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Activation of Heteroaromatic C−H Bonds in Furan and 2,5-Dimethylfuran

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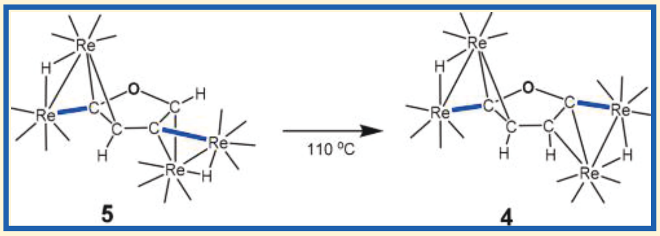
Supporting Information

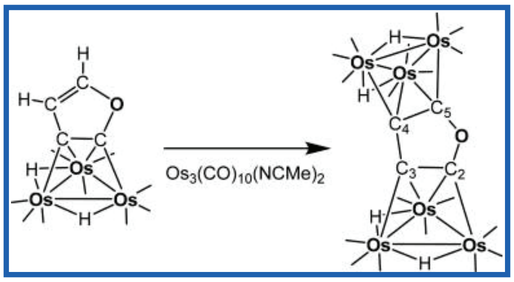


ABSTRACT: The reaction of $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$ (**1**) with furan in CH_2Cl_2 at 40 °C yielded two new isomeric dirhenium compounds, $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}2,3\text{-}C_4H_3O)(\mu\text{-}H)$ (**2**) and $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}3,2\text{-}C_4H_3O)(\mu\text{-}H)$ (**3**), which contain a bridging ($\sigma + \pi$)-coordinated furyl ligand formed by activation of the C−H bond at the 2 and 3 positions of furan, respectively. Compound **3** is the first example of a compound formed by C−H bond activation at the 3 position of a furan ring. Compound **3** was isomerized to **2** by heating to 80 °C for 7 days. The reaction of compound **2** with a second 1 equiv of **1** in CH_2Cl_2 at 40 °C yielded the doubly metalated furan-bis[$Re_2(CO)_8(\mu\text{-}H)$] product $[Re_2(CO)_8(\mu\text{-}H)]_2(\mu\text{-}\eta^2\text{-}2,3\text{-}\mu\text{-}\eta^2\text{-}5,4\text{-}C_4H_2O)$ (**4**) containing a 2,5-furdiyl ligand that is ($\sigma + \pi$)-coordinated to two $Re_2(CO)_8(\mu\text{-}H)$ groups by activation of the C−H bond at the 5 position of the furyl ligand in **2**. Compound **2** can also be formed as the major isomer, together with a small quantity of **4** by heating furan with $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n]$ in toluene to reflux. An isomer of **4**, $[Re_2(CO)_8(\mu\text{-}H)]_2(\mu\text{-}\eta^2\text{-}2,3\text{-}\mu\text{-}\eta^2\text{-}4,5\text{-}C_4H_2O)$ (**5**), was obtained from the reaction of **3** with **1** through C−H activation at the 4 position of the furyl ring in **3**. Compound **4** was also obtained from **5** by heating to 110 °C for 24 h. The reaction of **1** with 2,5-dimethylfuran (DMFUR) in CH_2Cl_2 at 40 °C yielded the new compound $[Re_2(CO)_8(\mu\text{-}\eta^2\text{-}3,2\text{-}(CH_3)_2C_4H_2O)](\mu\text{-}H)$ (**6**), which contains a bridging ($\sigma + \pi$)-coordinated 2,5-dimethylfuryl ligand formed by activation of the C−H bond at the 3 position of DMFUR. All of the new compounds were characterized structurally by single-crystal X-ray diffraction analysis.

INTRODUCTION

The activation of C−H bonds in arenes and heteroarenes has attracted great attention in recent years.[1] These reactions have been shown to play an important role in a range of organic syntheses.[2,3] Furans are an important family of heteroarenes derived from biomass and serve as platform chemicals and precursors to a range of higher-value products including biofuels.[4−9] There are very few examples of activation of the C−H bonds of furans by metal complexes.[10,11] In recent studies, our group has observed the first example of a quadruple CH activation of the furan molecule by the addition of two triosmium carbonyl clusters to the furan molecule, leading to the formation of the first furdiyne ligand in the bis(triosmium) complex $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}2,3\text{-}\mu_3\text{-}\eta^2\text{-}4,5\text{-}C_4O)Os_3(CO)_9(\mu\text{-}H)_2$ by complete removal of all four H atoms from the furan ring (Scheme 1).[11]

Scheme 1. Schematic of the Synthesis and Structure of the Tetrametalated Furdiyne-Ligated Complex $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}2,3\text{-}\mu_3\text{-}\eta^2\text{-}4,5\text{-}C_4O)Os_3(CO)_9(\mu\text{-}H)_2$[11]



We have also shown that the dirhenium carbonyl complex $Re_2(CO)_{10}(\mu\text{-}C_6H_5)(\mu\text{-}H)$ (**1**) is very effective at C−H bond activation in aromatic compounds,[12−15] and we have shown that compound **1** is also effective in producing activation of the C−H bonds and opening of the heteroaromatic ring of thiophene.[15]

We have now extended our CH activation studies with **1** and also with $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n]$ to include the reactions with furan and 2,5-dimethylfuran (DMFUR). DMFUR not only is a potential biofuel but also serves as a scavenger for singlet oxygen in Diels−Alder reactions.[16−21] To our knowledge, there are no previously reported examples of C−H bond activation in DMFUR.

