Metallacycles

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Synthesis and Characterization of Dirhenadehydro[12]annulenes

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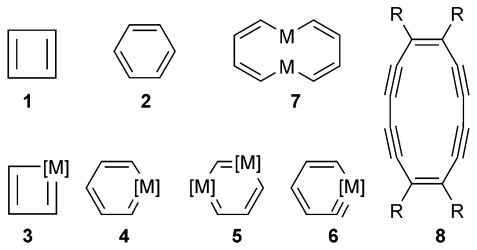
Abstract: *The 12-membered-ring metallacycles [mer-Re{≡CCH=C(R)C≡C–}Cl(PMe$_2$Ph)$_3$)]$_2$ (R = CMe$_3$, 1-adamantyl), which are organometallic analogues of antiaromatic octadehydro[12]annulene, are prepared by heating the methyl carbyne complexes mer-Re{≡CCH=C(R)C≡CH}(CH$_3$)Cl(PMe$_2$Ph)$_3$. An intermolecular σ-bond metathesis between the Re–CH$_3$ bond and the acetylenic C–H bond is proposed for their formation.*

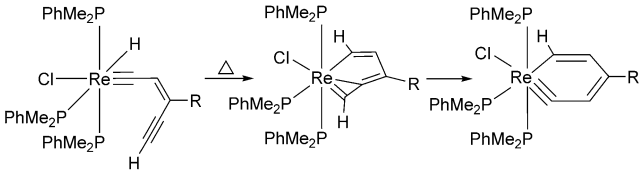
An [*n*]annulene is a monocyclic hydrocarbon comprising alternating single and double bonds (for example, cyclobutadiene (**1**), benzene (**2**)). Dehydroannulenes are annulene derivatives with one or more triple bonds (for example, benzyne). Annulenes and dehydroannulenes have inspired numerous theoretical and experimental studies as a result of their interesting properties.[1] For example, they can be used as aromaticity probes, as intermediates in the action of enediyne antitumor agents and as precursors in the preparation of novel carbon containing compounds.



Formal replacement of carbon atoms or CH groups in annulenes and dehydroannulenes by an isolobal transition-metal fragment would give metallaannulenes and metalladehydroannulenes. While annulenes with the number of ring carbon atoms up to 30 and dehydroannulenes with the number of ring carbon atoms up to 38 are known, reported examples of metallaannulenes and metalladehydroannulenes are mainly those with six or less ring atoms, for example, metallacyclobutadienes (**3**),[2,3] metallabenzenes (**4**),[4,5] dimetallabenzenes (**5**),[6] and metallabenzynes (**6**).[7,8] Larger metallaannulenes and metalladehydroannulenes are very rare. Very recently, Xi and his co-workers reported the synthesis and characterization of the first dimetalla-[10]annulenes (**7**).[9]

Herein, we report the synthesis and characterization of dimetalladehydro[12]annulenes which are closely related to octadehydro[12]annulenes **8**, species that have been previously studied for their aromaticity/antiaromaticity and interesting materials properties.[10]

We have shown that the rhenium hydridocarbyne complexes **9** can thermally isomerize to the rhenabenzynes **11** via bicyclic metallacycle complexes **10** (Scheme 1).[11] Continuing our efforts at making new metallabenzynes, we have prepared rhenium carbyne complexes **14** (see Scheme 2), analogous to **9** with the hydride ligand of **9** being replaced by a methyl group. These carbyne complexes may be expected to undergo similar methyl migration reactions to give bicyclic metallacycles, analogous to **10**, that can be converted to methyl-substituted rhenabenzynes.



Scheme 1. Formation of rhenabenzynes from hydridocarbyne complexes.

The precursor methyl carbyne rhenium complexes *mer*-Re{≡CCH=C(R)C≡CH}(CH$_3$)Cl(PMe$_2$Ph)$_3$ (R = CMe$_3$, **14a**; 1-adamantyl, **14b**) were prepared by the route shown in Scheme 2. Treatment of the SiMe$_3$-protected dichloro carbyne complexes *mer*,*cis*-Re{≡CCH=C(R)C≡CSiMe$_3$}Cl$_2$(PMe$_2$Ph)$_3$ (**12**) with CH$_3$MgCl in THF gave the methyl carbyne complexes **13**, which were isolated as green solids (Scheme 2). The desired carbyne complexes **14** were then obtained by desilylation of the complexes **13** with *n*Bu$_4$NF.

