Metallabenzenes

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Synthesis and Characterization of Stable Ruthenabenzenes**

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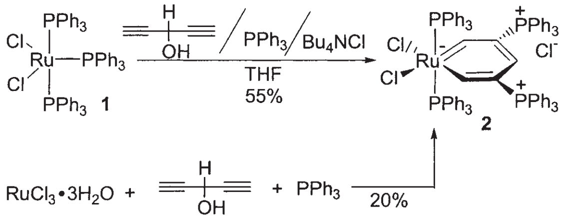
Transition-metal-containing metallabenzenes[1–3] are an interesting class of compounds because they exhibit chemical properties of both organometallic compounds[1] and aromatic organic compounds.[1,4] The first stable transition-metal-containing metallabenzenes were reported in 1982 by Roper et al.[5] Since then a number of stable metallabenzenes have been successfully isolated and characterized. Most of the well-characterized stable metallabenzenes are those with a transition metal atom from the third transition series, especially osmium,[4–7] iridium,[2a–d,g–h,8] and platinum.[2e,9] In contrast, well-characterized metallabenzenes with a metal atom from the first or the second transition series are still very rare, although such species was predicted theoretically as early as 1979.[10] Although coordinated metallabenzenes with metal atoms from the first[11] and the second[12,13] transition series and 1,3-dimetallabenzenes[14] of Nb and Ta were isolated and well characterized, free metallabenzenes with a metal atom from the first or the second transition series have been isolated rarely. The ruthenabenzene [CpRu{C(Ph)CHCHC(Ph)C(OEt)}(CO)] (Cp = cyclopentadienyl), and related ruthenaphenoxide and ruthenaphenanthrene oxide reported by Jones and co-workers represent rare examples (and the only reported examples, to the best our knowledge) of spectroscopically characterized metallabenzenes with a metal from the second transition series.[15a] However, these species are thermally unstable at ambient temperature. Other metallabenzenes such as ferrobenzene,[16a] ruthenaphenanthrene,[15a] ruthenaphenol,[15b] and chromobenzene[16b] have been proposed as reactive intermediates, but no direct observation of such species have been made. Herein we report the isolation and characterization of thermally stable ruthenabenzenes.

We recently reported a convenient method for the preparation of osmabenzenes starting from the reactions of $[OsCl_2(PPh_3)_3]$ with $HC\equiv CCH(OH)C\equiv CH$.[7] We found that the method can also be used to prepare ruthenabenzenes. Treatment of $[RuCl_2(PPh_3)_3]$ (**1**)[17] with $HC\equiv CCH(OH)C\equiv CH$, PPh_3, and Bu_4NCl in THF produced cationic ruthenabenzene **2**, which was isolated as a green solid in 55% yield (Scheme 1). Interestingly, **2** can even be obtained from the one-pot reaction of $RuCl_3$, PPh_3, and $HC\equiv CCH(OH)C\equiv CH$ in $CHCl_3$, although the yield is lower.



Scheme 1. Preparation of the stable ruthenabenzene **2**.

Complex **2** was characterized by solution NMR spectroscopy and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ showed two singlets at $\delta = 18.2$ and 8.1 ppm ($CPPh_3$ and $RuPPh_3$, respectively). The presence of the metallacycle is clearly indicated by the ^1H and ^{13}C NMR data. In particular, the ^1H NMR spectrum in $CDCl_3$ showed the characteristic signal for RuCH at $\delta = 17.5$ ppm and for γ-CH at $\delta = 8.2$ ppm. The ^1H NMR chemical shift for RuCH ($\delta = 17.5$ ppm) is significantly downfield relative to that for the vinyl complex $[Ru\{CH{=}CH(C_6H_4\text{-}p\text{-}OMe)\}Cl(CO)(PPh_3)_2]$ ($\delta = 8.13$ ppm),[18] but is close to those for ruthenium carbene complexes, for example, $[(PCy_3)(RO)_2Ru{=}CHPh]$ (Cy = cyclohexyl; R = *t*Bu: $\delta = 15.5$ ppm; $R = C(CF_3)_2(CH_3)$: $\delta = 17.5$ ppm; $R = C(CF_3)_3$: $\delta = 19.2$ ppm).[19] The $^{13}C\{^1H\}$ NMR spectrum (in CD_2Cl_2) showed the signals for RuCH, $\mathit{C}PPh_3$, and γ-CH at $\delta = 284.3$, 108.3, and 146.0 ppm, respectively. The NMR data suggest that the metallacycle of **2** has a delocalized symmetrical structure.