RESULTS AND DISCUSSION

The reaction of **1** with furan in CH_2Cl_2 at 40 °C for 15 h yielded two new isomeric dirhenium compounds, $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}2,3\text{-}C_4H_3O)(\mu\text{-}H)$ (**2**) and $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}3,2\text{-}C_4H_3O)(\mu\text{-}H)$ (**3**), in 55% and 37% yield, respectively.

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Both products were characterized by a combination of IR and NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of compound **2** is shown in Figure 1.

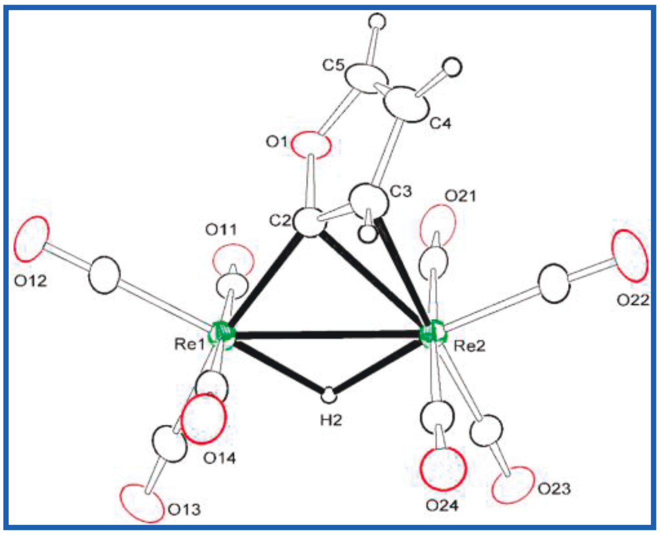

Figure 1. ORTEP diagram of the molecular structure of **2** showing 25% thermal ellipsoid probability. Selected interatomic bond distances (Å): Re1−Re2 = 3.0626(13), Re1−H2 = 1.87(6), Re2−H2 = 1.86(6), Re1−C2 = 2.163(8), Re2−C2 = 2.445(6), Re2−C3 = 2.584(6), O1−C2 = 1.411(7), O1−C5 = 1.358(9), C2−C3 = 1.352(10), C3−C4 = 1.439(10), C4−C5 = 1.317(12).

Compound **2** contains a ($\sigma + \pi$)-coordinated furyl ligand bridging the dirhenium metal−metal bond at the C2−C3 double bond. Atom C2 is σ-bonded to atom Re1 [Re1−C2 = 2.163(8) Å], and atoms C2 and C3 are π-bonded to Re2 [Re2−C2 = 2.445 (6) Å and Re2−C3 = 2.584(6) Å]. The furyl ligand was formed by a CH bond activation at the C atom at the 2 position of the furan ring, following elimination of the phenyl and hydrido ligands from **1** in the form of benzene. The mechanism of activation of the C−H bond is assumed to be similar to that of the oxidative addition of the C−H bond of benzene to **1**.[14] Compound **2** is structurally similar to its thiophene homologue, $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}2,3\text{-}C_4H_3S)(\mu\text{-}H)$, which has similar Re−C bond distances: Re1−C2 = 2.186(4) Å, Re2−C2 = 2.474(4) Å, and Re2−C3 = 2.623(4) Å.[15] The C−C distances in **2** [C2−C3 =1.352(10) Å, C3−C4 = 1.439(10) Å, and C4−C5 = 1.317(12) Å] are similar to those in $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}2,3\text{-}C_4H_3S)(\mu\text{-}H)$ [C2−C3 = 1.392(6) Å, C3−C4 = 1.440(7) Å, and C4−C5 = 1.338(8) Å] and in furan [free molecule, 1.322(6) and 1.428(7) Å, adjusted for the effects of π-bonding to the Re atom in the complex].[22] The molecule contains a Re−Re single bond [3.0626 (13) Å], which is very similar to that found in $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}2,3\text{-}C_4H_3S)(\mu\text{-}H)$ [Re1−Re2 = 3.061(2) Å]. Compound **2** also contains one bridging hydrido ligand H2 across the Re−Re bond (δ = −12.96). The ^{13}C NMR spectrum of **2** shows four resonances (δ = 156.67, 155.49, 112.72, and 108.65) for the furyl ligand. The resonances at 156.67 and 155.49 ppm have shifts similar to that of the O-bound C atoms in free furan, 143.6 ppm,[23] and are assigned accordingly. The ^{13}C resonances of the non-O-bound C atoms at 112.72 and 108.65 ppm are also similar to the non-O-bound C atoms in free furan, 110.4 ppm[23] and are so assigned. The DEPT ^{13}C NMR spectrum of **2** shows only three resonances (δ = 156.67, 112.72, and 108.65), indicating that the missing resonance at 155.49 ppm is the one belonging to the σ-metalated atom C2. There are only four resonances [δ = 186.75 (2CO), 184.42 (2CO), 183.02 (2CO), and 181.83 (2CO)] for the CO ligands in **2**. This can be explained by a dynamical averaging process through which the coordinated π bond of the furyl ligand flips back and forth between the two Re atoms, thereby averaging the CO ligands into four pairs. A similar averaging process was observed for the bridging thienyl ligand in the structurally similar complex $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}2,3\text{-}C_4H_3S)(\mu\text{-}H)$.[15] The 2-furyl ligand in **2** serves as a three-electron donor to the metal atoms; thus, both Re atoms are formally electronically saturated; i.e., they have 18-electron configurations.

