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Bond Activation |*Hot Paper*|

Multiple C–H Bond Activations in Corannulene by a Dirhenium Complex

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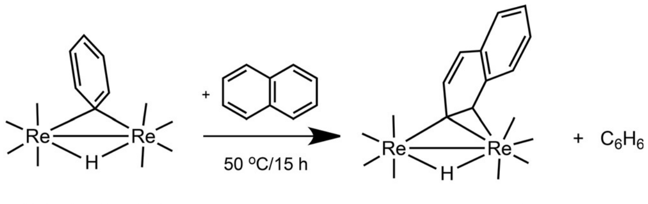
Abstract: The reaction of $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1** with corannulene ($C_{20}H_{10}$) yielded the product $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}C_{20}H_9)$, **2** (65% yield) containing a Re_2 metalated corannulene ligand formed by loss of benzene from **1** and the activation of one of the CH bonds of the nonplanar corannulene molecule by an oxidative-addition to **1**. The corannulenyl ligand has adopted a bridging $\eta^2\text{-}\sigma+\pi$ coordination to the $Re_2(CO)_8$ grouping. Compound **2** reacts with a second equivalent of **1** to yield three isomeric doubly metalated corannulene products: $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}10,11\text{-}C_{20}H_8)\text{-}Re_2(CO)_8(\mu\text{-}H)$, **3** (35% yield), $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}2,1\text{-}\mu\text{-}\eta^2\text{-}10,11\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **4** (12% yield), and $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}11,10\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **5** (12% yield), by a second CH activation on a second rim double bond on the corannulene molecule. The isomers differ by the relative orientations of the coordinated $Re_2(CO)_8(\mu\text{-}H)$ groupings. All new products were characterized structurally by single crystal X-ray diffraction analysis.

Introduction

Bowl-shaped polycyclic aromatic compounds, such as corannulene, have attracted considerable attention because of their remarkable multi-electron transfer redox properties and their potential for the storage of electrical charge.[1,2] There are a number of examples of π-coordinated metal groupings to the rings of corannulenes in both η^6- and η^2-coordination modes.[3] Metalated corannulenes have been obtained by the oxidative addition of the C–X, X = halide, bonds of halocorannulenes to $Pt(PEt_3)_4$ and related complexes.[4] Thompson has reported the first examples of cyclometalated-platinum and -iridium corannulenes by using pyridyl-substituted derivatives of corannulene.[5]

The oxidative addition of aromatic CH bonds to metal complexes has attracted great interest in recent years.[6] It was recently shown that the dirhenium complex $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1** which contains a bridging η^1-phenyl ligand and a bridging hydrido ligand across its unsaturated Re–Re bond[7] will eliminate benzene under very mild conditions and then react with other arenes by binuclear oxidative addition of C–H bonds to yield new dirhenium complexes containing bridging aryl ligands, see Scheme 1.[8] In 2016, the mechanism for the binuclear oxidative addition for the activation of an aromatic CH bond of benzene to the dirhenium octacarbonyl group of **1** was established by a density functional theory analysis.[8]



$Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}Ph)$, **1**

$Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}C_{10}H_7)$

Scheme 1. A schematic for benzene-naphthalene exchange in compound **1**. CO ligands are represented only as lines to the rhenium atoms.

In recent studies we have shown that **1** can undergo reductive elimination of benzene, and undergo multiple CH activations to naphthalene and anthracene in the presence of an excess of **1**.[9]

We have now investigated the reactions of bowl-shaped corannulene, $C_{20}H_{10}$, with **1** and have obtained not only the first example of direct aromatic CH bond activation in this molecule, but we have also obtained three isomeric doubly metalated corannulenes by the oxidative addition of two CH bonds to corannulene. These results are reported herein.

Experimental Details

General Data. All reactions were performed under a nitrogen atmosphere by using the standard Schlenk glassware techniques. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Nicolet IS10 Midinfrared FT-IR spectrophotometer. ^1H NMR

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and ^{13}C NMR were recorded on a Bruker Advance III-HD spectrometer operating at 300 and 400 MHz, respectively. Mass spectrometric (MS) measurements performed by a direct-exposure probe by using electron impact ionization (EI) were made on a VG 70S instrument. $Re_2(CO)_{10}$ was obtained from STREM and was used without further purification. Corannulene was prepared by a previously reported method.[10] $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1** was prepared according to previously reported procedure.[7] Product separations were performed by TLC in air on Analtech 0.25 or 0.5 mm silica gel 60 Å F_{254} glass plates.