When a toluene solution of complex **14a** was heated, the expected bicyclic metallacycle or rhenabenzyne complex was not obtained. Instead, the reaction produced the 12-membered metallacycle dirhenadehydro[12]annulene **15a** as

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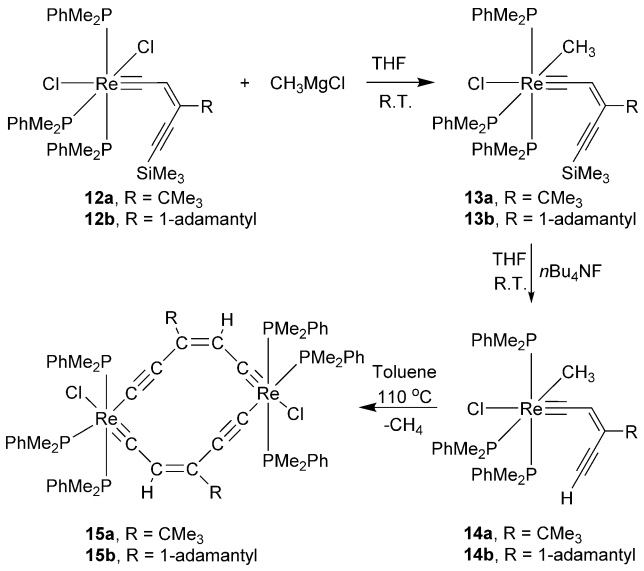

Scheme 2. Preparation of dirhenadehydro[12]annulenes **15a** and **15b**.

a result of σ-bond metathesis between the Re–CH_3 bond and the acetylenic C–H bond. Under similar reaction condition, complex **14b** was converted into the analogous dirhenadehydro[12]annulene **15b** with an adamantyl substituent (Scheme 2).

Complexes **15a** and **15b** were isolated as red solids in 36.8% and 31.6% yield, respectively. They have been characterized by NMR spectroscopy and elemental analysis. The structure of **15a** has also been confirmed by a single-crystal X-ray diffraction study. As shown in Figure 1, the complex **15a** contains an essentially planar, twelve-membered metallacycle. The maximum deviation from the mean plane through Re1 and C1–C5 is 0.08 Å for the Re1 atom. The Re≡C bond distance (1.770(4) Å) is similar to that (1.774-(3) Å) for the precursor rhenium carbyne complex **14b** (see Supporting Information). The Re–C≡ single bond is 2.100-(3) Å, which is within the range of those reported for rhenium acetylide complexes.[12] The Re-C-C angle (175.0(3)°) is close to 180°, indicating that the ring strain of the metallacycle is negligible. The solid-state structure is consistent with the solution NMR data. For example, the $^{31}P\{^1H\}$ NMR spectrum of **15a** shows a doublet at $\delta = -23.5$ ppm and a triplet at −26.7 ppm with a coupling constant of 17.3 Hz. The ^1H NMR spectrum displayed the proton signal of Re≡C-CH at $\delta =$ 4.75 ppm. The $^{13}C\{^1H\}$ NMR spectrum displayed the signals of carbon atoms of the metallacycle at $\delta = 267.8$ (Re≡C), 158.3 (Re-*C*≡C), 147.0 (Re≡C-CH=*C*), 129.0 (Re≡C-*CH*=C) and 124.5 (Re-C≡*C*) ppm. Complex **15b** has NMR data similar to those of **15a**, except those of adamantyl and *t*-butyl groups.

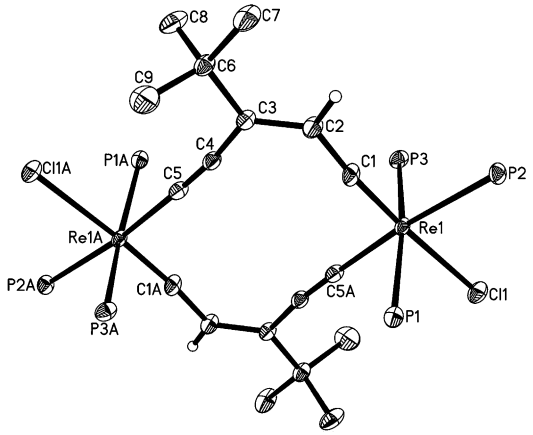

Figure 1. ORTEP drawing of **15a**. Thermal ellipsoids are set at 35% probability. All the C atoms of the PMe_2Ph ligands and H atoms except those on the metallacycle are omitted for clarity. Selected bond lengths [Å] and angles [°]: Re1-Cl1 2.5750(9), Re1-C1 1.770(4), Re1-C5A 2.100(3), C1-C2 1.412(5), C2-C3 1.370(5), C3-C4 1.423(5), C4-C5 1.199-(5); C1-Re1-C5A 98.33(14), C2-C1-Re1 175.0(3), C2-C3-C4 121.5(3), C3-C2-C1 125.6(3), C4-C5-Re1A 176.8(3), C5-C4-C3 172.5(4).