Compound **3** (Figure 2) contains a μ-η^2-3-furyl ligand formed by the reductive elimination of benzene from **1** and oxidative addition of the C−H bond at the 3 position of the furan to the dirhenium unit. Atom C3 is bonded to Re1 [Re1−C3 = 2.192(8) Å], and the C2−C3 double bond is coordinated to Re2 in the $\sigma + \pi$ coordination mode [Re2−C3 = 2.462(8) Å and Re2−C2 = 2.564(7) Å].

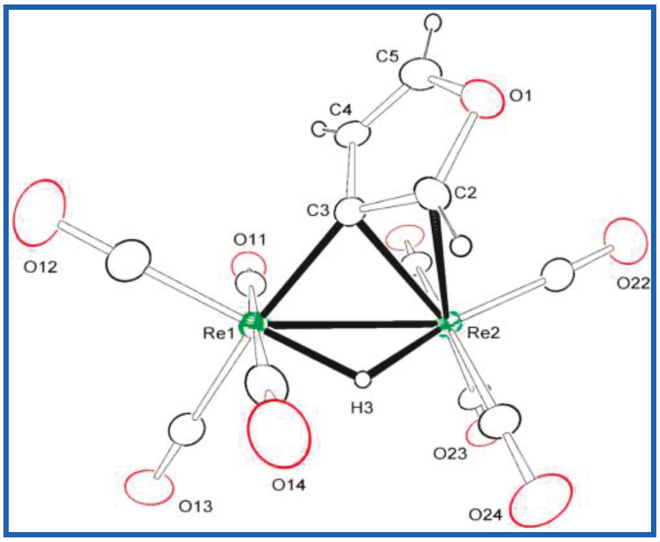

Figure 2. ORTEP diagram of the molecular structure of **3** showing 25% thermal ellipsoid probability. Selected interatomic bond distances (Å): Re1−Re2 = 3.0516(4), Re1−H3 = 1.79(3), Re2−H3 = 1.81(3), Re1−C3 = 2.192(8), Re2−C3 = 2.462(8), Re2−C2 = 2.564(7), O1−C2 = 1.363(9), O1−C5 = 1.374(12), C2−C3 = 1.383(11), C3−C4 = 1.445(11), C4−C5 = 1.333(13).

The coordinated double bond distance C2−C3 = 1.383 (11) Å and the Re−Re single bond distance Re1−Re2 = 3.0516 (4) Å are similar to those in **2**. The uncoordinated bonds remain mostly unaffected and are almost the same as those in the free furan molecule.[22] Compound **3** also contains a bridging hydrido ligand H3 across the Re−Re bond (δ = −13.54). The ^{13}C NMR spectrum of **3** shows four resonances (δ = 147.24, 132.98, 129.14, and 100.88). The DEPT ^{13}C NMR spectrum of **2** shows only three resonances (δ = 147.24, 132.98, and 129.14), indicating that the resonance at 100.88 ppm is the one due to the σ-metalated C atom that bridges the two Re atoms. This is fairly close to the resonance of the bridging C atom in **1** at 117.84 ppm (see the Supporting Information, SI). As in **2**, both Re atoms in **3** are electronically saturated with 18 electrons each. A schematic of the synthesis of compounds **2** and **3** is shown in Scheme 2.

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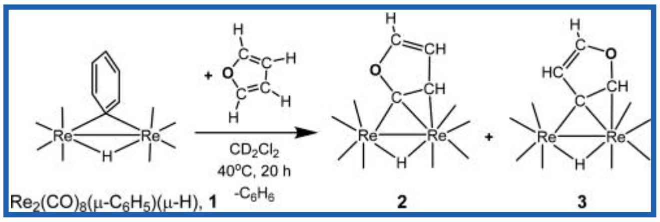
Scheme 2. Schematic of the Synthesis of Compounds 2 and 3 from the Reaction of 1 with Furan[a]



[a] CO ligands on the Re atoms are represented only as lines.

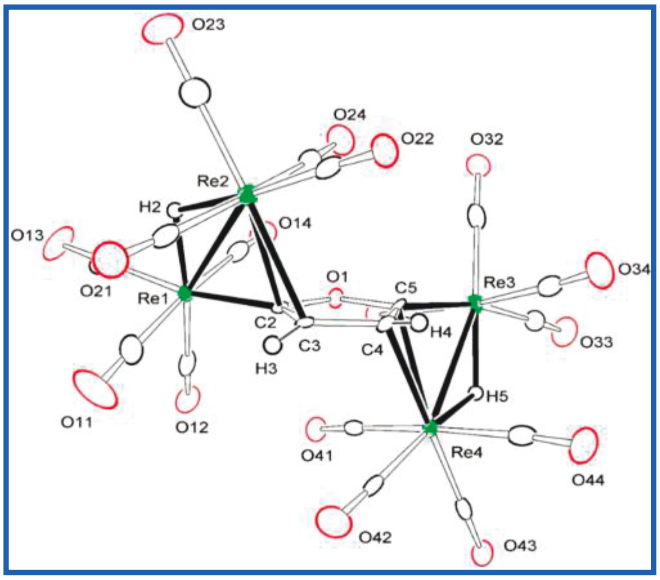


Figure 3. ORTEP diagram of the molecular structure of **4** showing 50% thermal ellipsoid probability. Selected interatomic bond distances (Å): Re1−Re2 = 3.0902(2), Re3−Re4 = 3.0825(3), Re1−C2 = 2.132(4), Re2−C2 = 2.453(3), Re2−C3 = 2.462(4), Re3−C5 = 2.139(4), Re4−C5 = 2.455(4), Re4−C4 = 2.472(4), Re1−H2 = 1.83(4), Re2−H2 = 1.92(4), Re3−H5 = 1.89(6), Re4−H5 = 1.83(6), O1−C2 = 1.407(5), O1−C5 = 1.409(4), C2−C3 = 1.391(6), C3−C4 = 1.467(5), C4−C5 = 1.383(6).