Reaction of $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, 1 with corannulene in a 1:2 ratio

A 25.0 mg (0.037 mmol) amount of **1** and 8.0 mg (0.072 mmol) of corannulene, $C_{20}H_{10}$, were dissolved in 1.6 mL CD_2Cl_2 and placed in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then heated to 40 °C for 24 h. A ^{1}H NMR spectrum obtained after this period showed a new hydride resonance at $\delta = -13.44$. The contents were then put into a flask and solvent was removed in vacuo. The residue was extracted in CH_2Cl_2 and separated by TLC by using hexane to give a yellow band of 20.0 mg of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}C_{20}H_9)$, **2**, 65 % yield as major product and a yellow band of 5.0 mg of $[Re_2(CO)_8(\mu\text{-}H)](\mu\text{-}1\text{-}\mu\text{-}3\text{-}C_6H_4)[Re_2(CO)_8(\mu\text{-}H)]$ in 21 % yield.[9] Spectral data for **2**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2112(m), 2083(s), 2018(vs.), 1989(sh), 1974(s), 1955(sh). ^{1}H NMR (CD_2Cl_2, δ in ppm) 8.02 (d, 1 H, $^3J = 8.7$ Hz), 7.98 (d, 1 H, $^3J = 8.7$ Hz), 7.83–7.92(m, 6 H), 6.69(s, 1 H), −13.44 (s, 1 H, hydride). Mass Spec. EI/MS *m/z*: 846, [M^+], 818, [$M^+ - CO$], 790, [$M^+ - 2CO$]. The isotope distribution pattern in these ions is consistent with the presence of two rhenium atoms.

Reaction of 1 with corannulene in a 3:1 ratio

A 40.0 mg (0.059 mmol) amount of **1** and 5.0 mg (0.020 mmol) of corannulene were dissolved in 1.6 mL CD_2Cl_2 and placed in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen gas. The NMR tube was then heated to 40 °C for 24 h. A ^{1}H NMR spectrum obtained after this period showed three new hydride resonances at $\delta = -13.46$, -13.49 and -13.50 in addition to the one of **2**. The contents were then transferred to a flask and solvent was removed in vacuo. The residue was then dissolved in CH_2Cl_2 and then separated by TLC by using hexane solvent to give in order of elution: a yellow band of 15.0 mg of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}10,11\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **3**, 35 % yield and another yellow band of 5.0 mg of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}2,1\text{-}\mu\text{-}\eta^2\text{-}10,11\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **4**, 12 % yield, yellow band of 5.0 mg of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}11,10\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **5**, 12 % yield along with 10.0 mg of **2**, 20 % yield and 7.0 mg of $[Re_2(CO)_8(\mu\text{-}H)](\mu\text{-}1\text{-}\mu\text{-}3\text{-}C_6H_4)[Re_2(CO)_8(\mu\text{-}H)]$, 19 % yield.[9] Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2111(m), 2084(s), 2020(vs.), 1991(sh), 1975(s), 1957(sh). ^{1}H NMR (CD_2Cl_2, δ in ppm) 7.88–8.07(m, 6 H), 6.69(s, 2 H), −13.46 (s, 1 H, hydride) and −13.50 (s, 1 H, hydride). Spectral data for **4**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2110(m), 2083(s), 2019(vs.), 1991(sh), 1976(s), 1956(sh). ^{1}H NMR (CD_2Cl_2, δ in ppm) 8.04(d, 2 H, $^3J = 8.7$ Hz), 8.07 (d, 2 H, $^3J = 8.7$ Hz), 7.91(s, 2 H), 6.71(s, 2 H), −13.49 (s, 2 H, hydride). Spectral data for **5**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2110(m), 2083(s), 2019(vs.), 1991(sh), 1974(s), 1957(sh). ^{1}H NMR (CD_2Cl_2, δ in ppm) 8.11(s, 2 H), 7.88 (d, 2 H, $^3J = 7.5$ Hz), 7.93 (d, 2 H, $^3J = 7.5$ Hz), 6.73(s, 2 H), −13.46 (s, 2 H, hydride).