Unambiguous confirmation for the structure of **2** was provided by X-ray diffraction (Figure 1).[20] The complex contains an essentially planar six-membered metallacycle with two PPh_3 substituents. The coplanarity is reflected by the small deviations (0.0426 Å) from the RMS planes of the best fit through the six atoms Ru1, C1, C2, C3, C4, and C5. Within the metallacycle, the C–C bond lengths are in the range 1.378(7)–1.395(7) Å, and there is no significant C–C bond-

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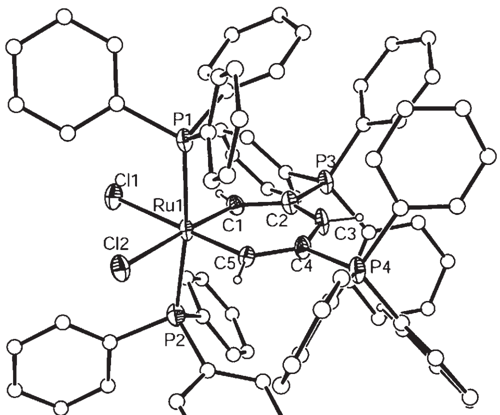


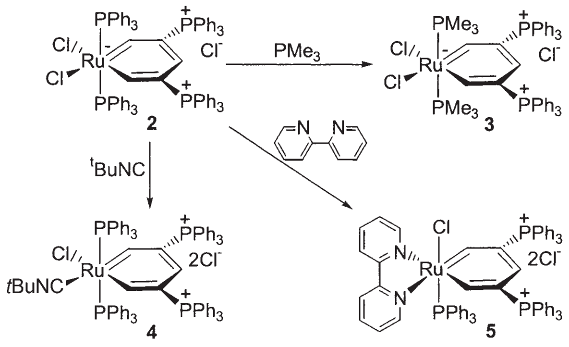
Figure 1. Molecular structure of **2** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Ru1–C1 1.922(5), C1–C2 1.382(7), C2–C3 1.395(7), C3–C4 1.378(7), C4–C5 1.391(7), C5–Ru1 1.911(5), C2–P3 1.790(5), C4–P4 1.792(5), Ru1–P1 2.4148(15), Ru1–P2 2.3926(15), Ru1–Cl1 2.5046(13), Ru1–Cl2 2.5196(13); C1-Ru1-C5 90.4(2), C1-Ru1-P1 92.25(15), C1-Ru1-P2 93.10(15), C5-Ru1-P1 93.17(15), C5-Ru1-P2 91.63(15), P1-Ru1-P2 172.78(5), Cl1-Ru1-Cl2 94.85(5), C2-C1-Ru1 129.5(4), C4-C5-Ru1 128.6(4), C1-C2-P3 123.3(4), C3-C4-P4 114.6(4), C3-C2-P3 114.3(4), C5-C4-P4 122.2(4), C1-C2-C3 122.2(5), C2-C3-C4 125.2(5), C3-C4-C5 123.2(4).

length alternation, as one might expect for a delocalized structure. To the best of our knowledge, this is the first structurally characterized uncomplexed metallabenzene with a metal atom from the second transition series.

In the solid state, ruthenabenzene **2** is air-stable. Its thermal stability is also remarkable, and **2** remains nearly unchanged when heated at 100 °C in air for 5 h. The higher thermal and air stability of ruthenabenzene **2** is probably related to the protecting effect of the bulky phosphine substituents and/or ligands. The electronic properties may also play an important role in the stability of **2**. To our knowledge, no metallabenzenes with a metal of the first or second transition series that are stable at room temperature have been reported previously. Thus, **2** is a rare example of thermally stable metallabenzenes with a transition metal atom from the second transition series.