Although complexes **15** have a skeleton similar to that of octadehydro[12]annulenes **8** with two ≡C atoms of **8** being replaced by two ≡$[ReCl(PMe_2Ph)_3]$ groups for **15**, they displayed properties different from those of their organic counter parts. We noted that the parent octadehydro-[12]annulene with hydrogens at the vinyl carbons is unknown. Alkyl substituted octadehydro[12]annulenes such as 5,6:11,12-bis(tetramethylene)-1,3,7,9-octadehydro-[12]annulene rapidly decompose on exposure to air at room temperature.[13] Octadehydro[12]annulenes that are stable at room temperature have been reported only for those with alkynyl groups at the vinyl carbons,[10,14] and those fused with benzo and related moieties.[10,15] In contrast, the dirhenium complexes **15** are air-stable and can be stored for months in air without appreciable decomposition. A TGA analysis shows that complex **15b** is thermally stable up to 205 °C. The high thermal stability of complexes **15** could be related to the fact that octadehydro[12]annulenes have ring strain[16] while complexes **15** are not strained, as reflected by the angles associated with the metallacycles.

The difference in the electronic structures may also contribute to the varied thermal stability and reactivity. Octadehydro[12]annulenes are antiaromatic according to the Hückel rule. The antiaromatic character is supported by the NMR[17] and UV/Vis spectroscopic data,[18] as well as calculated NICS values.[19] We have carried out a theoretical study to determine if dirhenadehydro[12]annulene complexes **15** are also antiaromatic. Our calculations at the GIAO-B3LYP/6-311 + G(d,p) + lanl2dz//B3LYP/6-31G(d) + lanl2dz level show that the model dirhenadehydro[12]annulene complex **16** (see Figure 2 for its structure) has NICS (0) and NICS (1) values of −0.47 and −0.32, respectively. For comparison, with the same computational method, the NICS (0) and NICS (1) values of the antiaromatic compound **19** (see Figure 2 for its structure) were calculated to be 17.1 and 15.1 respectively.[20] The results suggest that the dirhenadehydro[12]annulene **16**, unlike **19**, is not an antiaromatic species.

To further confirm that **16** is not antiaromatic, we have also calculated its stability relative to the isomer **17** with an *exo*-methylene group,[21] as well as the free energy change for hydrogenation of **16** to **18**.[22] Calculations at the B3LYP/6-31G(d) level indicate that the complex **16** is 13.9 kcal mol^{-1} more stable than the isomer **17** (Figure 2). For comparison, toluene (**22**) and the antiaromatic octadehydro[12]annulene

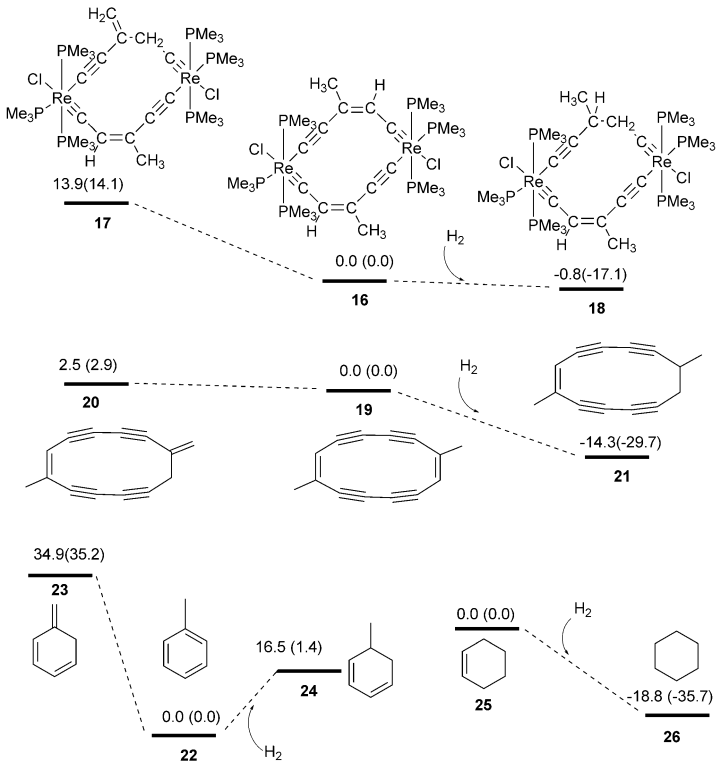

Figure 2. Relative stability of isomers of dirhenadehydro[12]annulene **16**, dehydro[12]annulene **19**, and toluene (**22**), and free reaction energy changes in the hydrogenation of **16**, **19**, toluene (**22**), and cyclohexene (**25**) calculated at the B3LYP/6-31G(d) + lanl2dz level in the gas phase. The relative free energies and electronic energies (in parentheses) are given in kcal mol^{-1}.

