Multiple Aromatic C-H Bond Activations by a Dirhenium Carbonyl Complex

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Multiple Aromatic C-H Bond Activations by a Dirhenium Carbonyl Complex

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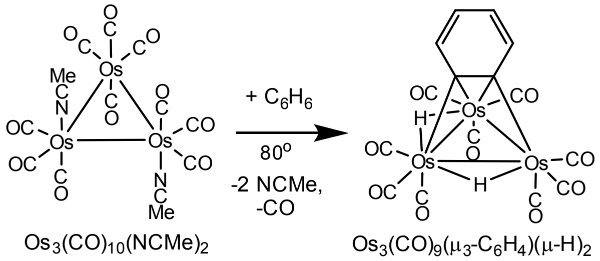
Multiple aromatic CH activations by a dirhenium complex has provided meta-related dimetallated arene rings in the complexes $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}3,4\text{-}C_{14}H_8)Re_2(CO)_8(\mu\text{-}H)$, 3 and $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}1,\mu\text{-}\eta^1\text{-}3\text{-}C_6H_4)Re_2(CO)_8(\mu\text{-}H)$, 4. Both products were characterized structurally by single crystal X-ray diffraction and DFT molecular orbital analyses.

The activation of CH bonds in hydrocarbons has attracted considerable research interest in recent years.[1,2] Multiple activations of CH bonds have received considerably less attention.[3] Multiple CH activations generally proceed by an oxidative addition at a metal atom and are followed by a β-elimination at a neighboring carbon atom. Catalytic dehydrogenations of alkanes generally proceed by a combination of these two steps to yield an olefin.[4] Multiple CH bond activation in aromatic compounds on a single ring are rare.[5,6] There a few examples of polynuclear metal complexes having benzyne ligands[6] that were formed by CH activations at neighboring carbon atoms of the benzene ring, e.g. Scheme 1.[6a]



Scheme 1. Synthesis of a benzyne ligand by CH activations at neighboring C atoms in benzene by a triosmium cluster.

We now report a new form of multiple aromatic CH activation reactions which involves multiple additions of the metal containing reagent to a single arene substrate and thus it does not need occur at neighboring carbon sites of the arene. The reaction of $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1** with anthracene, $C_{14}H_{10}$, has been found to yield the new compound $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}C_{14}H_9)(\mu\text{-}H)$, **2** in 73% yield by reductive-elimination of the bridging phenyl and bridging hydrido ligands of **1** as benzene and the oxidative-addition of the CH bond at the 2-position of the anthracene to the two rhenium atoms of **1**.

Compound **2** contains a $\mu\text{-}\eta^2\text{-}C_{14}H_9$ ligand that exhibits the classical σ-π coordination mode observed for bridging alkenyl ligands. The molecular structure of **2** was confirmed crystallographically, see Supporting Information, and it resembles that of the naphthyl compound $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}C_{10}H_7)(\mu\text{-}H)$ that was reported previously.[7] The most interesting feature of the reaction of **1** with anthracene is that compound **2** will react with a second equivalent of **1** by the elimination of benzene and the oxidative addition the bridging $C_{14}H_9$ ligand at the *meta*-related 4-position to the second Re_2 group. This produces the "doubly" CH activated anthracenyl complex $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}3,4\text{-}C_{14}H_8)Re_2(CO)_8(\mu\text{-}H)$, **3**, in 56% yield, see Scheme 2.

The molecular structure of **3** was established crystallographically and an ORTEP drawing of its molecular structure is shown in Figure 1. Atoms C1 – C2 of the anthracenyl ligand are π–bonded to Re1 and atoms C3 and C4 are π–bonded to Re3. C2 is σ–bonded to Re2 and C4 is σ–bonded to Re4. As expected, the C(1)-C(2) and C(3)-C(4) bond distances, 1.383(9) Å and 1.403(8) Å, respectively, are slightly longer than those in anthracene itself, 1.361(3) Å.[8] Despite the presence of four metal atoms on the one ring, this ring appears to have retained the bulk of its aromatic character, at least based on the NMR shifts of the hydrogen atoms on C1 and C3 which remain highly deshielded, δ = 7.02 (s, H1) and 7.43 (s, H3).[9]