Compound **3** was isomerized to **2** in 100% conversion by heating to 80 °C for 7 days. The transformation is tantamount to a 1,2-hydrogen shift from atom C2 to C3 accompanied by a reverse shift of the σ-bonded atom Re1 from C3 to C2. Unfortunately, the mechanism for this isomerization has not been established, and it could involve a multistep process involving the bridging hydrido ligand on the Re atoms.

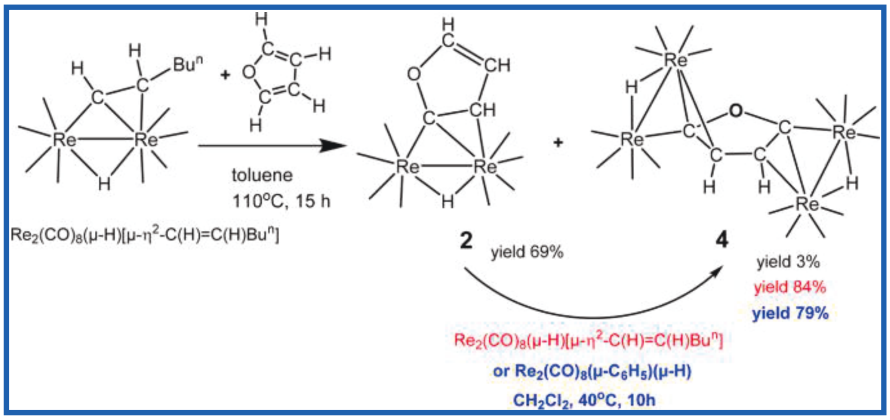
Compound **2** can also be obtained from the reaction of $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n]$ with furan (excess) as a major isomeric product (69% yield), together with a small amount of the new compound $[Re_2(CO)_8(\mu\text{-}H)]_2(\mu\text{-}\eta^2\text{-}2,3\text{-}\mu\text{-}\eta^2\text{-}5,4\text{-}C_4H_2O)$ (**4**; 3% yield) when heated to reflux in toluene for 9 h (Scheme 3).

The molecular structure of compound **4** was confirmed by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 3. Compound **4** contains a bridging furan ligand formed by the activation of two furan CH bonds, one at the 2 position and one at the 5 position, and is the first example of a "furdiyl" ligand. Both "double" bonds of the furdiyl ligand are coordinated to a $HRe_2(CO)_8$ subunit of the complex in the $\eta^2-(\sigma + \pi)$ bridging coordination mode. The two Re−C σ-bonding interactions [Re1−C2 = 2.132(4) Å and Re3−C5 = 2.139(4) Å] are significantly shorter than the π-bonding interactions [Re2−C2 = 2.453(3) Å, Re2−C3 = 2.462(4) Å, Re4−C5 = 2.455(4) Å, and Re4−C4 = 2.472(4) Å], which are similar to those observed in **2** and **3**. The structure of **4** resembles that of the thiendiyl compound $[Re_2(CO)_8(\mu\text{-}H)]_2(\mu\text{-}\eta^2\text{-}2,3\text{-}\mu\text{-}\eta^2\text{-}5,4\text{-}C_4H_2S)$, which has a coordination mode similar to that of its doubly metalated thiophene ligand. The two hydrido ligands in compound **4** are equivalent because of its C_2 molecular symmetry; thus, there is only one hydride resonance in the ^1H NMR spectrum (δ = −13.39). Because of the symmetry of the complex, there are only two ^{13}C resonances for the furdiyl ligand [δ = 177.85 (C2 and C5) and 91.27 (C3 and C4)]. The former is due to the metalated C atoms and the latter to the hydrogen-bonded C atoms. All of the C−C bonds in the coordinated furdiyl ligand have increased in length compared to the free furan molecule,[22] as a result of diminished π-bonding character between the coordinated C atoms in the ring system.

As expected, compound **4** can be obtained in higher yield (79%) by heating a solution of compound **2** and **1** to reflux in CH_2Cl_2 to 40 °C for 10 h or in 84% yield by heating a solution of **2** with a $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n]$/toluene solvent to reflux for 15 h (Scheme 3).

