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Tetrarhena-heterocycle from the Palladium-Catalyzed Dimerization of $\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)(\mu\text{-H})$ Exhibits an Unusual Host–Guest BehaviorRichard D. Adams,^{*,†} William C. Pearl, Jr.,[†] Yuen Onn Wong,[†] Qiang Zhang,[†] Michael B. Hall,^{*,‡} and Justin R. Walensky^{‡,§}[†]Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States[‡]Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States

S Supporting Information

ABSTRACT: The six-membered heavy atom heterocycles $[\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)(\mu\text{-H})]_2$, **5**, and $\text{Pd}[\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)(\mu\text{-H})]_2$, **7**, have been prepared by the palladium-catalyzed ring-opening cyclo-dimerization of the three-membered heterocycle $\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)(\mu\text{-H})$, **3**. The palladium atom that lies in the center of the heterocycle **7** was removed to yield **5**. The palladium removal was found to be partially reversible leading to an unusual example of host–guest behavior. A related dipalladium complex $\text{Pd}_2\text{Re}_4(\text{CO})_{16}(\mu_4\text{-SbPh})(\mu_3\text{-SbPh}_2)(\mu\text{-Ph})(\mu\text{-H})_2$, **6**, was also formed in these reactions of palladium with **3**.

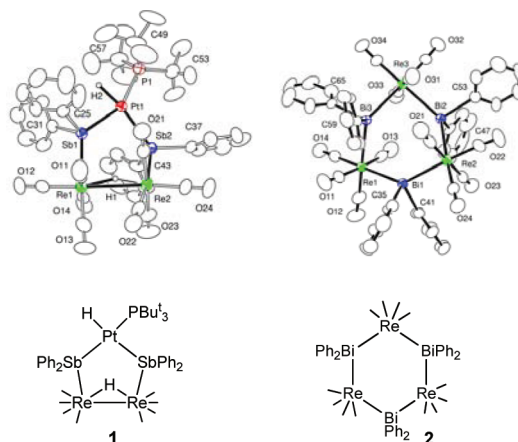
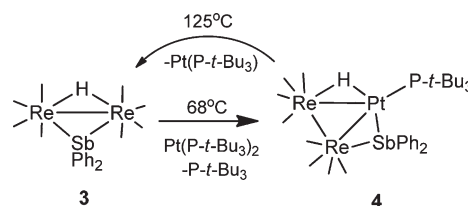
Host–guest phenomena have been one of the most exciting methods for gaining control over the reactivity of ions, molecules, metal complexes, and nanomaterials in recent years.^{1–5} Crown ethers, cryptands, metallacycles, cavitands, and capsules are well-known for their ability to complex ions and molecules in solutions.^{1–5} We now wish to report on what may prove to be a potential new family of hosts, heavy atom metallaheterocycles, that could add a new direction to this important field, namely, the ability to complex uncharged metal atoms reversibly.

In recent studies, our group has synthesized some unusual new metallaheterocycles, e.g. $\text{HPtRe}_2(\text{CO})_8(\text{P-}t\text{-Bu}_3)(\mu\text{-SbPh}_2)_2(\mu\text{-H})$,⁶ **1**, and $[\text{Re}(\text{CO})_4(\mu\text{-BiPh}_2)]_3$,⁷ **2**, by linking heavy transition metal groupings with heavy atom bridging ligands, such as diphenylantimony and diphenylbismuth, derived from the main group elements (Figure 1).

The three-membered heterocycle $\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)(\mu\text{-H})$,⁸ **3**, has been shown to react with $\text{Pt}(\text{P-}t\text{-Bu}_3)_2$ by a reversible ring-opening insertion of a $\text{Pt}(\text{P-}t\text{-Bu}_3)$ group into one of its Re-Sb bonds to yield the compound $\text{Re}_2[\text{Pt}(\text{P-}t\text{-Bu}_3)](\mu\text{-SbPh}_2)(\text{CO})_8(\mu\text{-H})$, **4**, Scheme 1.