19 were calculated to be 34.9 and 2.5 kcal mol^{-1}, respectively, more stable than the corresponding isomers (**23** and **20**) each having an *exo*-methylene group. The hydrogenation of **16** to give **18** has a free energy change of only −0.8 kcal mol^{-1}, which is significantly less exothermic than that for the hydrogenation of antiaromatic octadehydro[12]annulene **19** (−14.3 kcal mol^{-1}) and non-aromatic cyclohexene (**25**, −18.8 kcal mol^{-1}). We noted that hydrogenation of toluene has a free energy change of 16.5 kcal mol^{-1}. These computational data indicate that the dirhenadehydro[12]annulene **16** can be regarded as being not antiaromatic.[23] In this regards, we noted that the ^{1}H NMR signals of Re≡CC*H* of the metallacyclic complexes **15** appeared at $\delta \approx 4.7$ ppm, which is downfield from those of Re≡CC*H* of the related rhenium carbyne complexes **14** ($\delta \approx 4.4$ ppm).

How were complexes **15** formed? Our computational studies suggest that the model rhenium methyl carbyne complex **27** can react with HC≡CCH=CH$_2$ to give the alkynyl carbyne complex **31** via the proton transfer process shown in Figure 3. The key step involves intermolecular σ-bond metathesis between the Re–CH$_3$ bond and the acetylenic C–H bond.[24,25] We believe that complexes **15** are presumably formed through a similar pathway. The energy profile shown in Figure 3 implies that addition of excess phosphine should slow down the rate for the formation of **15**. This expectation has been confirmed experimentally through studying the effect of added PMe$_2$Ph on the rate for the formation of **15b** from **14b**. For example, as monitored by in situ NMR spectroscopy, approximately 45% of **14b** is converted into **15b** after heating a solution of **14b** in toluene at 110 °C for 45 mins. Under similar condition, only trace of **15b** can be observed when 0.5 equivalent of PMe$_2$Ph was added.

Note that, on heating, the hydridocarbyne rhenium complexes **9** isomerize initially to bicyclic metallacycles **10** (via hydride migration to the carbyne carbon)[26] and finally to rhenabenzynes **11**, but do not undergo σ-bond metathesis reactions to give rhenadehydro[12]annulene derivatives, while the methyl carbyne rhenium complexes **14** undergo σ-bond metathesis reactions to give dirhenadehydro[12]annulenes **15** rather than isomerization reactions to give bicyclic metallacycles or rhenabenzynes. Our calculations at the B3LYP/6-31G(d) + lanl2dz level suggest that the different reactivity is of kinetic, rather than thermodynamic, origin. In the case of the hydridocarbyne rhenium