Interestingly, the reaction of compound **3** with **1** at 40 °C in CH_2Cl_2 solvent for 18 h yielded a second bis$[Re_2(CO)_8(\mu\text{-}H)]$

Scheme 3. Schematic of Various Routes for the Synthesis of Compounds 2 and 4[a]



[a] CO ligands on the Re atoms are represented only as lines from the Re atoms.

furdiyl compound $[Re_2(CO)_8(\mu\text{-}H)]_2(\mu\text{-}\eta^2\text{-}2,3\text{-}\mu\text{-}\eta^2\text{-}4,5\text{-}C_4H_2O)$ (**5**) in 86% yield by activation of the C−H bond at the 5 position of the furyl ring in **3**. Compound **5** is an isomer of **4**. Its molecular structure has also been determined by a single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of **5** is shown in Figure 4. Compound **5** contains two η^2−(σ + π) bridging $Re_2(CO)_8(\mu\text{-}H)$ subunits on a single bridging furdiyl ligand, but unlike **4**, one of the Re−C σ bonds is located at the 2 position of the furan ring and the other one is located at the 4 position. The Re−C σ-bond distances [C2 = 2.158 (9) Å and Re2−Re3−C4 = 2.175(11) Å] are similar to those in **4**. The Re−C π-bond distances are also similar to those in **4**. The furdiyl ring contains only two H atoms: one on C3 and another on C5. Accordingly, two resonances were observed in the ^{1}H NMR spectrum at 7.59 (s, 1H) and 6.51 (s, 1H) ppm. The hydride ligands in **5** are inequivalent, and two separate resonances were observed for these ligands in the ^{1}H NMR spectrum [δ = −13.04 (s) and −13.58 (s)]. The ^{13}C NMR spectrum of **5** contains four resonances for the furdiyl ligand: 166.79 (C2), 135.14 (C5H), 120.41 (C3H), and 109.51 (C4). The first is due to the metalated atom C2 that is bonded to the O atom, and the last is due to the metalated atom C4 that is not bonded to O. The two remaining resonances are for the atoms C3 and C5 that contain H atoms.

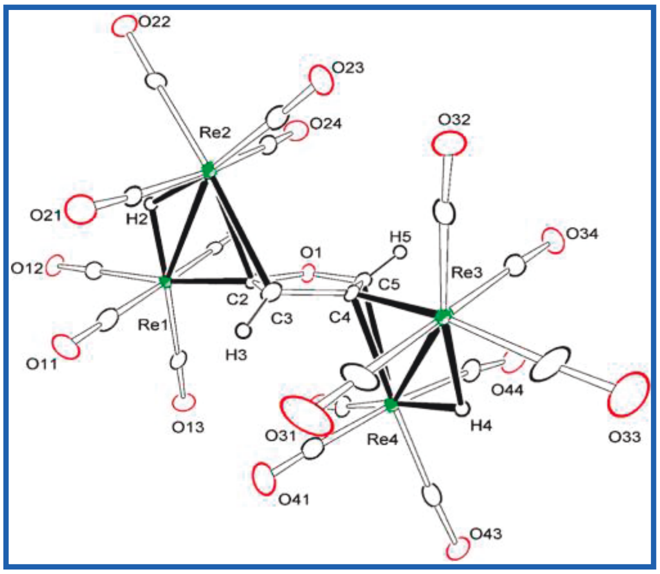
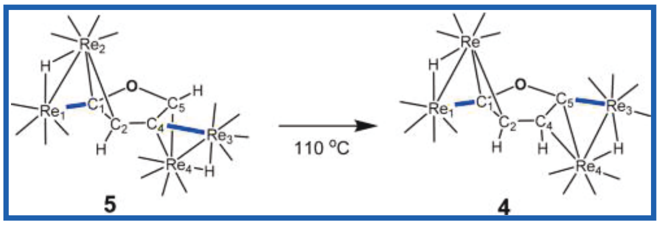


Figure 4. ORTEP diagram of the molecular structure of **5** showing 30% thermal ellipsoid probability. Selected interatomic bond distances (Å): Re1−Re2 = 3.0734(6), Re3−Re4 = 3.0447(6), Re1−C2 = 2.158(9), Re2−C2 = 2.424(9), Re2−C3 = 2.624(10), Re3−C4 = 2.175(11), Re4−C4 = 2.453(10), Re4−C5 = 2.525(10), O1−C2 = 1.416(12), O1−C5 = 1.387(13), C2−C3 = 1.386(14), C3−C4 = 1.496(14), C4−C5 = 1.404(15), Re1−H2 = 1.76(14), Re2−H2 = 1.87(14), Re3−H4 = 1.99(10), Re4−H5 = 1.76(11).

Similar to the isomerization of **3** to **2** (see above), compound **5** can be isomerized to **4** together with the formation of some **2** by heating a solution of **5** in a toluene-d_8 solvent to 110 °C for 24 h. ^{1}H NMR spectra showed complete conversion of **5** into a mixture of compounds **2** formed by the loss of a $Re_2(CO)_8$ subunit and **4** in a 10:7 ratio. A schematic of the isomerization of **5** to **4** is shown in Scheme 4. The isomerization is tantamount to a 1,2-hydrogen shift from atom C5 to C4 with a compensatory 1,2-Re shift of the σ-bonded $Re(CO)_4$ group (atom Re_3) from C4 to C5. Note that the mechanism has not been established, and we cannot rule out a multistep process involving the hydrido ligand on the Re3−Re4 bond. Efforts to obtain **5** by heating solutions of **4** were unsuccessful, indicating that **4** is the more stable of the two products.

Scheme 4. Schematic of the Isomerization of 5 to 4[a]



[a] Bonds shown in blue are the Re−C σ bonds to the furdiyl ligand. CO ligands on the Re atoms are represented only as lines from the Re atoms.