Preparation of 3, 4 and 5 from reaction of 2 with 1

A 25.0 mg (0.037 mmol) amount of **1** and 20.0 mg (0.024 mmol) of **2** were dissolved in 1.6 mL CD_2Cl_2 and placed in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then heated to 40 °C for 24 h. The contents were then put into a flask and solvent was removed in vacuo. The residue was extracted in CH_2Cl_2 and separated by TLC by using hexane to give a yellow band of 14.0 mg of **3**, 40 % yield, 4.0 mg of **4**, 15 % yield and 5.0 mg of **5**, 11 % yield along with 5.0 mg of $[Re_2(CO)_8(\mu\text{-}H)](\mu\text{-}1\text{-}\mu\text{-}3\text{-}C_6H_4)[Re_2(CO)_8(\mu\text{-}H)]$, 20 % yield.[9]

Thermolysis of 3 at 40 °C

10.0 mg (0.007 mmol) of **3** was dissolved in 1.6 mL CD_2Cl_2 and placed in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen and was then heated to 45 °C for 40 h. A ^{1}H NMR spectrum taken after 40 h showed hydride resonances for **2**, **3**, **4** and **5**. Approximately, 90 % of the **3** had been converted into **2**. Compounds **3**, **4** and **5** were present in the ratio of 4:1:2, respectively, in addition to a small amount of $Re_2(CO)_8(\mu\text{-}Cl)(\mu\text{-}H)$.

Crystallographic Analyses: Yellow single crystals of **2**, **3**, **4**, and **5** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from solutions in pure hexane or a mixture of hexane and benzene at 20 °C in the open air. X-ray intensity data were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo K_α radiation, $\lambda = 0.71073$ Å).[11] Correction for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections were applied using the program SADABS.[12] All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2, using the SHELXTL software packages.[13] For further information, see the Supplementary Material. Crystal data, data collection parameters, and results for the analyses are listed in Table S1. CCDC 1883385–1883388 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre

Results and Discussion

The reaction of $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1** with corannulene in a 1:2 molar ratio in CD_2Cl_2 at 40 °C for 24 h yielded the new compound $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}C_{20}H_9)$, **2** (65 % yield) together with the known compound $[Re_2(CO)_8(\mu\text{-}H)](\mu\text{-}1\text{-}\mu\text{-}3\text{-}C_6H_4)$-$[Re_2(CO)_8(\mu\text{-}H)]$ in 21 % yield which is a product of the condensation of **1** with itself.[9]

Compound **2** was characterized by IR, ^{1}H NMR spectroscopy, mass spectrometry and structurally by a single-crystal X-ray diffraction analysis. Compound **2** crystallized with two symmetry-independent molecules in the asymmetric crystal unit. Both molecules are structurally similar. An ORTEP diagram of the molecular structure of one of these two symmetry-independent molecules of **2** is shown in Figure 1. The complex contains a bowl-shaped corannulenyl ligand that has undergone a CH activation at one of the rim CH bonds, C1. The carbon atoms C1 and C2 are coordinated to a $Re_2(CO)_8(\mu\text{-}H)$ grouping in the traditional $\eta^2\text{-}\sigma+\pi$ coordination mode exhibited by bridging alkenyl ligands. See the related compound $\{Re_2(CO)_8\text{-}[\mu\text{-}HCC(H)C_4H_9]_2(\mu_4\text{-}Hg)\}$, **6**, as an example of a compound that contains an $\eta^2\text{-}\sigma+\pi$ bridging alkenyl ligand coordinated to a Re_2 metal grouping.[14] Atom Re1 is σ-coordinated to C1 and Re2 is η^2-π-coordinated to the atoms C1 and C2 of the rim

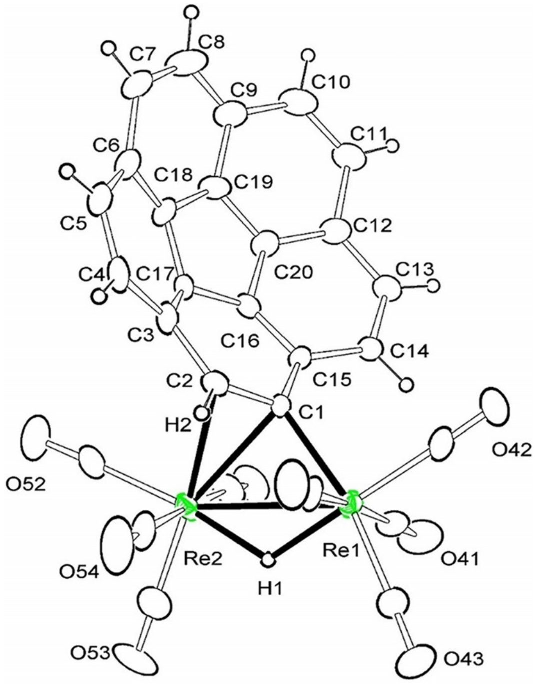


Figure 1. An ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}C_{20}H_9)$, **2** showing 25 % thermal ellipsoid probability. Selected interatomic bond lengths (Å) are as follow: Molecule 1: Re(1)–Re(2) = 3.0442(7), Re(1)–C(1) = 2.210(9), Re(2)–C(1) = 2.464(9), Re(2)–C(2) = 2.504(10), C(1)–C(2) = 1.420(13), C(2)–C(3) = 1.460(14), C(3)–C(4) = 1.428(15), C(1)–C(15) = 1.480(13), C(3)–C(17) = 1.354(14), C(4)–C(5) = 1.388(17), C(15)–C(16) = 1.379(13), C(16)–C(17) = 1.418(13); Molecule 2: Re(3)–Re(4) = 3.0426(7), Re(3)–C(21) = 2.217(10), Re(4)–C(21) = 2.451(9), Re(4)–C(22) = 2.509(11), C(21)–C(22) = 1.422(14), C(21)–C(35) = 1.483(14), C(22)–C(23) = 1.453(15), C(23)–C(37) = 1.336(15), C(23)–C(24) = 1.426(16), C(24)–C(25) = 1.401(19), C(35)–C(36) = 1.379(14).

double bond. The σ-bond lengths, Re(1)–C(1) = 2.210(9) Å [molecule 2, Re(3)–C(21) = 2.217(10) Å] and the Re–C π-bond lengths: Re(2)–C(1) = 2.464(9) Å, Re(2)–C(2) = 2.504(10) Å [molecule 2, Re(4)–C(21) = 2.451(9) Å, Re(4)–C(22) = 2.509(11) Å], are similar to those in the hexenyl compound **6**: σ-bonds, Re(1)–C(1) = 2.129(9) Å, Re(3)–C(7) = 2.151(11) Å and π-bonds: Re(2)–C(1) = 2.324(9) Å, Re(2)–C(2) = 2.481(9) Å, Re(4)–C(7) = 2.411(11) Å, Re(4)–C(8) = 2.505(15) Å, and also to those in the naphthyl complex, $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}C_{10}H_7)$, **7**: σ-bond, Re(2)–C(1) = 2.196(4) Å, and π-bonds: Re–C(1) = 2.433(4) Å, Re–C(2) = 2.599(4) Å, respectively.[8] The π-coordinated C–C bond in **2**, C(1)–C(2) = 1.420(13) Å [C(21)–C(22) = 1.422(14) Å] is not significantly longer than the corresponding C–C double bonds in the free corannulene molecule, 1.402(5) Å.[15] The hydride-bridged Re–Re bond in **2**, Re(1)–Re(2) = 3.0442(7) Å [Re(3)–Re(4) = 3.0426(7)], is similar to that in **7**, Re–Re = 3.0531(3) Å. The hydrido ligand exhibits a typical highly shielded resonance, $\delta = -13.44$, in the ^{1}H NMR spectrum. The resonance shown at $\delta = 6.69$ is attributed to H2 of the coordinated double bond and it is shifted upfield significantly from its position in corannulene the free molecule, $\delta = 7.82$. Note: For steric reasons the Re_2 fragment is coordinated to the outside (*exo*-side) of the corannulene bowl. By virtue of the σ+π coordination, the corannulenyl ligand serves as a three-electron donor to the $Re_2(CO)_8(\mu\text{-}H)$ group and with the existence of a hydride-bridged Re–Re single bond, both rhenium atoms formally achieve an 18-electron configuration.

