Metallacycles

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# Synthesis and Characterization of Rhenabenzenes**

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There has been much interest in the chemistry of transition-metal-containing metallabenzenes.[1] These compounds are interesting because they often display the chemical properties of both organometallic compounds and aromatic organic compounds. The isolation and characterization of stable examples represent one of the major challenges in metallabenzene chemistry. Previous studies have led to the isolation of an impressive number of stable metallabenzene compounds that contain a late transition metal, such as osmium,[2–4] ruthenium,[5,6] iridium,[7–10] and platinum.[11]

In contrast, the isolation of stable metallabenzenes that contain an early or middle transition metal (Group 3–7) has so far met with limited success,[12] although manganabenzenes were predicted theoretically 30 years ago.[13] Whilst metallabenzenes, such as rhenabenzene,[14] rhenaphenathrene,[15] chromabenzene,[16] and tungstabenzene[17] have been suggested as reaction intermediates, no direct observation of such species has been made. Herein, we report the preparation and structural characterization of the first stable rhenabenzenes.

One of the major difficulties in the isolation of stable metallabenzenes is that such complexes may have low thermal stability and tend to rearrange to more thermodynamically stable cyclopentadienyl complexes.[4a,8c,9a] In our previous work on the chemistry of osmabenzynes, we found that a methoxy substituent at the α carbon atom of a metallabenzene can stabilize the metallabenzene relative to cyclopentadienyl complexes.[4a] Therefore, we envisioned that stable rhenabenzene compounds might be obtained by attaching alkoxy groups onto the rhenabenzene ring. To test this possibility, and to provide a guide for our experimental work, we carried out computational studies[18,19] on the relative stability of various substituted rhenabenzenes and their corresponding cyclopentadienyl complexes (Figure 1). The unsubstituted rhenabenzene **1** is very unstable with respect to the Cp complex **2** (Figure 1). The introduction of an OMe group onto the rhenabenzene ring at the γ (**3**) or α position (**5**) significantly increased the relative stability of the rhenabenzene compounds (Figure 1). Most interestingly, the formation of Cp complex **7** from rhenabenzene **6**, which contains two OMe substituents, was found to be unfavorable in terms of the reaction energy. These computational results were encouraging, as they implied that rhenabenzenes that contain two OR substituents should be sufficiently stable for isolation.

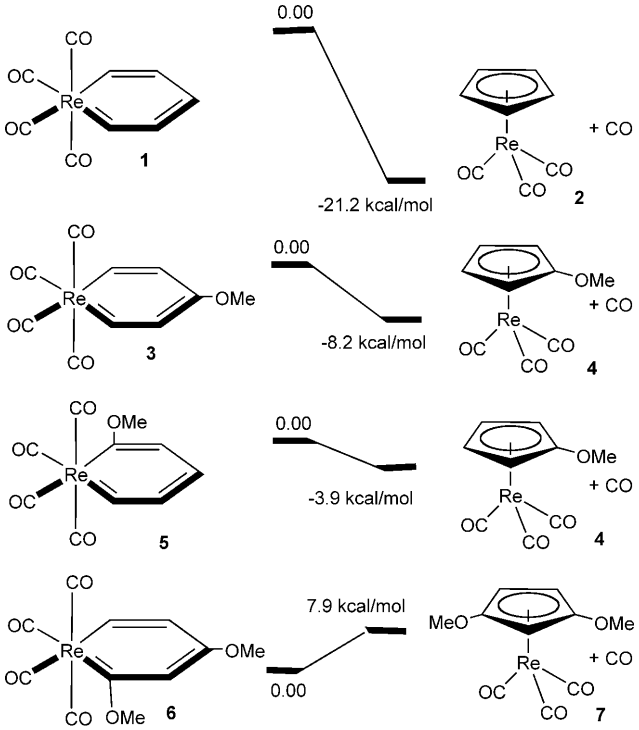


***Figure 1.*** Relative reaction energies of rhenabenzenes and their corresponding cyclopentadienyl complexes.

Plantevin and Wojcicki reported a series of reactions of rhenacyclobutadienes with alkynes that afforded substituted cyclopentadienyl complexes.[14] It was suggested that the cyclopentadienyl complexes were formed via rhenabenzene intermediates that were not isolated or detected, probably because of their low thermal stability. We reasoned that the reactions of HC≡COR with rhenacyclobutadiene complexes that contain ethoxy substituents would give rhenabenzenes with two OR substituents, which our computations indicated should be stable.