It has now been found that when **3** is heated to 45 °C in the presence of $\text{Pd}(\text{P-}t\text{-Bu}_3)_2$, it undergoes a remarkable ring-opening cyclo-dimerization to form the new six-membered tetrarhena-heterocycle $\text{Re}_4(\text{CO})_{16}(\mu\text{-SbPh}_2)_2(\mu\text{-H})_2$, **5**, in 29% yield. Compound **5** was characterized by single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 2.

The structure of compound **5** consists of a puckered six-membered $\text{Re}_2\text{SbRe}_2\text{Sb}$ ring in a chair-like conformation. The SbPh_2 ligands lie at opposite sides of the molecule. The molecule contains two-fold rotational symmetry in the solid state. Compound **5** contains two equivalent hydrido ligands that bridge the

Figure 1. Structural diagrams for **1** and **2**.Scheme 1. Schematic of the Reversible Addition of $\text{Pt}(\text{P-}t\text{-Bu}_3)_2$ to **3**

Re-Re bonds, $\text{Re1-Re2} = 3.2607(4)$ Å, in the two $\text{Re}_2(\text{CO})_8$ groupings, $\delta = -14.94$. Interestingly, the hydrido ligands lie inside the ring. There was no spectroscopic evidence for formation of **5** even by heating **3** to 100 °C for 2 h in the absence of a source of palladium. There was a second product, $\text{Pd}_2\text{Re}_4(\text{CO})_{16}(\mu_4\text{-SbPh})(\mu_3\text{-SbPh}_2)(\mu\text{-Ph})(\mu\text{-H})_2$, **6**, obtained in only 4% yield that contains two mutually bonded palladium atoms; see Figure 3. Formally, compound **6** contains two ring-opened equivalents of **3**, but they are separated by the Pd atoms and a phenyl ring has been cleaved from one of the original SbPh_2 ligands. This phenyl ring serves as a bridging ligand across the Re(2)-Pd(2) bond in **6**.

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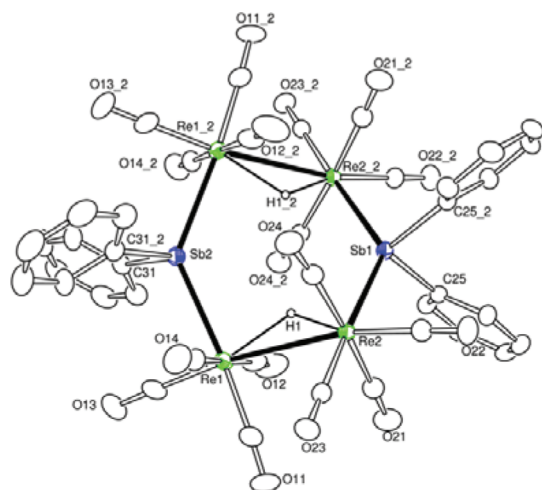


Figure 2. ORTEP diagram of the molecular structure of compound **5** showing 30% thermal ellipsoid probabilities. Selected interatomic bond distances (Å) and angles (deg) are as follow: Re1–Re2 = 3.2607(4), Re1–Sb2 = 2.8002(4), Re2–Sb1 = 2.7959(3), Re1–H1 = 2.02(5), Re2–H1 = 1.65(5).

When a concentrated solution of compound **3** was treated with $\text{Pd}(\text{dba})_2$, dba = dibenzylideneacetone at 45 °C, compound **5** together with a second product, $\text{Pd}[\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)(\mu\text{-H})_2]$, **7**, was obtained. Because of their structural similarities, the two compounds cocrystallize from the reaction mixture. The ratio of the two compounds in the crystalline form varies from reaction to reaction and crystal to crystal depending on the original concentrations of **3** and $\text{Pd}(\text{dba})_2$ in the reaction solution. It is possible to find samples that contain as much as 96% of **7**.¹⁰ Compound **7** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 4.