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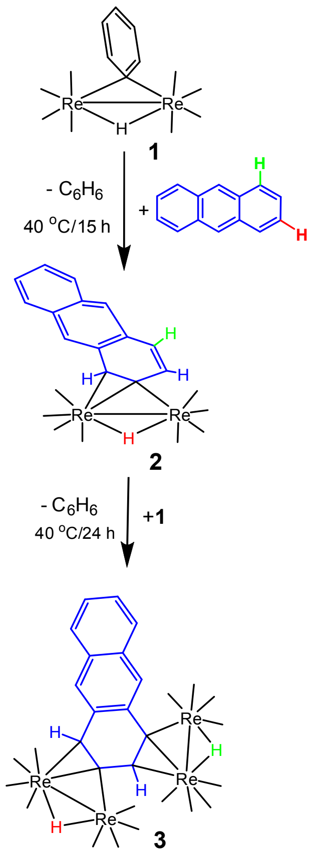


Scheme 2. A schematic of the reactions of 1 with anthracene.

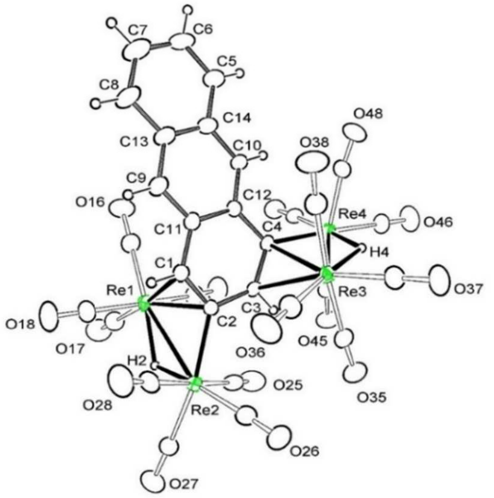


Figure 1. An ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}3,4\text{-}C_{14}H_8)Re_2(CO)_8(\mu\text{-}H)$, 3, showing 25% thermal ellipsoid probability. Selected interatomic bond distances(Å) are as follow: Re(1)-Re(2)=3.0566(4), Re(1)-C(1)=2.500(6), Re(1)-C(2)=2.463(6), Re(2)-C(2)=2.202(6), Re(3)-Re(4)=3.0484(3), Re(3)-C(3)=2.519(6), Re(3)-C(4)=2.462(6), Re(4)-C(4)=2.217(5), C(1)-C(2)=1.383(9), C(1)-C(11)=1.459(8), C(2)-C(3)=1.474(8), C(3)-C(4)=1.403(8), C(4)-C(12)=1.470(8), C(11)-C(12)=1.428(8).

Compound **1** is so aggressive toward aromatic CH activation that in the absence of a substrate it will even attack another molecule of its own kind. In this way we have found that **1** will react with another molecule of **1** by the elimination of benzene to yield the complex, $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}1,\mu\text{-}\eta^1\text{-}3\text{-}C_6H_4)Re_2(CO)_8(\mu\text{-}H)$, **4** in 51% yield simply by heating a solution in CH_2Cl_2 solvent to 40 °C for 24 h. An ORTEP diagram of the molecular structure **4** is shown in Figure 2. Compound **4** contains two $Re_2(CO)_8(\mu\text{-}H)$ groupings attached to a single C_6H_4 ring. One $Re_2(CO)_8(\mu\text{-}H)$ group is attached to the carbon atom C(1) in a $\mu\text{-}\eta^1$-fashion and a second $Re_2(CO)_8(\mu\text{-}H)$ group is attached to the carbon atom C(3) in a similar arrangement, i.e. the $Re_2(CO)_8(\mu\text{-}H)$ groups are positioned on the ring in *meta*-related sites, see Scheme (3). The C – C bond distances in the C_6H_4 ring that are involved in coordination to a metal atom, C(1)-C(2)=1.410(5) Å, C(2)-C(3)=1.421(5) Å, C(1)-C(6)=1.431(5) Å, C(3)-C(4)=1.413(5) Å, are significantly longer than those that are not bonded to the metal atoms, C(4)-C(5)=1.393(6) Å, C(5)-C(6)=1.367(6) Å, but like **3**, despite the present of four metal atoms on the ring, on the basis of the observed chemical shifts of the resonances of the ring hydrogen atoms, δ = 8.68 (s, 1H, H2, ^4J = 1.5 Hz), δ = 8.07 (dd, 2H, H4, H6, ^3J = 7.2 Hz, ^4J = 1.5 Hz), δ = 7.05-7.10 (t, 1H, H5, ^3J = 7.2 Hz), this ring also appears to have retained most its aromatic character.