Stable ethoxy-containing rhenacyclobutadiene complexes **9** and **10**, to be used as rhenabenzene precursors, were synthesized from the reaction of $Na[Re(CO)_5]$ with RC≡$CCO_2Et$, followed by treatment with propionyl chloride and ethanol (Scheme 1). This route has been used previously for

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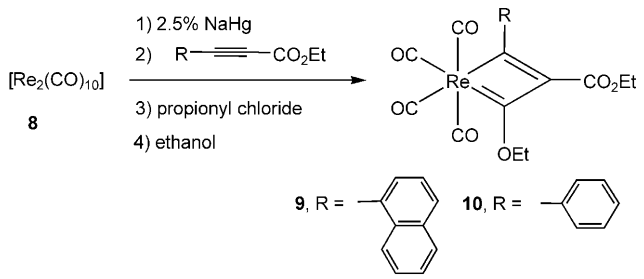
the synthesis of analogous rhenacyclobutadiene complexes.[20] Compounds **9** and **10** were obtained as orange and orange-brown crystalline solids in 52 and 37% yield, respectively.




***Scheme 1.*** Preparation of stable rhenacyclobutadienes **9** and **10**.

Both complexes were characterized by spectroscopic methods and the structure of **9** was also confirmed by single-crystal X-ray diffraction (Figure 2).[21]

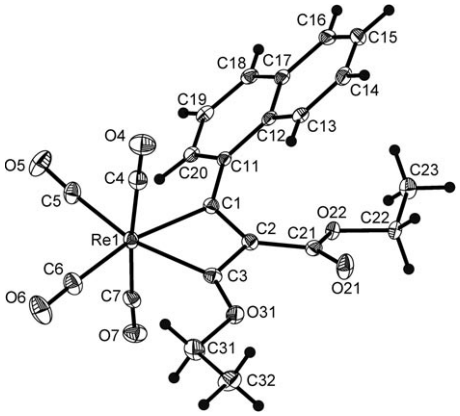
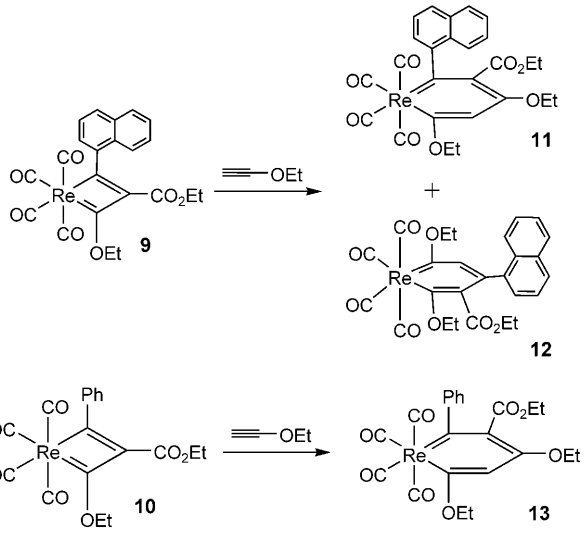


***Figure 2.*** Molecular structure of **9** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Re(1)–C(3) 2.145(3), Re(1)–C(1) 2.188(3), C(1)–C(2) 1.383(4), C(2)–C(3) 1.432(4); C(3)-Re(1)-C(1) 60.63(11), C(2)-C(1)-C(11) 127.4(3), C(2)-C(1)-Re(1) 98.50(19), C(1)-C(2)-C(3) 102.0(3).

Treatment of the rhenacyclobutadienes **9** and **10** with alkyne 1-ethoxyethyne resulted in the formation of stable rhenabenzene compounds (Scheme 2). In the case of the naphthyl-substituted compound **9**, the reaction gave a mixture of products, from which rhenabenzene **11** was isolated as orange block-shaped crystals in 10% yield, and the isomeric rhenabenzene **12** was isolated as a yellow oil in 15% yield (Scheme 2). The phenyl analogue **10** also gave a mixture, including rhenabenzene **13,** which was isolated as an orange solid.