Compound **7** contains a slightly puckered six-membered Re_4Sb_2 ring similar to that of **5**, but it also contains a palladium atom in the center of the ring. This particular crystal contained only 51% Pd (determined by occupancy refinement) in the center of the Re_4Sb_2 ring. The palladium atom is bonded to all four Re atoms, Pd(1)–Re(1) = 2.9348(18) Å, Pd(1)–Re(2) = 2.9455(19) Å, Pd(1)–Re(3) = 2.9820(18) Å, Pd(1)–Re(4) = 2.9823(19) Å. The Re–Re bond distances, Re(1)–Re(2) = 3.4235(7) Å, Re(3)–Re(4) = 3.3592(6) Å, have all increased as a result of the insertion of the Pd atom into the ring.¹¹ Although these Re–Re distances seem long, they are not unprecedented. The hydride-bridged Re–Re interactions are 3.439(24) Å¹² in $\text{Re}_4(\text{CO})_{16}(\mu\text{-H})_4$ and 3.2742(4) in **1**.⁶ The observed Pd–Sb distances, Pd(1)–Sb(1) = 2.6306(18) Å, Pd(1)–Sb(2) = 2.6351(18) Å, in **7** are short enough to expect significant bonding interactions between these atoms. The Pd–Sb bond distances in the compounds $\text{Pd}(\text{SbPh}_3)_2(\text{Ph})\text{X}$, X = Cl and Br, are 2.5568(5) and 2.5421(5) Å respectively.¹³ The two equivalent hydride ligands H1 and H2, $\delta = -17.89$, were located and refined in this low temperature structural analysis, and they serve as triply bridging ligands across the two oppositely positioned Re_2Pd triangles, Pd(1)–H(1) = 1.90(10) Å, Pd(1)–H(2) = 1.76(10) Å.

The nature of the bonding of the palladium atom to the heterocycle was further established by geometry-optimized density functional theory (DFT) molecular orbital calculations.¹⁴ The bonding between the palladium atom and the p- and

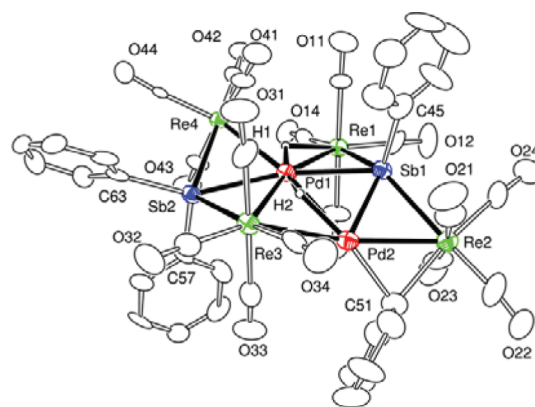


Figure 3. ORTEP diagram of the molecular structure of compound **6** showing 30% thermal ellipsoid probabilities. Selected interatomic bond distances (Å) are as follow: Re(1)–Sb(1) = 2.7439(17), Re(1)–Pd(1) = 2.9317(18), Re(2)–Sb(1) = 2.7434(18), Pd(1)–Pd(2) = 2.848(2), Re(2)–Pd(2) = 2.839(2), Re(3)–Pd(2) = 2.961(2), Re(3)–Pd(1) = 3.0949(19), Re(4)–Pd(1) = 2.7895(19), Re(4)–Sb(2) = 2.8527(17), Pd(1)–Sb(2) = 2.736(2), Pd(2)–Sb(1) = 2.547(2), Pd(1)–Sb(1) = 2.666(2), Pd(1)–H(1) = 1.75(1), Re(1)–H(1) = 1.75(1), Pd(1)–H(2) = 1.37(14), Pd(2)–H(2) = 1.83(14).