Other thermally stable ruthenabenzenes can be obtained by substitution reactions of **2**. Treatment of **2** with PMe_3 produced complex **3**, which can be isolated as a green solid (Scheme 2). The structure of **3** is supported by NMR spectroscopic data. The $^{31}P\{^1H\}$ NMR spectrum showed a signal for $CPPh_3$ at $\delta = 18.1$ ppm and for $RuPMe_3$ at $\delta = -13.9$ ppm. Two signals for the metallacycle in the ^1H NMR spectrum ($\delta = 17.0$ (RuCH) and 7.9 ppm (γ-CH)) and three in the $^{13}C\{^1H\}$ NMR spectrum ($\delta = 279.6$ (RuCH), 143.3 (CH), and 107.3 ppm ($CPPh_3$)) verifies the symmetrical structure of **3**.

Addition of *t*BuNC to a solution of **2** in dichloromethane led to the formation of the isocyanide-containing complex **4**. The structure of ruthenabenzene **4** was readily assigned on the basis of the NMR spectroscopic data. In particular, the $^{31}P\{^1H\}$ NMR spectrum showed three singlets at $\delta = 25.1$ ($RuPPh_3$), 23.3 ($CPPh_3$), and 18.3 ppm ($CPPh_3$). In the ^1H NMR spectrum, the two signals for RuCH appeared at $\delta = 15.6$ and 15.5 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the five signals for the metallacycle appeared at $\delta = 286.1$ (RuCH), 280.6 (RuCH), 149.1 (γ-CH), 113.7 ($CPPh_3$), and 113.6 ppm ($C(PPh_3)$).



Scheme 2. Ligand-substitution reactions of ruthenabenzene **2**.

Treatment of **2** with 2, 2′-dipyridyl led to the replacement of one chloride and one PPh_3 ligand by 2,2′-dipyridyl to give ruthenabenzene **5** (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ showed the signal for $CPPh_3$ at $\delta = 19.0$ ppm and for $RuPPh_3$ at $\delta = 45.6$ ppm. The ^1H NMR spectrum in $CDCl_3$ showed characteristic signals for RuCH at $\delta = 15.6$ and for γ-CH at $\delta = 8.2$ ppm. The $^{13}C\{^1H\}$ NMR spectrum showed three signals for the metallacycle at $\delta = 293.6$ (RuCH), 147.7 (γ-CH), and 120.2 ppm ($CPPh_3$), thus indicating that the metallacycle has a delocalized symmetrical structure.

The structure of **5** was also determined by X-ray diffraction (Figure 2).[20] Unlike complex **2**, the metallaben-