The structures of rhenabenzenes **11** and **13** were determined by single-crystal X-ray diffraction and are shown in Figures 3 and 4, respectively. Both compounds are structurally similar; however, the structure of **13** was determined to a greater accuracy and its geometry is used in the discussion below. Both compounds contain an essentially planar rhenabenzene unit with no deviations from the mean plane greater




***Scheme 2.*** Preparation of rhenabenzenes.

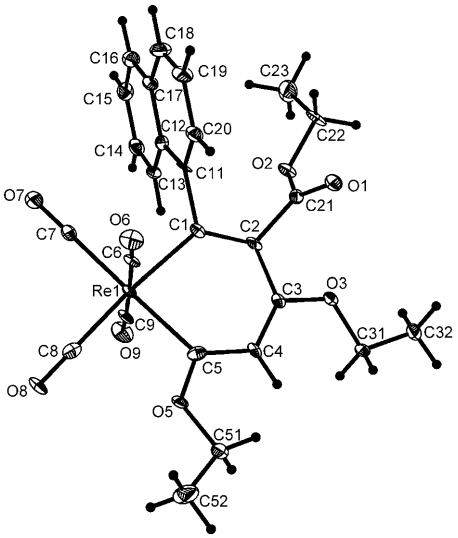


***Figure 3.*** Molecular structure of **11** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Re(1)–C(5) 2.153(7), Re(1)–C(1) 2.175(7), C(1)-C(2) 1.363(10), C(2)–C(3) 1.451(10), C(3)–C(4) 1.372(10), C(4)–C(5) 1.416(10), C(3)–O(3) 1.345(8), C(5)–O(5) 1.325(9); C(5)-Re(1)-C(1) 86.0(3), C(2)-C(1)-Re(1) 126.1(5), C(1)-C(2)-C(3) 125.9(7), C(4)-C(3)-C(2) 127.6(7), C(3)-C(4)-C(5) 122.8(7), C(4)-C(5)-Re(1) 128.2(6).

than 0.15 Å. The Re–C bonds have an intermediate length in between a Re=C carbene bond, which has an average of 2.06(5) Å from over 20 hits from the Cambridge Structural Database, and a Re–C single bond, which has an average of 2.22(7) Å from 400 hits.[22] The Re–C(OEt) bond is significantly shorter (Re(1)–C(5) = 2.142(4) Å) than the Re–C(Ph) bond (Re(1)–C(1) = 2.184(3) Å), because of the electronic asymmetry of the substituent groups. A similar pattern for the Re–C bond lengths was found for rhenacylocbutadiene **9**. In both **11** and **13** there is some degree of C(1)=C(2)–C(3) bond

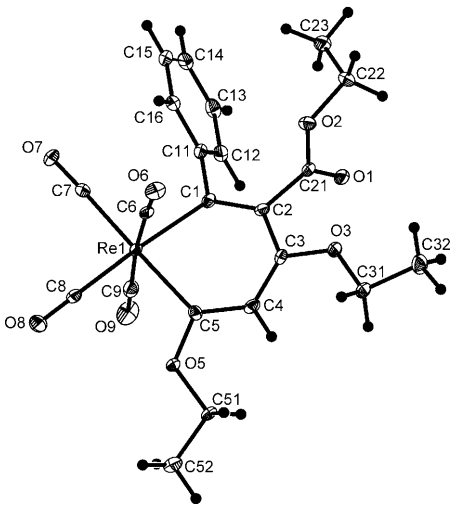



***Figure 4.*** Molecular structure of **13** (thermal ellipsoids set at 50% probability) Selected bond lengths [Å] and angles [°]: Re(1)–C(05) 2.142(4), Re(1)–C(1) 2.184(3), C(1)–C(2) 1.356(5), C(2)–C(3) 1.444(5), C(3)–C(4) 1.392(5), C(4)–C(5) 1.391(5), C(3)–O(3) 1.340(4), C(5)–O(5) 1.353(4); C(5)-Re(1)-C(1) 85.57(13), C(4)-C(5)-Re(1) 128.5(3), C(2)-C(1)-Re(1) 125.0(3), C(1)-C(2)-C(3) 125.7(3), C(4)-C(3)-C(2) 127.9(3), C(5)-C(4)-C(3) 122.0(3).

localization, but overall, the Re–C and C–C bond lengths within the six-membered ring, together with its planar nature, indicate that the metallacycle has a generally delocalized structure.