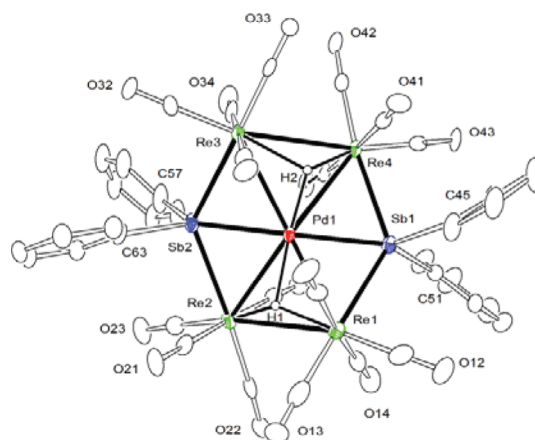


Figure 4. ORTEP diagram of the molecular structure of compound **7** showing 30% thermal ellipsoid probabilities. Selected interatomic distances (Å) are as follow:¹¹ Re(1)–Re(2) = 3.4235(7), Re(3)–Re(4) = 3.3592(6), Pd(1)–Re(1) = 2.9348(18), Pd(1)–Re(2) = 2.9455(19), Pd(1)–Re(3) = 2.9820(18), Pd(1)–Re(4) = 2.9823(19), Re(1)–Sb(1) = 2.7825(10), Re(2)–Sb(2) = 2.8007(10), Pd(1)–Sb(1) = 2.6306(18), Pd(1)–Sb(2) = 2.6351(18), Pd(1)–H(1) = 1.90(10), Pd(1)–H(2) = 1.76(10), Re(1)–H(1) = 1.92(10), Re(2)–H(1) = 1.67(10), Re(3)–H(2) = 2.05(9), Re(4)–H(2) = 1.75(10).

sp-orbitals on the Sb atoms are shown in the orbitals HOMO–29 and HOMO–30, Figure 5. Interactions between the palladium atom and the two hydride ligands are shown in the HOMO–44. These bonding interactions stabilize the molecule to a surprisingly large degree as the neutral Pd atom's binding energy is 40 kcal mol^{–1}.

There is a remarkable relationship between **5** and **7** that takes the form of a host/guest behavior. For example, when a solution of a **5/7** mixture (12%/88%) was treated with PCy_3 , Cy = C_6H_{11} (cyclohexyl), the palladium atom was removed from **7** with conversion to **5** in 3 h at 25 °C; no **7** remained as determined by ¹H NMR spectroscopy. Interestingly, the palladium atom can be

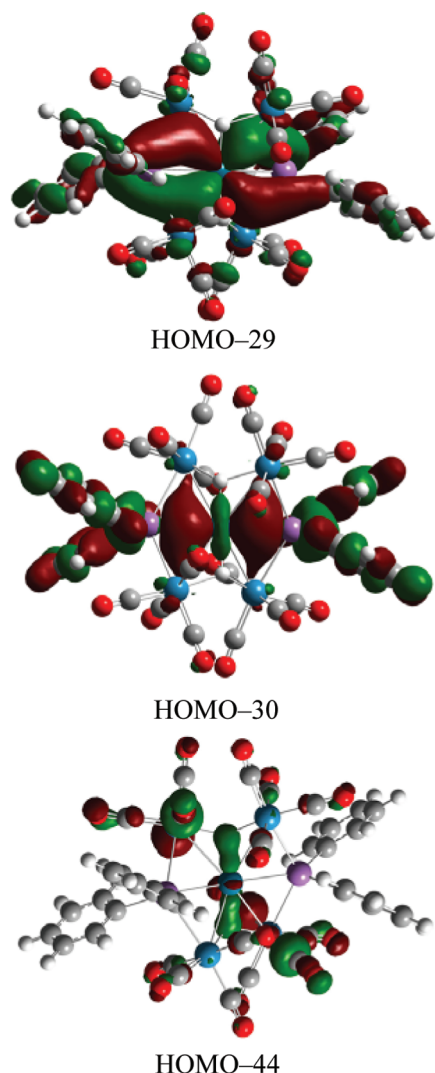
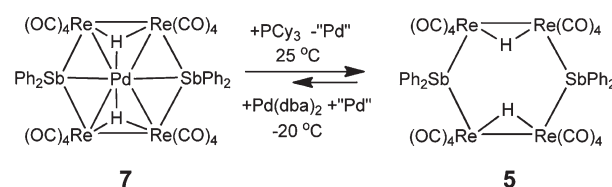


Figure 5. