2CH<sub>2</sub>Cl<sub>2</sub>, **4b**•CH<sub>2</sub>Cl<sub>2</sub>, and **4b'**

	<b>2a</b> •2CH <sub>2</sub> Cl <sub>2</sub>	<b>4b</b> •CH <sub>2</sub> Cl <sub>2</sub>	<b>4b'</b>
formula	C <sub>47</sub> H <sub>42</sub> NCl <sub>5</sub> OP <sub>2</sub> Ru	C <sub>56</sub> H <sub>56</sub> NCl <sub>3</sub> O <sub>3</sub> P <sub>2</sub> Ru	C <sub>55</sub> H <sub>54</sub> NClO <sub>3</sub> P <sub>2</sub> Ru
fw	977.14	1060.44	975.51
cryst system	monoclinic	triclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>m</i> (No. 11)	<i>P</i> -1 (No. 2)	<i>P</i> -1 (No. 2)
color of crystal	orange	amber	amber
crystal size (mm)	0.35 x 0.15 x 0.06	0.80 x 0.40 x 0.03	0.20 x 0.20 x 0.20
<i>a</i> (Å)	9.523(3)	10.957(1)	12.712(2)
<i>b</i> (Å)	22.815(7)	15.466(1)	12.742(1)
<i>c</i> (Å)	10.988(2)	17.537(2)	15.986(2)
<i>α</i> (deg)	90	78.638(2)	80.906(2)
<i>β</i> (deg)	103.112(4)	71.9489(9)	75.435(2)
<i>γ</i> (deg)	90	71.3085(8)	88.018(2)
<i>V</i> (Å <sup>3</sup> )	2324.9(11)	2660.7(5)	2474.6(5)
<i>Z</i>	2	2	2
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.396	1.324	1.309
$\mu$ (cm <sup>-1</sup> )	7.28	5.48	4.78
2 $\theta_{\text{max}}$ (deg)	55.0	55.0	55.0
no. of all reflns collected	19792	23134	21470
no. of unique reflns	5302	11356	10553
<i>R</i> <sub>int</sub>	0.067	0.027	0.034
no. of obsd reflns <sup>a</sup>	2441	6974	6957
no. of parameters	266	595	568
<i>R</i> <sup>b</sup>	0.135	0.091	0.068
<i>Rw</i> <sup>c</sup>	0.191	0.122	0.086
GOF <sup>d</sup>	1.15	1.40	1.02

<sup>a</sup> All data. <sup>b</sup>  $R = \Sigma |Fo^2 - Fc^2| / \Sigma Fo^2$ . <sup>c</sup>  $Rw = \{\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2\}^{1/2}$ .

<sup>d</sup> GOF =  $[\{\Sigma w (|Fo| - |Fc|)^2\} / (No - Np)]^{1/2}$ , where *No* and *Np* denote the number of data and parameters.

## References

- [1] (a) M. B. Fairy, R. J. Irving, *J. Chem. Soc., (A)*, **1966**, 64, 475. (b) S. D. Robinson, M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, **1972**, 1.