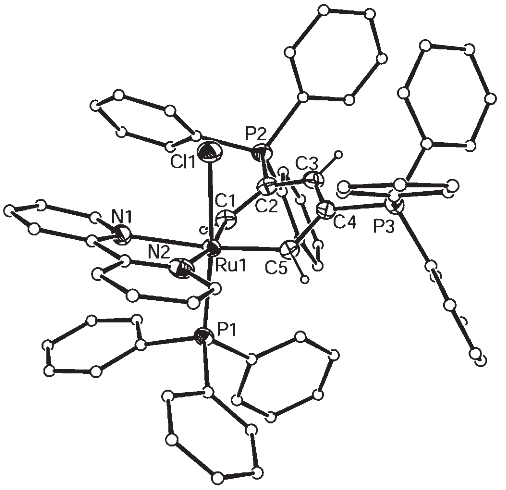


Figure 2. Molecular structure of **5** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Ru1–C1 1.935(4), C1–C2 1.382(6), C2–C3 1.387(7), C3–C4 1.396(7), C4–C5 1.407(6), C5–Ru1 1.914(4), C2–P2 1.793(5), C4–P3 1.790(5), Ru1–P1 2.3178(12), Ru1–Cl1 2.4407(13), Ru1–N1 2.210(4), Ru1–N2 2.189(4); C1-Ru1-C5 89.43(19), C1-Ru1-P1 94.23(14), C1-Ru1-Cl1 89.00(14), C5-Ru1-P1 96.47(14), C5-Ru1-Cl1 88.76(14), P1-Ru1-Cl1 173.87(4), N1-Ru1-N2 74.51(16), C2-C1-Ru1 123.9(3), C4-C5-Ru1 123.5(3), C1-C2-P2 117.2(4), C3-C4-P3 118.3(3), C3-C2-P2 118.8(4), C5-C4-P3 118.4(3), C1-C2-C3 123.9(4), C2-C3-C4 123.6(4), C3-C4-C5 122.8(4).

zene ring of **5** is, unexpectedly, distorted with the ruthenium center tilted out of the plane of the C_5 backbone. Atoms C1–C5 are coplanar, with a maximum deviation from the least-squares plane of 0.0207 (32) Å for C2. The C–C bond lengths of the C1–C5 chain are in the range 1.382(6)–1.407(6) Å, and there is no C–C bond-length alternation. The ruthenium center lies −0.6722 (56) Å out of the plane of the ring carbon atoms (C1, C2, C3, C4, C5). The dihedral angle between this plane and the C1/Ru/C5 plane is 29.3°. The tilt angle is even larger than that in the coordinated ruthenabenzene $[(C_5H_5)Ru(\mu\text{-}C_7H_9)Ru(C_5Me_5)(CH_3CN)]PF_6$ (27.2°).[12a] It is not very clear why the metallabenzene ring of **5** deviates significantly from planarity, whereas that of the closely related ruthenabenzene **2** is essentially planar. Although not common, other nonplanar metallabenzenes are known. For example, in iridabenzenes supported by Tp ligand, the iridium metal is also bent by 0.57 to 0.76 Å out of the plane of the metallacyclic carbon atoms.[2a,h]

In summary, we have prepared and structurally characterized several ruthenabenzenes. Ruthenabenzenes **2**–**5** are rare examples of stable metallabenzenes with a transition metal of the second transition series.

Experimental Section

2: Method A: A mixture of $[RuCl_2(PPh_3)_3]$ (0.60 g, 0.63 mmol), HC≡CCH(OH)C≡CH (55 mg, 0.69 mmol), PPh_3 (0.83 g, 3.2 mmol), and Bu_4NCl (0.40 g, 5.4 mmol) in THF (10 mL) was stirred at room temperature for about 10 h to give a brownish-green suspension. The green solid was collected by filtration, washed with THF (5 × 2 mL), and then dried under vacuum (0.45 g, 55 %). Method B: A mixture of $[RuCl_3{\cdot}3H_2O]$ (0.10 g, 0.38 mmol), PPh_3 (0.60 g, 2.3 mmol), and HC≡CCH(OH)C≡CH (34 mg, 0.42 mmol) in $CHCl_3$ (15 mL) was stirred at room temperature for about 20 h to give a brownish-black solution. The volume of the mixture was reduced to approximately 3 mL under vacuum. Addition of diethyl ether (20 mL) to the residue produced a brown solid, which was collected by filtration, washed with THF (2 × 5 mL) and diethyl ether (2 × 5 mL), and dried under vacuum (0.10 g, 20 %). ^{1}H NMR (300.1 MHz, $CDCl_3$): $\delta = 17.5$ (d, ^3J(PH) = 18.9 Hz, 2 H; RuCH), 8.2 (t, ^3J(PH) = 14.0 Hz, 1 H; RuCHC(PPh_3)C*H*), 7.9–6.6 ppm (m, 60 H; PPh_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 18.2$ (s; $CPPh_3$), 8.1 ppm (s, $RuPPh_3$); $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2): $\delta = 284.3$ (d, ^2J(PC) = 11.6 Hz; Ru*C*H), 146.0 (t, ^2J(PC) = 21.4 Hz; RuCHC(PPh_3)*C*H), 137.3–126.8 (m, PPh_3), 108.3 ppm (dd, ^1J(PC) = 73.2 Hz, ^3J(PC) = 12.1 Hz; RuCH*C*(PPh_3)); elemental analysis: calcd for $C_{77}H_{63}Cl_3P_4Ru$ (%): C 70.08, H 4.81; found: C 69.65, H 4.88.

3: A solution of PMe_3 in THF (1.0 M; 4.5 mL, 4.5 mmol) was added to a solution of **2** (0.40 g, 0.31 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for about 12 h to give a brown solution. The volume of the mixture was reduced to approximately 1 mL under vacuum. The residue was purified by column chromatography (neutral alumina, eluent: acetone/methanol 5:1) to give **3** as a green solid (0.17 g, 58 %). ^{1}H NMR (500.4 MHz, $CDCl_3$): $\delta = 17.0$ (d, ^3J(PH) = 16.5 Hz, 2 H; RuCH), 7.9 (t, ^3J(PH) = 14.5 Hz, 1 H; RuCHC(PPh_3)C*H*), 7.8–7.2 ppm (m, 30 H; PPh_3), 0.88 (t, *J*(PH) = 4.1 Hz, 18 H; $RuPMe_3$); $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$): $\delta = 18.1$ (s; $CPPh_3$), −13.9 ppm (s; $RuPMe_3$); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): $\delta = 279.6$ (d, ^2J(PC) = 12.7 Hz; RuCH), 143.3 (t, ^2J(PC) = 23.0; RuCHC(PPh_3)*C*H), 134.9–128.4 (m; PPh_3), 107.3 (dd, ^{1}J(PC) = 75.2 Hz, ^3J(PC) = 12.0 Hz; RuCH*C*(PPh_3)), 15.7 ppm (t, *J*(PC) = 15.4 Hz; PMe_3); elemental analysis: calcd for $C_{47}H_{51}Cl_3P_4Ru$ (%): C 59.60, H 5.43; found: C 59.79, H 4.96.

4: *t*BuNC (0.53 mL, 4.5 mmol) was added to a solution of **2** (0.40 g, 0.31 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for about 1 h to give a brown solution. The volume of the mixture was reduced to approximately 1 mL under vacuum. The residue was purified by column chromatography (neutral alumina, eluent: acetone/methanol 5:1) to give **4** as a green solid (0.23 g, 52 %). ^{1}H NMR (500.4 MHz, $CDCl_3$): $\delta = 15.6$ (d, ^3J(PH) = 23.3 Hz, 1 H; RuCH), 15.5 (d, ^3J(PH) = 19.0 Hz, 1 H, RuCH), 8.0 (t, ^3J(PH) = 13.5 Hz, 1 H; RuCHC(PPh_3)C*H*), 7.8–6.7 (m, 60 H; PPh_3), 1.1 ppm (s, 9 H; $(CH_3)_3CNC$); $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$): $\delta = 25.1$ (s; $RuPPh_3$), 23.3 ppm (s; $CPPh_3$), 18.3 ppm (s; $CPPh_3$); $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2): $\delta = 286.1$ (d, ^2J(PC) = 9.8 Hz; RuCH), 280.6 (d, ^2J(PC) = 10.2 Hz; RuCH), 149.1 (t, ^2J(PC) = 22.1; RuCHC(PPh_3)*C*H), 136.3–128.4 (m; PPh_3), 123.3 (s; $(CH_3)_3$CN*C*), 113.7 (d, ^1J(PC) = 72.3 Hz; RuCH*C*(PPh_3)), 113.6 (d, ^1J(PC) = 72.8 Hz; RuCH*C*(PPh_3)), 58.7 (s; $(CH_3)_3$*C*NC), 29.2 ppm (s; ($^{}$*C*$H_3)_3$CNC); elemental analysis: calcd for $C_{82}H_{72}NP_4Cl_3Ru$ (%): N 1.00, C 70.21, H 5.17; found: N 1.35, C 70.24, H, 5.51.

5: 2,2′-Dipyridyl (94 mg, 0.60 mmol) was added to a solution of **2** (0.40 g, 0.31 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for about 5 h to give a brown-green solution. The volume of the mixture was reduced to approximately 1 mL under vacuum. The residue was purified by column chromatography (neutral alumina, eluent: acetone/methanol 5:1) to give **5** as a green solid (0.21 g, 49 %). ^{1}H NMR (500.4 MHz $CDCl_3$,): $\delta = 15.6$ (dd, ^3J(PH) = 16.0 Hz, ^3J(PH) = 8.0 Hz, 2 H; RuCH), 9.0 (d, ^3J(HH) = 8.0 Hz, 2 H; NCH), 8.2 (t, ^3J(PH) = 8.0 Hz, 1 H; RuCHC(PPh_3)C*H*), 7.8–6.7 ppm (m, 51 H; PPh_3, 2,2′-dipyridyl); $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$): $\delta = 45.6$ (t, ^4J(PP) = 2.6 Hz; Ru(PPh_3)), 19.0 ppm (d, ^4J(PP) = 2.6 Hz; $CPPh_3$); $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2): $\delta = 293.6$ (d, ^2J(PC) = 12.6 Hz; RuCH), 154.0 (s; $N(CH)_4$*CC*$(CH)_4N$), 147.7 (t, ^2J(PC) = 22.8 Hz; RuCHC(PPh_3)*C*H), 147.5 (s; N(*C*H)(CH)(CH)(CH)C), 140.0 (s; N(CH)(*C*H)(CH)(CH)C), 136.3–128.4 (m; PPh_3), 126.0 (s; N(CH)(CH)(*C*H)(CH)C), 124.9 (s; N(CH)(CH)(CH)(*C*H)C), 120.2 ppm (dd, ^1J(PC) = 75.8 Hz, ^3J(PC) = 13.1 Hz; RuCH*C*(PPh_3)); elemental analysis: calcd for $C_{69}H_{56}N_2P_3Cl_3Ru$ (%): N 2.31, C 68.29, H 4.65; found: N 2.06, C 68.13, H 4.87.

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[20] Crystal data for **2**: $C_{77.50}H_{71}Cl_4O_{3.50}P_4Ru$, $M_r = 1425.09$, monoclinic, $P2(1)/n$, $Z = 4$, $a = 17.580(2)$, $b = 24.385(3)$, $c = 18.446(3)$ Å, $\alpha = 90$, $\beta = 110.948(2)$, $\gamma = 90°$, $V = 7385.3(17)$ Å^3; 53143 reflections, 12954 independent reflections ($R_{int} = 0.0705$); $R_1 = 0.0757$, $wR_2 = 0.1916$ for 847 parameters and 10129 reflections with $[I > 2\sigma(I)]$. Crystal data for **5**: $C_{70.50}H_{65}Cl_6N_2O_3P_3Ru$, $M_r = 1394.92$, triclinic, $P\bar{1}$, $Z = 2$, $a = 13.915(2)$, $b = 14.921(2)$, $c = 18.165(3)$ Å, $\alpha = 104.201(2)$, $\beta = 106.209(3)$, $\gamma = 102.962(3)°$, $V = 3332.6(9)$ Å^3; 33450 reflections, 12344 independent reflections ($R_{int} = 0.0357$); $R_1 = 0.0699$, $wR_2 = 0.1776$ for 784 parameters and 11133 reflections with $[I > 2\sigma(I)]$. Crystals of **2** and **5** suitable for X-ray diffraction were grown from a solution in CH_2Cl_2 layered with diethyl ether. Intensity data were collected on a Bruker SMART CCD Area Detector with graphite-monochromated $Mo_{K\alpha}$ radiation at temperature of 223 K. The structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares methods on F^2 by using the Bruker SHELXTL (Version 6.10) program package. All non-hydrogen atoms were refined anisotropically. CCDC-294492, and CCDC-294494 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.