The solution NMR data of **11** and **13** are consistent with their solid-state structures. In particular, the $^1$H NMR spectrum of **11** displayed a characteristic $^1$H signal at 6.27 ppm, which corresponds to the proton on the metallacyclic ring. The $^{13}C\{^1H\}$ NMR spectrum showed Re*C*(OEt) and Re*C*-(Naph) signals at $\delta = 258.7$ and 203.1 ppm, respectively. The other $^{13}$C signals of the metallacycle were found at $\delta =$ 103.1 ppm (β-*C*H), $\delta = 155.3$, and 166.6 ppm.

The structure of isomer **12** was inferred from its $^1$H and $^{13}$C NMR data. The $^1$H NMR spectrum displayed a characteristic $^1$H signal at $\delta = 4.83$ ppm; the $^{13}C\{^1H\}$ NMR spectrum showed two ReC(OEt) signals at $\delta = 242.0$ and 213.7 ppm. Other $^{13}$C signals of the metallacycle were observed at $\delta =$ 94.2 ppm (β-*C*H), 161.4, and 166.8 ppm. The remaining NMR data are similar to those of **11**.

In summary, through both computational and experimental efforts, we have successfully isolated and structurally characterized three rhenabenzene compounds, **11**–**13**, which represent rare examples of stable metallabenzenes that contain a Group 7 transition metal.

