ORGANIC LETTERS

2002
Vol. 4, No. 17
2889−2892

In Situ Generation of Endohedral Metallocenophanes of Cobalt and Rhodium with One Cyclopentadienone Unit

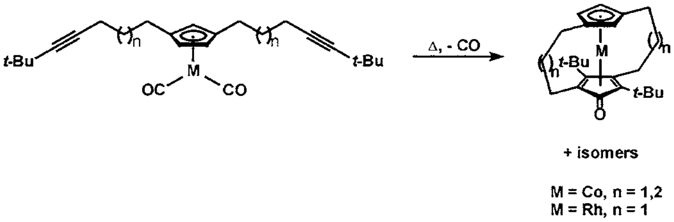
Gerald Scholz, Carsten Schaefer, Frank Rominger, and Rolf Gleiter*

Organisch-Chemisches Institut, Universität Heidelberg, INF 270,
D-69120 Heidelberg, Germany

rolf.gleiter@urz.uni-heidelberg.de

Received June 3, 2002

ABSTRACT

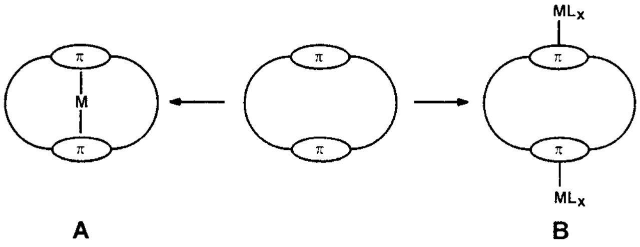


Endohedral metallocenophanes of cobalt and rhodium were prepared using thermolysis of cyclopentadienylmetaldicarbonyl complexes bearing two alkyne units. In the case of the rhodium cyclopentadienonophanes, the structures of two isomeric complexes were confirmed by X-ray diffraction analysis.

In [*n.n*]cyclophanes,[1−3] at least two cyclic conjugated π-systems face each other forced by at least two bridges, such as hydrocarbon chains, creating a cage structure with an inside and outside face. This arrangement allows two ways for binding a metal atom or metal fragment to the π-systems: inside the cage (endohedral, A) or outside the cage (exohedral, B) as shown in Scheme 1.[4] Endohedral metallocenes deserve special interest because the hydrocarbon cage is able to stabilize low oxidation states of the incorporated metals. This has been demonstrated by complexing Ga(I) and Ge(II) in [2.2.2]paracyclophane.[5]

There are various procedures described in the literature for creating endohedral metallocenophanes: either by reacting metal atoms or metal ions with the appropriate cyclophanes (route a in Scheme 2)[5,6] or by building the tethers on a metallocene (route b in Scheme 2).[7] Recently, we pointed out a third path (route c in Scheme 2) by using a template synthesis to generate one of the π-systems.[8] This seems to

Scheme 1

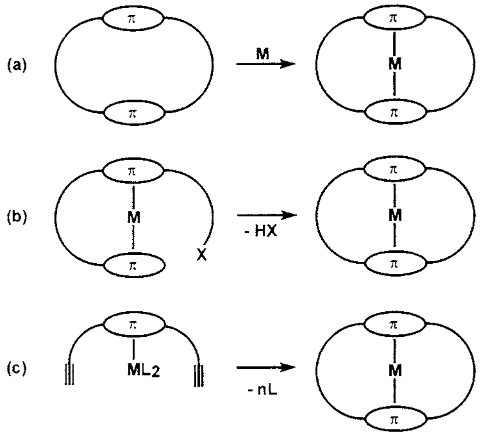


---

[1] Vögtle, F. *Cyclophane Chemistry: Synthesis, Structures and Reactions*; Wiley: Chichester, 1993.
[2] Keehn, P. M., Rosenfeld, S. M., Eds. *Cyclophanes*; Academic Press: New York, 1983.
[3] Diederich, F. *Cyclophanes*; The Royal Society of Chemistry: London, 1991.
[4] Schulz, J., Vögtle, F. *Top. Curr. Chem.* **1994**, *172*, 41−86.
[5] Schmidbaur, H. *Angew. Chem.* **1985**, *97*, 893−904; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 893−904.