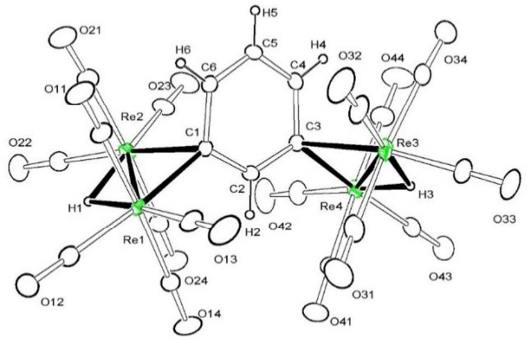
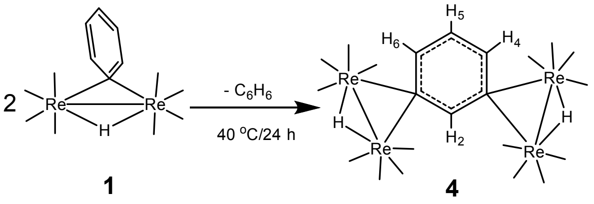


Figure 2. An ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}1,\mu\text{-}\eta^1\text{-}3\text{-}C_6H_4)Re_2(CO)_8(\mu\text{-}H)$, 4, showing 30% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follow: Re(1)–Re(2)=3.0046(2), Re(3)–Re(4)=3.0240(2), Re(1)-H(1)=1.85(5), Re(2)-H(1)=1.89(5), Re(3)-H(3)=1.92(5), Re(4)-H(3)=1.72(5), Re(1)-C(1)=2.224(4), Re(2)-C(1)=2.417(4), Re(3)-C(3)=2.424(4), Re(4)-C(3)=2.224(4), C(1)-C(2)=1.410(5), C(2)-C(3)=1.421(5), C(1)-C(6)=1.431(5), C(3)-C(4)=1.413(5), C(4)-C(5)=1.393(6), C(5)-C(6)=1.367(6).



Scheme 3. Reaction of 1 with itself yields the doubly *meta*-CH activated complex 4.

ADF DFT molecular orbital calculations have revealed the nature of the bonding of the rhenium atoms to the carbon atoms of the anthracene ring. The HOMOs of compound **3** and anthracene shown in Figure 3 show the bonding of the metal atoms in **3** in relation to the most relevant π-orbital in anthracene.

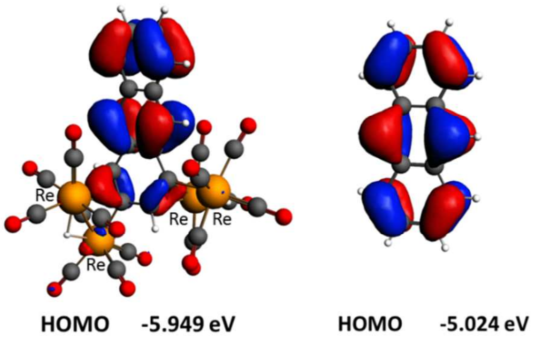


Figure 3. The highest occupied molecular orbital (HOMO) of compound 3 (left) and anthracene (right), ISO value equal 0.03. The energy in eV is given under the orbital. Atom color code: Orange = Re, Gray = C, Red = O.

ADF DFT molecular orbitals that show the nature of the bonding of the $Re_2(CO)_8(\mu\text{-}H)$ fragments to the relevant ring π-orbitals of the C_6H_4 ligand in **4** are shown in Figure 4. The dirhenium groups in **4** are both formally electronically unsaturated having only 32 valence electrons each. In previous studies, we have found that aryl rings bond to the metal atoms in related unsaturated μ-η^1-coordination modes by a combination of σ-donation and π-donation.[7,10] This seems to be the case in **4** too.

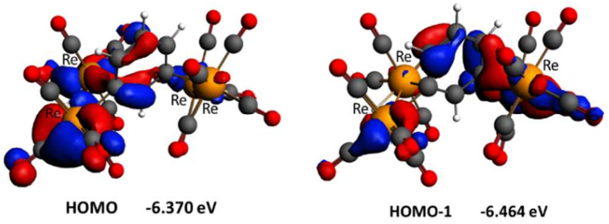


Figure 4. The HOMO and HOMO-1 of compound 4, ISO value equal 0.03. Energy in eV is given under the orbital. Atom color code: Orange = Re, Gray = C, Red = O.

It is anticipated that multiple aromatic CH activation products as represented by compounds **3** and **4** will open the door to new pathways for the "multiple" functionalization reactions in aromatic ring systems.

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Conflicts of interest

"There are no conflicts to declare".

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