## *Experimental Section*

Synthesis of **11** and **12**: A hexane solution of ethyl ethynyl ether (40%, 1.32 mL, 5.42 mmol) was added to a solution of **9** (1.047 g, 1.81 mmol) in acetonitrile (80 mL) at 0 °C. The resultant mixture was stirred at this temperature for one hour and then at room temperature for about 18 h to give a dark brown solution. The solvents were then removed under reduced pressure. The mixture was purified by column chromatography on silica gel. The column was first eluted with hexane/$Et_2O$ (6:1) followed by hexane/$Et_2O$ (1:1) to afford three fractions. The first fraction was a yellow solution. A yellow oil, which was identified to be **12** (180 mg, 15.3% yield), was obtained after removal of the solvents. The second fraction was collected as a yellow solution. Removal of the solvents under reduced pressure afforded a brown solid which was identified to be the starting material, rhenacyclobutadiene complex **9** (204 mg, 19.5% yield). The third fraction was a reddish orange solution. A dark-orange sticky material was obtained after removing the solvents. The $^1$H NMR spectrum showed 3 singlets at $\delta = 5.61$, 5.65, and 6.84 ppm in an integration ratio of 0.7:0.25:1. The residue was extracted with a minimal amount of petroleum ether/dichloromethane (20:1). Storing the resultant orange solution in a freezer at −30 °C for 2 days afforded bright orange crystals that were collected by filtration, washed with ice-cooled hexane, and dried under vacuum. The solid was identified to be rhenabenzene **11** (117 mg, 10% yield). Crystals suitable for X-ray analysis were obtained by refrigerating a solution of the rhenabenzene in tetrahydrofuran/cyclohexane (1:30) for one week. Compound **11**: $^1$H NMR (400.1 MHz, $CD_3CN$): $\delta = 0.57$ (t, $J = 7.2$ Hz, 3H, $CH_3$), 1.39 (t, $J = 7.2$ Hz, 3H, $CH_3$), 1.54 (t, $J = 7.2$ Hz, 3H, $CH_3$), 3.56 (q, $J = 7.2$ Hz, 2H, $OCH_2$), 4.35 (q, $J = 7.2$ Hz, 2H, $OCH_2$), 4.46 (q, $J = 7.2$ Hz, 2H, $OCH_2$), 6.27 (s, 1H, ReC(OEt)C*H*), 6.83 (d, , $J =$ 7.2 Hz, 1H, Naph), 7.41 (m, 3H, Naph), 7.57 (d, $J = 8.4$ Hz, 1H, Naph), 7.70 (d, $J = 8.0$ Hz, 1H, Naph), 7.75 ppm (d, $J = 7.2$ Hz, 1H, Naph); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CD_3CN$): $\delta = 12.2$ (s, $CH_3$), 12.7 (s, $CH_3$) 12.9 (s, $CH_3$), 59.0 (s, $OCH_2$), 66.2 (s, $OCH_2$), 68.3 (s, $OCH_2$), 103.1 (s, ReC(OEt)C*H*),123.9. 124.0, 124.4, 125, 126.2, 126.3, 127.3, 132.8, 136.7, 155.1, 166.6 (s, $CO_2$Et), 186.3 (s, CO), 187.2 (s, CO), 187.4 (s, CO), 189.7 (s, CO), 203.1 (s, Re*C*(Naph)), 258.7 ppm (s, Re*C*-(OEt)). Elemental analysis (%) calcd for $C_{26}H_{27}O_8Re$: C 47.77, H 4.16; found: C 48.00, H 3.81. Compound **12:** $^1$H NMR (300.1 MHz, $CD_3COCD_3$): $\delta = 0.30$ (t, $J = 7.2$ Hz, 3H, $CH_3$), 1.11 (t, $J = 7.2$ Hz, 3H, $CH_3$), 1.45 ( t, $J = 7.2$ Hz, 3H, $CH_3$), 3.07 (d, $J = 6.0$ Hz, 2H, $OCH_2$), 4.00 (q, $J = 7$ .2 Hz, 2H, $OCH_2$), 4.75 (q, $J = 7.2$ Hz, $OCH_2$), 4.83 (s, 1H, ReC(OEt)C*H*), 7.26–7.46 (m, 4H, Naph), 7.72 (d, $J =$ 8.1 Hz, 1H, Naph), 7.80 (dd, $J = 8.1$, 1.2 Hz, 1H, Naph), 7.90 ppm (d, $J = 8.1$ Hz, 1H, Naph). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CD_3COCD_3$): $\delta =$ 12.9 (s, $CH_3$), 14.2 (s, $CH_3$), 14.5 (s, $CH_3$), 59.3 (s, $OCH_2$), 64.2 (s, $OCH_2$), 79.7 (s, $OCH_2$), 94.2 (s, ReC(OEt)C*H*), 123.4, 125.5, 125.8, 126.3, 127.2, 128.2, 133.8, 146.4, 161.38, 166.8 (s, $CO_2$Et), 191.0 (s, CO), 192.0 (s, CO), 194.3 (s, CO), 211.0 (s, CO)), 213.7 (s, Re*C*-(OEt)CH), 242.0 ppm (s, Re*C*(OEt)C($CO_2$Et)). Elemental analysis (%) calcd for $C_{26}H_{27}O_8Re$: C 47.77, H 4.16; found: C 48.22, H 3.76.