Finally, the reaction of **1** with DMFUR was also studied and found to yield the complex $[Re_2(CO)_8(\mu\text{-}\eta^2\text{-}3,2\text{-}(CH_3)_2C_4H_2O)](\mu\text{-}H)$ (**6**) in 65% yield after 20 h at 40 °C by the loss of benzene from **1** and the addition of one molecule of DMFUR with CH activation by the "$Re_2(CO)_8$" grouping. Compound **6** was characterized by IR and ^{1}H NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of **6** is shown in Figure 5. The structure of **6** is similar to that of **3** with a bridging hydrido ligand and a C-coordinated η^1-bridging 2,5-dimethylfuryl ligand, but unlike compounds **2** and **3**, the Re2···C2 distance in **6** is very long, 2.880(2) Å, and is at best only very weakly bonding in this molecule. This may

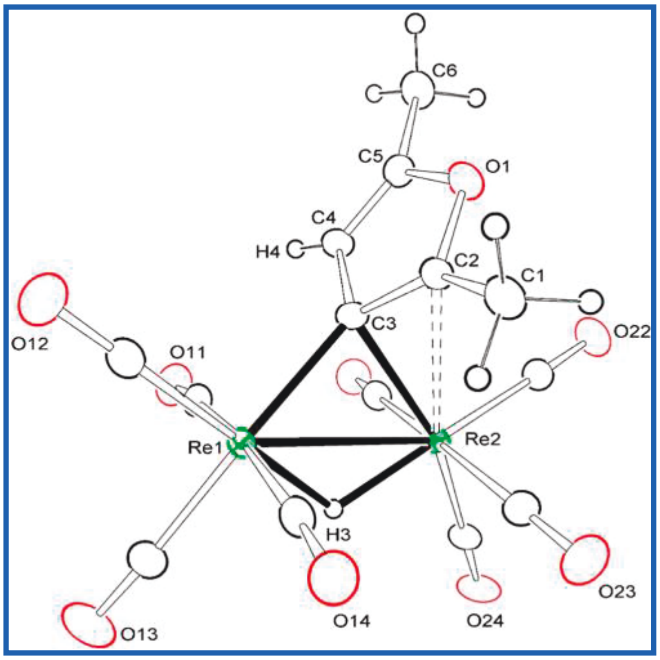


Figure 5. ORTEP diagram of the molecular structure of **6** showing 60% thermal ellipsoid probability. Selected interatomic bond distances (Å): Re1−Re2 = 3.00580(15), Re1−H3 = 1.79(3), Re2−H3 = 1.83(3), Re1−C3 = 2.225(2), Re2−C3 = 2.388(2), Re2−C2 = 2.880(2), O1−C2 = 1.366(3), O1−C5 = 1.387(3), C1−C2 = 1.490(3), C2−C3 = 1.390(3), C3−C4 = 1.474(3), C4−C5 = 1.337(3), and C5−C6 = 1.484(3).

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be due to steric interactions between the methyl group on C2 and one of the proximate carbonyl ligands on the atom Re2. The Re−Re bond distance, 3.0058(15) Å, in **6** is significantly shorter than that in **3**, Re−Re = 3.0516(4) Å, perhaps because of the decreased Re−C bonding between Re2 and C2. The other bond distances in the 2,5-dimethylfuryl ligand are comparable to compound **3** (Figure 2). Compound **6** also contains one hydrido ligand bridging the Re−Re bond (δ = −12.54). As expected, the ^{13}C NMR spectrum exhibits six resonances for the dimethylfuryl ligand: 175.19 (C5), 153.39 (C2), 131.42 (C4H), 86.01 (C3), 19.30 (CH_3), and 12.24 (CH_3). The resonance at 153.39 ppm is attributed to the atom C3 that bridges the two Re atoms.

Angelici et al. reported that $Re_2(CO)_{10}$ reacts with 2,5-dimethylthiophene in the presence of UV−vis irradiation by C−S bond cleavage to yield the metalated complex $Re_2(CO)_7(\mu\text{-2,5-SCMeCHCHCHCMe})$ containing a ring-opened bridging metalated thiapentadienyl ligand.[24] We did not obtain any evidence for ring opening of the 2,5-dimethylfuryl ligand under the milder conditions used in our studies.

SUMMARY AND CONCLUSIONS

In this work, we have shown that furan undergoes facile C−H bond activation not only at the 2 position but also at the 3 position in its reactions with **1** to yield compounds **2** and **3** under very mild conditions. Compound **2** can also be obtained in a good yield by the reaction of $Re_2(CO)_8(\mu\text{-H})[\mu\text{-}\eta^2\text{-C(H)=C(H)Bu}^n]$ with furan at 110 °C. Compound **3** was readily isomerized to **2** by heating to 80 °C. We also observed the first example of heteroaromatic CH activation in 2,5-DMFUR at the 3 position upon reaction with **1** to yield compound **6**. Compound **2** was found to react with a second 1 equiv of **1** through CH activation at the 5 position of the furyl ring to yield the first example of a doubly metalated 2,5-furdiyl ligand in the product **4**. Compound **3** was found to react with a second 1 equiv of **1** to yield compound **5** through CH activation at the 5 position of the furyl ring, leading to formation of the first example of a doubly metalated 2,4-furdiyl ligand. When heated to 110 °C for 24 h, compound **5** was isomerized to **4** (together with a significant amount of degradation to compound **2**) by interchanging the location of the Re−C σ bond on one of the two Re_2 groupings. Unlike our studies of the reactions of thiophene with **1**, we did not observe any ring opening of the Re-metalated furan ligands in these studies.[15] Our recent studies are revealing that polynuclear metal complexes are proving to be an important family of reagents for aromatic CH activation reactions.[11,13−15,25]