10.1021/ol026287h CCC: $22.00

Scheme 2

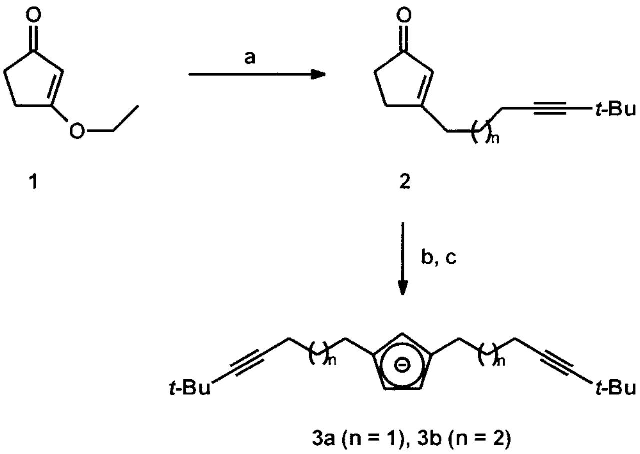


be the method of choice when at least one of the π-systems of the cyclophanes is unstable without complexation such as cyclobutadiene or cyclopentadienone. In this paper, we report the first examples of endohedral complexed cyclophanes with one cyclopentadienone ring.

To synthesize the cyclopentadienone system, we made use of the metal-supported [2 + 2 + 1] cycloaddition of two alkyne units and one CO group.[9] As metals we used cobalt and rhodium, following earlier work by others on CpCo(CO)$_2$ and CpRh(CO)$_2$.[10−13] To generate the cyclopentadienone ring systems, we used thermal conditions that were successful recently to generate tricyclic cyclopentadienones from cyclic alkynes.[14]

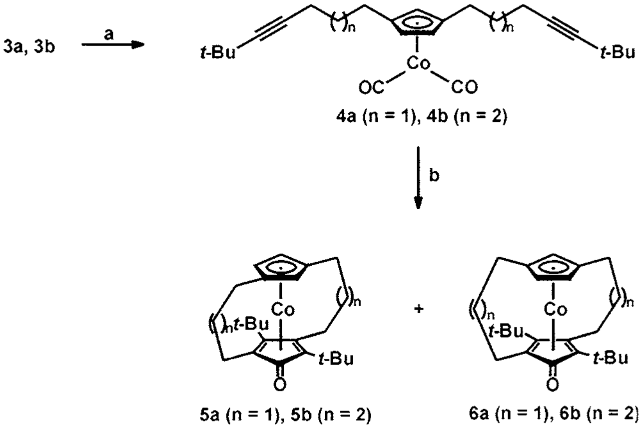
Our syntheses start similarly to those reported recently for endohedral complexed cyclophanes with a cyclobutadiene ring.[8] They commence with the 2-fold substituted cyclopentadiene system (Scheme 3) that could be synthesized in two steps from 3-ethoxycyclopent-2-en-1-one (**1**) and ω-chloroalkynes. Treatment of the cyclopentadienes with n-butyllithium generated the corresponding cyclopentadienyllithium salts **3**. These cyclopentadienyl anions were complexed by metal dicarbonyl fragments.

Scheme 3[a]



[a] Reagents: (a) ClMg(CH$_2$)$_{n+2}$-t-Bu, THF; (b) ClMg(CH$_2$)$_{n+2}$-t-Bu, THF; (c) n-BuLi, THF, −40 °C.

Scheme 4[a]



[a] Reagents: (a) Co$_2$(CO)$_8$/I$_2$, THF (60−65%); (b) decalin, 190 °C (2−10%).

In the case of the cobalt complexes, the reaction of the deprotonated cyclopentadienes with Co(CO)$_8$/I$_2$ was used to generate the cyclopentadienylcobalt dicarbonyl complexes **4a** and **4b** (Scheme 4).[15] Thermolysis of **4a** in decalin at 190 °C gave one C_1-symmetric cyclopentadienone complex (**5a** or **6a**) in 10% yield as a red oil.[16] On the basis of the spectroscopic data, a differentiation of **5a** and **6a** is not possible. Treatment of **4b** under the same conditions gave an equimolar mixture of **5b** and **6b** in 2% overall yield.[17]

The synthesis of the rhodium complexes (Scheme 5) started with the generation of the dicarbonyl complex **7** by

---

(6) Elschenbroich, C.; Möckel, R.; Zenneck, U. *Angew. Chem.* **1978**, *90*, 560−561. Koray, A. R.; Ziegler, M. L.; Blank, N. E.; Haenel, M. W. *Tetrahedron Lett.* **1979**, *26*, 2465−2466.