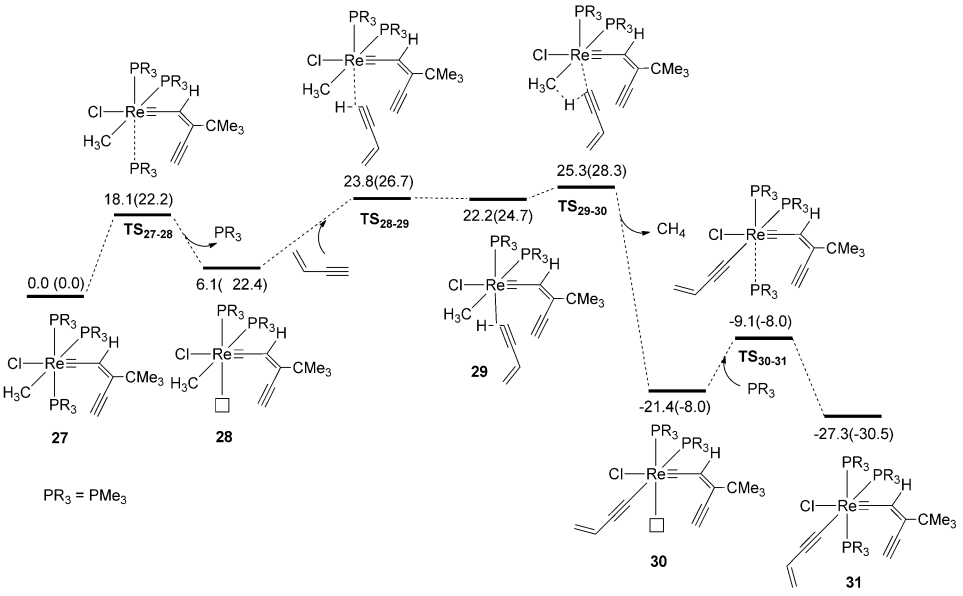

Figure 3. Energy profile calculated for the reaction of **27** with HC≡CCH=CH$_2$ to give **31** calculated at the B3LYP/6-31G(d) + lanl2dz level. The relative free energies and electronic energies (in parentheses) are given in kcal mol^{-1}.

complex *mer*-Re{≡C–CH=C(CMe_3)C≡CH}(H)Cl(PMe_3)$_3$, the barrier for the formation of the expected bicyclic metallacycle via hydride migration (Figure S4 in the Supporting Information) is lower than that for the σ-bond metathesis reaction with the terminal alkyne HC≡CCH=CH_2 (Figure S5). In the case of methyl carbyne rhenium complex **27**, the barrier for the formation of the expected bicyclic metallacycle via methyl migration (Figure S3) is higher than that for the σ-bond metathesis reaction with the terminal alkyne HC≡CCH=CH_2 (Figure 3).

In summary, we have successfully isolated and structurally characterized two interesting dirhenadehydro[12]annulenes. Theoretical studies suggest that, unlike their organic counter parts, these dirhenadehydro[12]annulenes are not antiaromatic. We are currently exploring the possibility of isolating other metallannulenes and metalladehydroannulenes with different ring sizes.

Acknowledgements

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[23] We noted that replacement of a carbon atom or a CH group in antiaromatic organic compounds, such as cyclobutadienes, see Ref. [3], pentalynes, or pentalenes, with an isolobal transition fragment can give stable aromatic metallacycles. a) C. Zhu, X. Zhou, H. Xing, K. An, J. Zhu, H. Xia, *Angew. Chem. Int. Ed.* **2015**, *54*, 3102 – 3106; *Angew. Chem.* **2015**, *127*, 3145 – 3149; b) C. Zhu, Q. Zhu, J. Fan, J. Zhu, X. He, X. Y. Cao, H. Xia, *Angew. Chem. Int. Ed.* **2014**, *53*, 6232 – 6236; *Angew. Chem.* **2014**, *126*, 6346 – 6350; c) C. Zhu, S. Li, M. Luo, X. Zhou, Y. Niu, M. Lin, J. Zhu, Z. Cao, X. Lu, T. Wen, Z. Xie, P. R. Schleyer, H. Xia, *Nat. Chem.* **2013**, *5*, 698 – 703.

[24] As a related example, the reactions of rhenium alkyl complexes $(CH_3)Re(CO)_3(PPh_3)(NCMe)$ with terminal alkynes $HC\equiv CR$ were reported to give acetylide complexes $Re(C\equiv CR)(CO)_3(PPh_3)(NCMe)$, which were proposed to proceed by oxidative addition of the C–H bonds of terminal alkynes followed by reductive elimination. J. G. Stack, R. D. Simpson, F. J. Hollander, R. G. Bergman, C. H. Heathcock, *J. Am. Chem. Soc.* **1990**, *112*, 2716 – 2729.

[25] σ-Bond metathesis reactions of transition-metal alkyl complexes L_nM-R with hydrocarbons R′-H to give L_nM-R′ and hydrocarbons R-H are known. D. Balcells, E. Clot, O. Eisenstein, *Chem. Rev.* **2010**, *110*, 749 – 823.

[26] It has been reported that rhenium hydride complexes can react with terminal alkynes to give acetylide complexes. For example, $\{(CMe_3)_2PCH_2SiMe_2)_2N\}ReH_4$, reacts at 23 °C with $RC\equiv CH$ ($R = CMe_3$, $SiMe_3$, Ph) to give H_2, $\{(CMe_3)_2PCH_2SiMe_2)_2N\}ReH_3(C\equiv CR)$ and $\{(CMe_3)_2PCH_2SiMe_2)_2N\}Re(C\equiv CR)_2$. O. V. Ozerov, L. A. Watson, M. Pink, M. H. Baik, K. G. Caulton, *Organometallics* **2004**, *23*, 4934 – 4943.

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