Reaction of **1** with corannulene in a 3:1 ratio at 40 °C for 24 h also yield **2**, in 20 % yield and $[Re_2(CO)_8(\mu\text{-}H)](\mu\text{-}1\text{-}\mu\text{-}3\text{-}C_6H_4)[Re_2(CO)_8(\mu\text{-}H)]$,[9] 19 % yield, but most importantly three new isomeric doubly $Re_2(CO)_8(\mu\text{-}H)$ metalated complexes: $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}10,11\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **3**, 35 % yield, $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}2,1\text{-}\mu\text{-}\eta^2\text{-}10,11\text{-}C_{20}H_8)\text{-}Re_2(CO)_8(\mu\text{-}H)$, **4**, 12 % yield, and $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}11,10\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **5**, 12 % yield were also obtained. Compounds **3**, **4**, and **5** can also be obtained in slightly better yields 40, 15 and 11 %, respectively, from the reaction of **2** with **1**.

Compounds **3**, **4**, and **5** were each characterized structurally by single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **3** is shown in Figure 2. Compound **3** contains two $Re_2(CO)_8(\mu\text{-}H)$ groups, one is η^2-σ+π coordinated to rim double bond at carbon atoms C(1)–C(2) as found in **2** and there is a second one at the rim double bond C(10)–C(11). The Re–C σ-bonds, Re(1)–C(1) = 2.196(4) Å, Re(3)–C(10) = 2.200(4) Å and the Re–C π-bonds, Re(2)–C(1) = 2.474(4) Å, Re(2)–C(2) = 2.463(4) Å and Re(4)–C(10) = 2.457(4) Å, Re(4)–C(11) = 2.460(4) Å are similar to those in **2**. The two $Re_2(CO)_8(\mu\text{-}H)$ groups are not related by symmetry and accordingly two resonances are observed for the inequivalent hydrido ligands, $\delta = -13.46$ (s) and -13.50 (s) in the ^{1}H NMR spectrum. The two coordinated C–C double bonds are also inequivalent, but they are not significantly different in length, C(1)–C(2) = 1.442(6) Å and C(10)–C(11) = 1.434(6) Å, as expected. The uncoordinated rim C–C double bonds, C(4)–C(5) = 1.376(6) Å, C(7)–C(8) = 1.382(6) Å, and C(13)–C(14) = 1.379(6) Å are slightly shorter in length than the coordinated double bonds.

Crystals of compound **3** were grown from hexanes solvent, a mixture of isomers. Curiously, the crystals of **3** contained one equivalent of methylcyclopentane which had cocrystallized from the hexanes crystallization solvent. Commercial hexanes contain about 1 % methylcyclopentane. The methylcyclopentane in the crystal, not shown in Figure 2, is located in the bowl of the corannulene ligand, see Figure S3 in the accompanying Supporting Information. It is somewhat surprising that compound **3** selectively separated the methylcyclopentane from the linear hexane (about 99 % in amount) during the crystallization process and in so doing has demonstrated a remarkable example of molecular recognition.

An ORTEP diagram of the molecular structure of **4** is shown in Figure 3. Compound **4** contains two $Re_2(CO)_8(\mu\text{-}H)$ groups and they are both η^2-σ+π coordinated to rim double bonds at carbon atoms C1–C2 and C10–C11 as in **3**, but in **4** the first $Re_2(CO)_8(\mu\text{-}H)$ group is σ-bonded to C2 by Re2, Re(2)–C(2) = 2.197(7) Å while the second $Re_2(CO)_8(\mu\text{-}H)$ group is σ-bonded to C10 by Re4, Re(4)–C(10) = 2.207(7) Å as found in **3**. By this change in coordination, compound **4** achieves an internal (non-crystallographic) reflection symmetry. Thus, the hydrido ligands on the two $Re_2(CO)_8(\mu\text{-}H)$ groups are equivalent, and only one resonance is seen in the ^{1}H NMR spectrum, $\delta = -13.49$ (s). The Re–C distances to the C–C π-bonds, Re(1)–