(7) Hisatome, M. *Rev. Heteroat. Chem.* **1992**, *6*, 142−176.

(8) Scholz, G.; Gleiter, R.; Rominger, F. *Angew. Chem.* **2001**, *113*, 2559−2561; *Angew. Chem., Int. Ed.* **2001**, *40*, 2477−2479.

(9) Hübel, W. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1968; Vol. 1, p 273. Pino, P.; Braca, G. *Ibid.* 1977; Vol. 2, 419−516. Schore, N. *Chem. Rev.* **1988**, *88*, 1081−1119 and references therein.

(10) Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888−3897.

(11) Gesing, E. R. F.; Tane, J. P.; Vollhardt, K. P. C. *Angew. Chem.* **1980**, *92*, 1057−1058; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1023−1024.

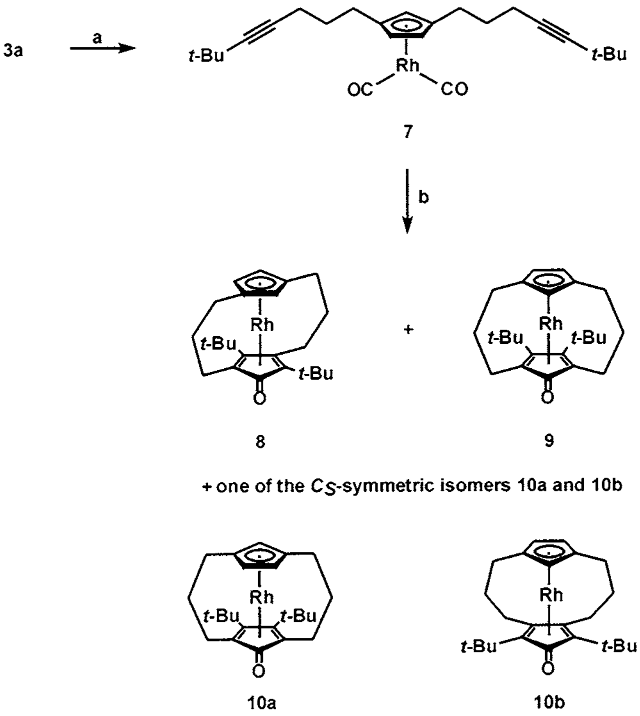
(12) Dickson, R. S.; Mok, C.; Connor, G. *Aust. J. Chem.* **1977**, *30*, 2143-2151.

(13) Dickson, R. S.; Johnson, S. H. *Aust. J. Chem.* **1976**, *29*, 2189−2199.

(14) Roers, R.; Rominger, F.; Nuber, B.; Gleiter, R. *Organometallics* **2000**, *19*, 1578−1588.

(15) **Analytical Data for 4a:** ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 1.24 (s, 18H), 1.46−1.52 (q, 4H), 2.01−2.08 (m, 8H), 4.48 (s, 2H), 4.61 (s, 1H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 18.7 (CH$_2$), 27.4 (CH$_2$), 27.6 (C), 30.3 (CH$_2$), 31.6 (CH$_3$), 78.1 (C), 83, 6 (CH), 85.6 (CH), 90.0 (C), 105.4 (C). **Analytical Data for 4b:** ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 1.22 (s, 18H), 1.29−1.43 (m, 6H), 1.85−1.90 (m, 4H), 1.99−2.04 (m, 6H), 4.49 (2H), 4.61 (1H); ^{13}C NMR (75 MHz, C$_6$D$_6$) δ 18.8 (C), 27.6 (C), 27.9 (CH$_2$), 29.1 (CH$_2$), 30.0 (CH$_2$), 31.6 (CH$_3$), 78.4 (C), 83.4 (CH), 85.4 (CH), 89.4 (C), 105.9 (C).