EXPERIMENTAL DETAILS

General Data. All reactions were performed under a nitrogen atmosphere. Reagent-grade solvents were dried by standard procedures and freshly distilled prior to use. IR spectra were recorded on a Nicolet IS10 mid-IR Fourier transform infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance III-HD spectrometer operating at 300 and 400 MHz, respectively. Mass spectrometry (MS) measurements performed by a direct-exposure probe by using electron impact ionization (EI) were obtained on a VG 70S instrument. $Re_2(CO)_{10}$, furan, and 2,5-dimethylfuran (DMFUR) were obtained from STREM and Sigma-Aldrich and used without further purification. $Re_2(CO)_8(\mu\text{-H})[\mu\text{-}\eta^2\text{-C(H)=C(H)Bu}^n]$ and $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-H})$ (**1**) were prepared according to previously reported procedures.[26,27] Product separations were performed by thin-layer chromatography (TLC) in air on Analtech 0.25 and 0.5 mm silica gel 60 F254 glass plates. For more details, see the SI.

Reaction of 1 with Furan. A 50.0 mg (0.074 mmol) amount of **1** and 1 mL (13.764 mmol) of furan were dissolved in 1.6 mL of CD_2Cl_2 in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The sample was then heated to 40 °C for 15 h. A ^{1}H NMR spectrum obtained after this period showed new hydride resonances at −12.96 and −13.54 ppm and a resonance at 7.15 ppm for benzene. The contents were then transferred to a vial, and the solvent was removed in vacuo. The residue was extracted in CH_2Cl_2 and separated by TLC using a hexane solvent to yield, in order of elution, a major yellow band of 27.0 mg of **2** (55% yield) and a minor yellow band of 18.0 mg of **3** (37% yield). Spectral data for **2**. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 2115(w), 2089(m), 2020(vs), 1997(sh), 1965(s). ^{1}H NMR (CD_2Cl_2): δ 8.05 (d, 1H, ^3J = 2.1 Hz), 6.56 (d, 1H, ^3J = 2.7 Hz), 6.52 (dd, 1H, ^3J = 2.4 Hz), −12.96 (s, 1H, H2, hydride). ^{13}C NMR (CD_2Cl_2, 100.66 MHz): δ 186.75 (2CO), 184.42 (2CO), 183.02 (2CO), 181.83 (2CO), 156.67 (C5H), 155.49 (C2), 112.72 (C3H), 108.65 (C4H). ^{13}C NMR (CD_2Cl_2, DEPT, 100.66 MHz): δ 156.67 (C5), 112.72 (C3), 108.65 (C4). EI/MS: *m/z* 664 (M^+), 636 (M^+ − CO). Spectral data for **3**. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 2114(w), 2085(m), 2016(vs), 1991(sh), 1968(s). ^{1}H NMR (CD_2Cl_2): δ 7.54 (s, 1H), 7.39 (s, 1H), 6.83 (s, 1H), −13.54 (s, 1H, H3, hydride). ^{13}C NMR (CD_2Cl_2, 100.66 MHz): δ 186.23 (2CO), 184.26 (2CO), 183.29 (2CO), 180.70 (2CO), 147.24 (1CH), 132.98 (1CH), 129.14 (1CH), 100.88 (C3). ^{13}C NMR (CD_2Cl_2, DEPT, 100.66 MHz): δ 147.24 (1CH), 132.98 (1CH), 129.14 (1CH). EI/MS: *m/z* 664 (M^+), 636 (M^+ − CO).

Reaction of $Re_2(CO)_8(\mu\text{-H})[\mu\text{-}\eta^2\text{-C(H)=C(H)Bu}^n]$ with Furan. A 120.0 mg (0.176 mmol) amount of $Re_2(CO)_8(\mu\text{-H})[\mu\text{-}\eta^2\text{-C(H)=C(H)Bu}^n]$ and 0.26 mL (3.52 mmol) of furan were dissolved in 25 mL of toluene. The solution was then heated to reflux for 9 h. The solution was then cooled, and the solvent was removed in vacuo. The residue was extracted in CH_2Cl_2 and separated by TLC using a hexane solvent to yield, in order of elution, a major yellow band of 80.0 mg of **2** (69% yield) and a minor yellow band of 6.0 mg of **4** (3% yield). Spectral data for **4**. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 2113(w), 2092(m), 2027(vs), 1999(sh), 1972(s). ^{1}H NMR (CD_2Cl_2): δ 5.97 (s, 2H, H3, H4), −13.39 (s, 2H, H2, H5, hydrides). ^{13}C NMR (CD_2Cl_2, 100.66 MHz): δ 185.65 (br, 2CO), 183.94 (br, 2CO), 182.19 (2CO), 181.54 (2CO), 177.85 (C2, C5), 91.27 (C3, C4). ^{13}C NMR (CD_2Cl_2, DEPT, 100.66 MHz): δ 91.27 (C3, C4). EI/MS: *m/z* 1262 (M^+), 1234 (M^+ − CO). The isotope distribution is consistent with the presence of four Re atoms.