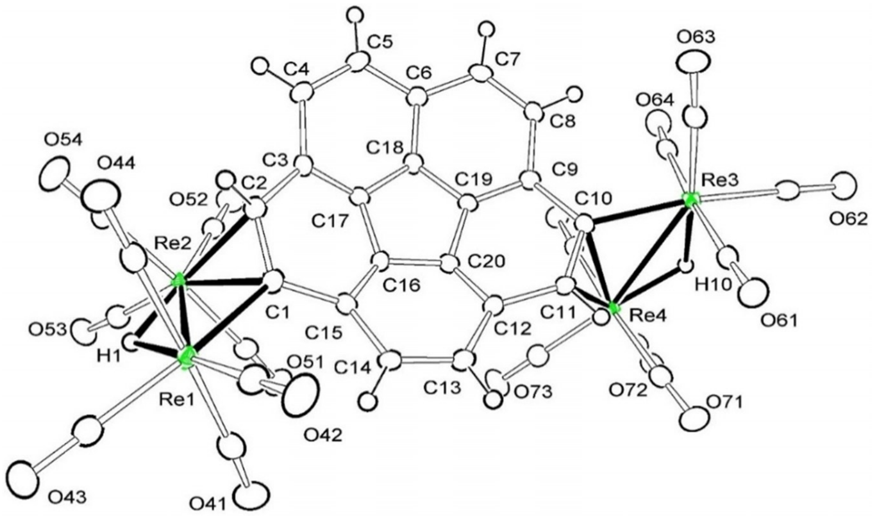


Figure 2. An ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}10,11\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **3**, showing 45 % thermal ellipsoid probability. Selected interatomic bond lengths (Å) are as follow: Re(1)–Re(2) = 3.065(3), Re(3)–Re(4) = 3.051(3), Re(1)–C(1) = 2.196(4), Re(2)–C(1) = 2.474(4), Re(2)–C(2) = 2.463(4), Re(3)–C(10) = 2.200(4), Re(4)–C(10) = 2.457(4), Re(4)–C(11) = 2.460(4), C(1)–C(2) = 1.442(6), C(1)–C(15) = 1.485(6), C(2)–C(3) = 1.467(6), C(10)–C(11) = 1.434(6) and C(11)–C(12) = 1.469(6).

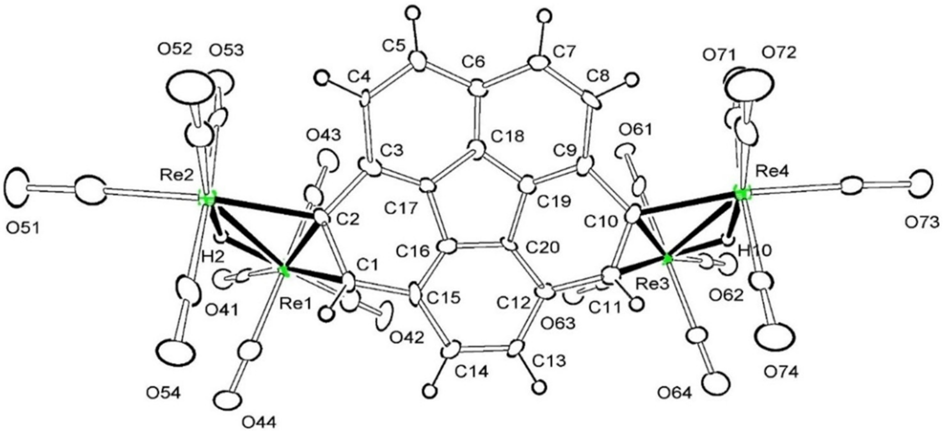


Figure 3. An ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}2,1\text{-}\mu\text{-}\eta^2\text{-}10,11\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **4**, showing 50 % thermal ellipsoid probability. Selected interatomic bond lengths (Å) are as follow: Re(1)–Re(2) = 3.0499(5), Re(3)–Re(4) = 3.0474(4), Re(1)–C(1) = 2.469(6), Re(1)–C(2) = 2.456(6), Re(2)–C(2) = 2.197(7), Re(3)–C(10) = 2.424(7), Re(4)–C(10) = 2.207(7), Re(3)–C(11) = 2.506(6), C(1)–C(2) = 1.441(9), C(1)–C(15) = 1.465(8), C(2)–C(3) = 1.503(9), C(10)–C(11) = 1.415(10), C(11)–C(12) = 1.479(9), C(4)–C(5) = 1.371(9), C(7)–C(8) = 1.379(10), C(13)–C(14) = 1.381(9).

C(1) = 2.469(6) Å, Re(1)–C(2) = 2.456(6) Å, Re(3)–C(10) = 2.424(7) Å, Re(3)–C(11) = 2.506(6) Å, are similar to those in **3**. Like **2**, compound **3** cocrystallized with a molecule of the crystallization solvent and it is also located in the bowl of the corannulene ligand, but in this case the molecule is benzene.

An ORTEP diagram of the molecular structure of **5** is shown in Figure 4. Compound **5** contains two $Re_2(CO)_8(\mu\text{-}H)$ groups and they are both $\eta^2\text{-}\sigma+\pi$ coordinated to rim double bonds C1–C2 and C10–C11 as in **3** and **4**, but in **5** it is the carbon atoms C1 and C11 that are σ-bonded to the metal atoms Re1 and Re3, Re(1)–C(1) = 2.199(5) Å and Re(3)–C(11) = 2.205(5) Å and Re2 and Re4 are π-bonded to the double bonds, Re(2)–C(1) = 2.439(5) Å, Re(2)–C(2) = 2.483(5) Å, Re(4)–C(10) = 2.467(5) Å and Re(4)–C(11) = 2.466(5). Compound **5** also contains non-crystallographic reflection symmetry and the two hydrido ligands are equivalent, $\delta = -13.46$ (s).

When a sample of **3** was heated to 45 °C for 40 h in CD_2Cl_2 solvent in a NMR tube, compounds **4** and **5** were formed in a 1:2 ratio but the majority of the complex (≈ 90 %) was decomposed to **2** by loss of one of the $Re_2(CO)_8$ units. A small amount of $Re_2(CO)_8(\mu\text{-}Cl)(\mu\text{-}H)$ was also found in this sample.

Summary and Conclusion

In this work we have prepared the first example of a CH activation in the nonplanar aromatic molecule corannulene, $C_{20}H_{10}$, by a metal complex by reductive elimination of benzene from **1** and by oxidative addition of one of the corannulene CH bonds to the dirhenium carbonyl group, see Scheme 2, to yield the new compound **2**. By using a larger amount of **1** relative to the corannulene, three additional products **3**, **4** and **5** which are isomers were formed by the activation of two CH

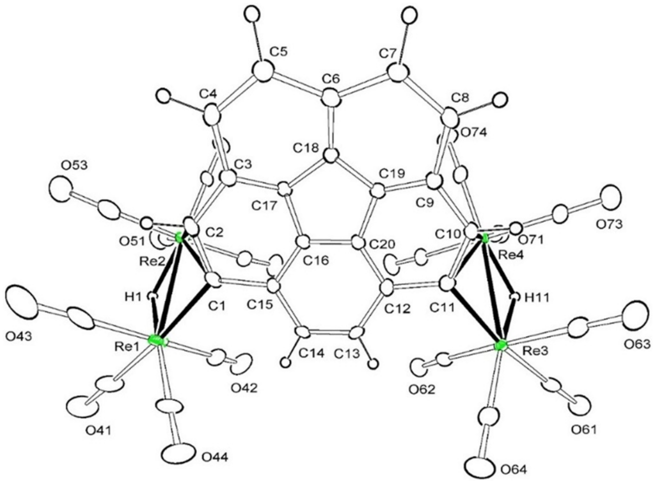
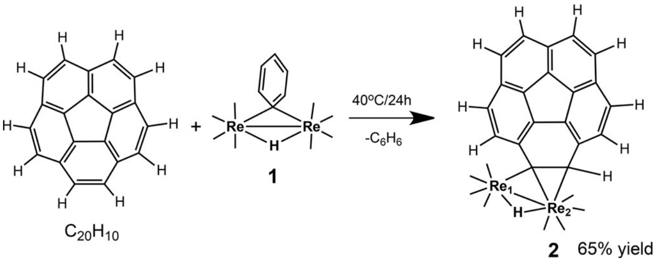