Scheme 5[a]



[a] Reagents: (a) $[RhCl(CO)_2]_2$, THF, 20 °C (58%); (b) cyclooctane, 160 °C (10%).

stirring the cyclopentadienyllithium salt **3a** with $[RhCl(CO)_2]_2$ in THF. Purification by flash column chromatography yielded dicarbonyl **7** as a yellow oil in 58% yield.[18]

Thermolysis of **7** in cyclooctane (160 °) gave a mixture of three diastereomeric cyclopentadienone complexes in 10% overall yield. ^{1}H NMR and ^{13}C NMR data showed the presence of one C_1-symmetric complex **8** and two C_s-symmetric complexes **9** and **10**.[19,20]

Single crystals suitable for X-ray diffraction analysis of two of the three isomers, namely **8** and **9**, could be obtained from a solution in *n*-hexane at 4 °C. To the best of our knowledge these crystal structures represent the first reported structures of cyclopentadienylrhodium cyclopentadienone complexes. In both structures, the cyclopentadienyl ring is bound η^5 to the rhodium atom and the cyclopentadienone ring in η^4-fashion. This can also be observed in the ^{13}C NMR spectrum: The cyclopentadienyl carbon atoms and four carbon atoms of the cyclopentadienone ring show rhodium−carbon coupling, whereas the carbonyl carbon does not.

The crystal structure of the C_1-symmetric complex **8** (Figure 1) shows very short Rh−C distances, resulting from the strain that is imposed by the two propylene bridges. The average Rh−C distance for the cyclopentadienyl ligand is 2.156 Å and for the cyclopentadienone unit 2.118 Å.[21] The strain leads to a bent cyclopentadiene ring. The ring systems are nearly parallel; the interplanar angle is 4.5°.

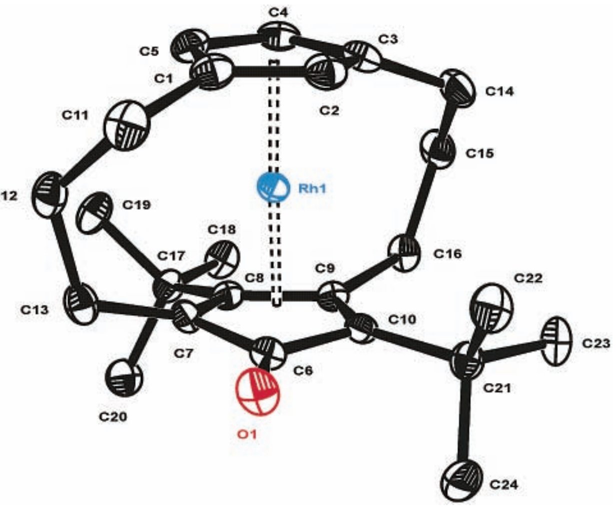


Figure 1. ORTEP drawing of **8** (50% probability thermal ellipsoids).

The carbon skeleton of **9** is less strained, resulting in slightly longer Rh−C distances compared to **8**: The average

---

(16) **Analytical Data for 5a or 6a:** ^{1}H NMR (500 MHz, CD_2Cl_2) δ 1.34 (s, 9H), 1.40 (s, 9H), 1.78−1.83 (br, 2H), 1.95−2.26 (br, 8H), 2.34−2.37 (br, 2H), 4.63 (s, 1H), 4.73 (s, 1H), 4.94 (s, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 21.46 (CH_2), 22.87 (CH_2), 23.45 (CH_2), 23.70 (CH_2), 30.62 (CH_3), 32.87 (CH_3), 33.26 (C), 33.56 (C), 37.88 (CH_2), 41.39 (CH_2), 75.64 (C), 80.59 (CH), 83.03 (C), 83.83 (CH), 85.97 (CH), 92.72 (C), 93.94 (C), 98.41 (C), 109.70 (C), 157.47 (CO); HRMS (FAB+) calcd for $C_{24}H_{34}OCo$ (M + H) 397.1942, found 397.1935.