Isomerization of 3 to 2. A 10.0 mg (0.015 mmol) amount of **3** was dissolved in 1.6 mL of C_6D_6 in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then heated to 80 °C for 1 week. ^{1}H NMR spectra were recorded daily. After 1 week, compound **3** had been converted to **2** in 100% yield.

Synthesis of 4 from $Re_2(CO)_8(\mu\text{-H})[\mu\text{-}\eta^2\text{-C(H)=C(H)Bu}^n]$ and 2. A 45.0 mg (0.066 mmol) amount of $Re_2(CO)_8(\mu\text{-H})[\mu\text{-}\eta^2\text{-C(H)=C(H)Bu}^n]$ and 30.0 mg (0.045 mmol) of **2** were dissolved in 25 mL of toluene. The solution was then heated to reflux for 15 h. The solution was then cooled, and the solvent was removed in vacuo. The residue was extracted in CH_2Cl_2 and separated by TLC by a 4:1 (v/v) hexane/methylene chloride solvent mixture to give a yellow band of **4** (24.0 mg, 84% yield).

Synthesis of 4 from 1 and 2. A 40.0 mg (0.059 mmol) amount of **1** and 40.0 mg (0.06 mmol) of **2** were dissolved 25 mL of methylene chloride. The solution was then heated to reflux for 10 h. The solution was then cooled, and the solvent was removed in vacuo. The residue was extracted in CH_2Cl_2 and separated by TLC by a 4:1 (v/v) hexane/methylene chloride solvent mixture to give a yellow band of **4** (30.0 mg, 79% yield).

Reaction of compound 3 with 1. A 20.0 mg (0.029 mmol) amount of **1** and 15.0 mg (0.022 mmol) of **3** were dissolved in 1.6 mL of CD_2Cl_2 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 18 h. A ^{1}H NMR spectrum obtained after this period showed new hydride resonances at −13.04 and −13.58 ppm. The contents were then transferred to a vial, and the solvent was removed in vacuo. The residue was extracted in CH_2Cl_2 and separated by TLC using a hexane solvent to give a major yellow band of 12.0 mg of **5** (86% yield). Spectral data for **5**. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 2110(w), 2091(m), 2026(vs), 2002(sh), 1981(s), 1962(s). ^1H NMR (CD_2Cl_2): δ 7.59 (s, 1H), 6.51 (s, 1H), −13.04 (s, 1H, hydrides), −13.58 (s, 1H, hydrides). ^{13}C NMR (CD_2Cl_2, 100.66 MHz): δ 185.63 (CO), 185.01 (CO), 183.88 (2CO), 183.65 (2CO), 180.66 (CO), 180.07 (CO), 166.79 (C2), 135.14 (C5H), 120.41 (C3H), 109.51 (C4). ^{13}C NMR (CD_2Cl_2, DEPT, 100.66 MHz): δ 135.14 (C5), 120.41 (C3). EI/MS: m/z 1262 (M^+), 1234 ($M^+ - n$CO, where n = 1−16). The isotope distribution is consistent with the presence of four Re atoms.

Isomerization of 5 to 4. A 10.0 mg (0.079 mmol) amount of **5** was dissolved in 1.6 mL of toluene-d_8 in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then heated to 110 °C for 24 h. ^1H NMR spectra recorded after a day showed 100% conversion of compound **5** into a mixture of compounds **2** and **4** in a 10:7 ratio, respectively.

Reaction of 1 with DMFUR. A 30.0 mg (0.044 mmol) amount of **1** and 0.1 mL (0.926 mmol) of DMFUR [2,5-$(CH_3)_2C_4H_2O$] were dissolved in 1.6 mL of CD_2Cl_2 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 20 h. A ^1H NMR spectrum obtained after this period showed a new hydride resonance at −12.50 ppm. The contents were then transferred to a flask, and the solvent was removed in vacuo. The residue was extracted in CH_2Cl_2 and separated by TLC using a hexane solvent to give the major yellow band of **6** (20.0 mg, 65% yield). Spectral data for **6**. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 2118(w), 2083(m), 2008(vs), 1989(sh), 1957(s). ^1H NMR (CD_2Cl_2): δ 6.22 (s, 1H, H4), 2.50 (s, 3H, methyl group), 2.12 (s, 3H, methyl group), −12.50 (s, 1H, H3, hydride). ^{13}C NMR (CD_2Cl_2, 100.66 MHz): δ 187.34 (2CO), 186.46 (2CO), 183.91 (2CO), 181.63 (2CO), 175.19 (C5), 153.39 (C2), 131.42 (C4), 86.01 (C3), 19.30 (CH_3), 12.24 (CH_3). ^{13}C NMR (CD_2Cl_2, DEPT, 100.66 MHz): δ 131.42. EI/MS: m/z 692 (M^+), 664 (M^+ − CO).

Crystallographic Analyses. Light-yellow single crystals of **2**−**6** suitable for X-ray diffraction analyses were obtained by the slow evaporation of solvent from a solution in pure hexane or a mixture of hexane and methylene chloride at 20 °C in the open air. X-ray-intensity data from the crystals 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 Kα radiation, λ = 0.71073 Å). All structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least squares on F^2 by using the *SHELXTL* software packages.[28] Crystal data and results of the structural refinements are given in Table S1.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00328.

> Details of the syntheses and characterizations of the new compounds, structural diagrams, and ^{13}C NMR spectra (PDF)

Accession Codes

CCDC 1893857−1893861 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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