**Synthesis of 13**: A solution of ethyl ethynyl ether in hexane (40%, 0.55 mL, 2.24 mmol) was added to a solution (30 mL) of **10** in acetonitrile (0.591 g, 1.12 mmol). The mixture was stirred at room temperature for about 18 h to give a dark brown solution. The solvents were removed under reduced pressure. The resulting oily mixture was purified by column chromatography on silica gel. The column was first eluted with heaxane/$Et_2O$ (10:1). Further elution of the column with hexane/$Et_2O$ (1:1) gave two fractions (one red and the other orange). The red fraction showed no $^1$H NMR signals in the region $\delta = 5$–7 ppm in the $^1$H NMR spectrum. The solvent of the orange fraction was removed under reduced pressure to give a dark-orange sticky material. The residue was extracted with hexane and stored in a freezer at −30 °C for 48 h to afford red-orange needle-shaped crystals. The crystalline solid was collected by filtration, washed with cold hexane, and dried under vacuum. The compound was identified to be **13** (34 mg, 5% yield). Bright orange block-shaped crystals that were suitable for X-ray analysis were obtained by storing a tetrahydrofuran/cyclohexane solution in a refrigerator at 0 °C for 2 days. $^1$H NMR (400.1 MHz, $CD_3CN$): $\delta = 0.94$ (t, $J = 7.2$ Hz, 3H $CH_3$), 1.37 (t, $J = 7.2$ Hz, 3H, $CH_3$), 1.51 (t, $J = 7.2$ Hz, 3H, $CH_3$), 3.76 (q, $J = 7.2$ Hz, 2H, $OCH_2$), 4.29 (q, $J = 7.2$ Hz, 2H $OCH_2$), 4.42 (q, $J =$ 7.2 Hz, $OCH_2$), 6.18 (s, 1H, ReC(OEt)C*H*), 6.84 (d, $J = 7.6$ Hz, 2H, Ph), 7.01 (t, $J = 7.6$ Hz, 1H, Ph), 7.28 ppm (t, $J = 7.6$ Hz, 2H Ph). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CD_3CN$): $\delta = 13.4$ (s, $CH_3$), 13.7 (s, $CH_3$), 60.0 (s, $OCH_2$), 66.9 (s, $OCH_2$), 68.9 (s, $OCH_2$), 103.6 (s, ReC-

(OEt)*C*H), 121.8, 124.5, 127.6, 137.0, 158.9, 167.4 (s, *C*$O_2$Et), 187.6 (s, *C*O), 187.9 (s, *C*O), 190.8 (s, *C*O), 191.0 (s, *C*O), 205.1 (s, Re*C*(Ph), 258.5 ppm (s, Re*C*(OEt)). Elemental analysis (%) calcd for $C_{22}H_{25}O_8Re$: C 43.77, H 4.17; found: C 44.28, H 3.72.

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**Keywords:** alkynes · arenes · metallacycles · rhenium · transition metals

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[21] Crystal data for **9** ($C_{22}H_{17}O_7Re$, $M_r = 579.56$): triclinic, $P\bar{1}$, $Z = 2$, $a = 7.7754(8)$, $b = 11.3457(12)$, $c = 11.8899(12)$ Å, $\alpha = 86.2570(10)$, $\beta = 79.4150(10)$, $\gamma = 86.6930(10)°$, $V = 1027.73(18)$ Å$^3$, 6736 reflections, $R1 = 0.0221$, $wR2 = 0.0510$ for 271 parameters and $R(\text{int}) = 0.0210 = 4284$ reflections with $[I > 2\sigma(I)]$. Crystal data for **13** ($C_{22}H_{21}O_8Re$, $M_r = 599.59$): triclinic, $P\bar{1}$, $Z = 2$, $a = 9.0242(8)$, $b = 9.4748(8)$, $c = 13.5816(12)$ Å, $\alpha = 100.5730(10)$, $\beta = 102.9210(10)$, $\gamma = 96.2170(10)°$, $V = 1099.04(17)$ Å$^3$, 7724 reflections, $R1 = 0.0232$, $wR2 = 0.0518$ for 283 parameters and $R(\text{int}) = 0.0190$ for 4171 reflections with $[I > 2\sigma(I)]$. Crystal data for **11** ($C_{32}H_{35}O_8Re$, $M_r = 733.80$) triclinic, $P\bar{1}$, $Z = 2$, $a = 7.1763(16)$, $b = 13.311(3)$, $c = 17.253(4)$ Å, $\alpha = 104.927(3)$, $\beta = 99.225(3)$, $\gamma = 103.506(2)°$, $V = 1505.1(6)$ Å$^3$, 7899 reflections, $R1 = 0.0520$, $wR2 = 0.1241$ for 370 parameters and $R(\text{int}) = 0.0372$ for 5674 reflections with $[I > 2\sigma(I)]$. Intensity data were collected on a Bruker SMART CCD Area Detector with graphite-monochromated $Mo_{K\alpha}$ radiation at a temperature of 173 K. The structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares methods on $F^2$ using the Bruker SHELXTL (Version 6.10) program package. All non-hydrogen atoms were refined anisotropically. CCDC 757667 (**9**), CCDC 757668 (**11**), and CCDC 757669 (**13**) 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.

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