(17) **Analytic Data for 5b and 6b:** ^{1}H NMR (500 MHz, CD_2Cl_2) δ 1.42 (s, 18H), 1.49 (s, 18H), 1.52−2.77 (br, 32H), 4.61 (s, 1H), 4.69 (s, 1H), 4.86 (s, 1H), 4.95 (s, 1H), 5.05 (s, 1H), 5.14 (s, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 24.14 (CH_2), 24.57 (CH_2), 25.12 (CH_2), 25.31 (CH_2), 25.57 (CH_2), 26.24 (CH_2), 26.47 (CH_2), 26.62 (CH_2), 26.73 (CH_2), 26.98 (CH_2), 27.44 (CH_2), 29.03 (CH_2), 30.04 (CH_2), 30.68 (CH_2), 31.41 (CH_3), 32.06 (CH_3), 33.23 (CH_3), 33.95 (CH_3), 34.01 (C), 34.14 (C), 34.23 (C), 34.30 (C), 70.96 (C), 77.73 (CH), 78.27 (CH), 79.45 (CH), 80.10 (CH), 81.34 (C), 83.07 (CH), 86.10 (CH), 87.56 (C), 88.52 (C), 90.97 (C), 93.60 (C), 97.23 (C), 97.75 (C), 98.16 (C), 99.93 (C), 100.74 (C), 103.26 (C), 159.87 (CO), 162.60 (CO); HRMS (FAB+) calcd for $C_{26}H_{38}OCo$ (M + H) 425.2254, found 425.2237.

(18) **Analytical Data for 7:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (s, 18H), 2.18 (m, 8H), 2.35 (t, 4H), 5.28 (s, 2H), 5.41 (s, 1H), 5.80 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.49 (CH_2), 27.31 (CH_2), 27.47 (C), 29.25 (CH_2), 31.53 (CH_3), 78.58 (C), 86.35 (CH, $J_{Rh,C} = 15$ Hz), 89.35 (CH, $J_{Rh,C} = 14$ Hz), 90.07 (C), 110.10 (C, $J_{Rh,C} = 14$ Hz); MS(FD) *m/z* 440 (M + −CO).

(19) **Analytical Data of 8:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 9H), 1.48 (s, 9H), 1.6−3.05 (m, 12H), 5.31 (s, 1H), 5.52 (s, 1H), 5.86 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.19 (CH_2), 22.79 (CH_2), 24.56 (CH_2), 25.94 (CH_2), 31.59 (CH_3), 33.50 (C), 33.70 (CH_3), 33.92 (C), 42.52 (CH_2), 44.73 (CH_2), 78.64 (C, $J_{Rh,C} = 8.3$ Hz), 86.95 (CH, $J_{Rh,C} = 6.2$ Hz), 88.55 (C, $J_{Rh,C} = 8.3$ Hz), 90.69 (CH, $J_{Rh,C} = 8.3$ Hz), 91.56 (CH, $J_{Rh,C} = 4.8$ Hz), 93.97 (C, $J_{Rh,C} = 5.5$ Hz), 95.99 (C, $J_{Rh,C} = 5.5$ Hz), 104.34 (C, $J_{Rh,C} = 9.0$ Hz), 107.42 (C, $J_{Rh,C} = 15$ Hz), 162.99 (CO); HRMS (FAB+) calcd for $C_{24}H_{34}ORh$ (M + H) 441.1665, found 441.1627.

(20) **Analytical data for the mixture of 8, 9, and 10:** ^{1}H NMR (500 MHz, $CDCl_3$, signals of **8** are omitted) δ 1.37, 1.38, 1.6−2.9, 5.04, 5.15, 5.50; ^{13}C NMR (125 MHz, $CDCl_3$, signals of **8** are omitted) δ 17.89 (CH_2), 21.65 (CH_2), 23.14 (CH_2), 23.63 (CH_2), 30.99 (CH_3), 32.22 (C), 33.11 (C), 34.92 (CH_2), 35.87 (CH_3), 39.80 (CH_2), 78.14 (C, $J_{Rh,C} = 8.5$ Hz), 82.78 (CH, $J_{Rh,C} = 5.7$ Hz), 85.03 (CH, $J_{Rh,C} = 7.5$ Hz), 89.67 (C, $J_{Rh,C} = 10$ Hz), 93.03 (CH, $J_{Rh,C} = 4.7$ Hz), 96.25 (C, $J_{Rh,C} = 6.6$ Hz), 97.66 (CH, $J_{Rh,C} = 6.6$ Hz), 99.31 (C, $J_{Rh,C} = 5.7$ Hz), 101.90 (C, $J_{Rh,C} = 10$ Hz), 109.21 (C, $J_{Rh,C} = 10$ Hz), 158.24 (CO), 167.28 (CO); HRMS (FAB+) calcd for $C_{24}H_{34}ORh$ (M + H) 441.1665, found 441.1632.