Figure 4. An ORTEP diagram of the molecular structure of Re$_2$(CO)$_8$(μ-H)(μ-η^2-1,2-μ-η^2-11,10-C$_{20}$H$_8$)Re$_2$(CO)$_8$(μ-H), **5**, showing 45 % thermal ellipsoid probability. Selected interatomic bond lengths (Å) are as follow: Re(1)–Re(2) = 3.0346(3), Re(3)–Re(4) = 3.0655(3), Re(1)–C(1) = 2.199(5), Re(2)–C(1) = 2.439(5), Re(2)–C(2) = 2.483(5), Re(3)–C(11) = 2.205(5), Re(4)–C(11) = 2.466(5) and Re(4)–C(10) = 2.467(5), C(1)–C(2) = 1.435(7), C(1)–C(15) = 1.501(7), C(2)–C(3) = 1.470(7), C(9)–C(10) = 1.475(6), C(10)–C(11) = 1.435(7), C(11)–C(12) = 1.499(7).



Scheme 2. A schematic showing the reaction of corannulene with **1**. CO ligands are represented only as lines to the rhenium atoms.

bonds on the same molecule of corannulene by the oxidative addition to two Re$_2$(CO)$_8$ groupings, see Scheme 3. The isomers are distinguished by the formation of different conformations of the $\sigma+\pi$ coordination of the two Re$_2$(CO)$_8$(μ-H) groupings on the double bonds of the corannulene molecule. The doubly metalated compound **3** readily loses one Re$_2$(CO)$_8$ grouping upon heating by returning to the singly metalated compound **2**, but small amounts of **4** and **5** were also formed.

Multiple aromatic CH oxidative additions by metal complexes are extremely rare.[9,16] The multiple metalations observed in this work are distinguished from other multiple CH activations[16] by addition of two equivalents of the metal complex to the same aromatic molecule.

The activation of the CH bonds in corannulene is the first step toward the functionalization of corannulenes and related "bowl" compounds in general.[17–19] The observation of multiple (two) CH activations in the same molecule increases the potential for functionalization reactions even further. However, we have observed that the CH activations are reversible at least for the doubly metalated complexes and this property may limit their usefulness for further chemical transformations.

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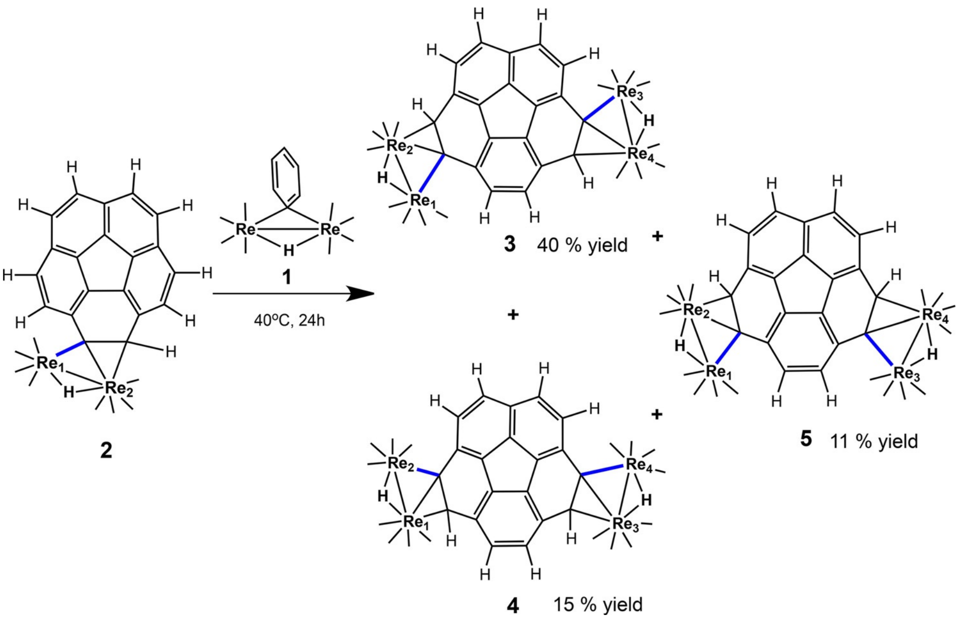
Conflict of interest

The authors declare no conflict of interest.



Scheme 3. A schematic showing the structures of the products formed from the reaction of **2** with **1**. The blue lines show the locations of the Re–C σ-bonds to the corannulene rings. CO ligands are represented only as lines to the rhenium atoms.

Keywords: C–H activation · corannulene · metalation · oxidative addition · rhenium

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