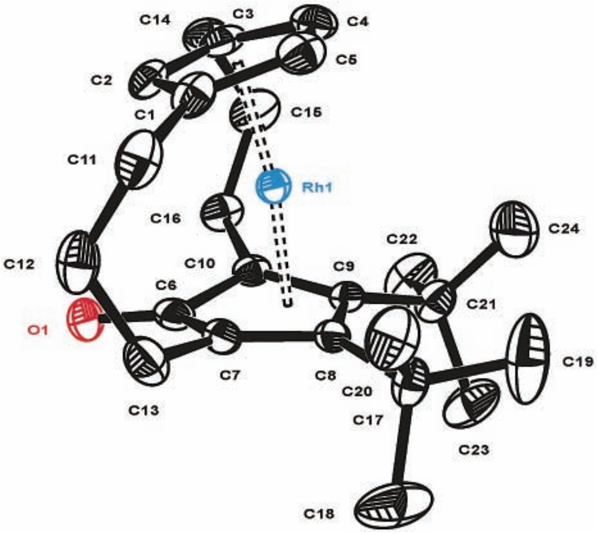


Figure 2. ORTEP drawing of **9** (50% probability thermal ellipsoids).

Rh−C distance for the cyclopentadienyl ligand is 2.175 Å and for the cyclopentadienone unit 2.122 Å. With an interplanar angle of 9.1°, the rings are more inclined toward each other (Figure 2).

In conclusion, we were able to show that two alkyne units tethered to a $CpCo(CO)_2$ fragment can be thermolyzed at 190 °C to yield, as the main product, a CpCo-stabilized cyclopentadienone ring, whereas at 120 °C only a CpCo-stabilized cyclobutadiene unit is generated. If two alkyne units are tethered to a $CpRh(CO)_2$ unit the thermolysis to the corresponding CpRh-stabilized cyclopentadienone takes place at 160 °C.

Supporting Information Available: Synthetic procedures for **4**−**10** and crystallographic data for **8** and **9**. ^1H and ^{13}C NMR spectra for **8**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL026287H

---

(21) **Crystal structure determination for 8**: $C_{24}H_{33}ORh$; MW = 440.41; yellow; needle; orthorhombic; space group $P2_12_12_1$; $a = 11.0586(1)$ Å; $b = 11.5946(1)$ Å; $c = 15.3264(1)$ Å; $V = 1965.15(3)$ Å^3; $Z = 4$; $T = 200(2)$ K; $d_{calcd} = 1.489$ g/cm^3; $F(000) = 920$; $\mu = 0.879$ mm^{-1}; 20 385 reflections collected; 4495 independent reflections ($R_{int} = 0.0306$); 4284 reflections observed ($I > 2\sigma(I)$); $R(F) = 0.019$; $R(F^2) = 0.043$; S (GOF) on $F^2 = 1.06$. $(\Delta\rho)_{max} = 0.39$ e/Å^3; $(\Delta\rho)_{min} = -0.44$ e/Å^3. **Crystal structure determination for 9**: $C_{24}H_{33}ORh$; MW = 440.41; brownish; polyhedron; monoclinic; space group $P2_1/c$, $a = 13.6091(5)$ Å; $b = 11.3557(4)$ Å; $c = 13.8620(6)$ Å; $\beta = 110.874(1)$°; $V = 2001.64(13)$ Å^3; $Z = 4$; $T = 200(2)$ K; $d_{calcd} = 1.461$ g/cm^3; $F(000) = 920$; $\mu = 0.863$ mm^{-1}; 20 364 reflections collected; 4585 independent reflections ($R_{int} = 0.0829$); 3039 reflections observed ($I > 2\sigma(I)$); $R(F) = 0.040$; $R(F^2) = 0.067$; S (GOF) on $F^2 = 1.00$. $(\Delta\rho)_{max} = 0.71$ e/Å^3; $(\Delta\rho)_{min} = -0.51$ e/Å^3.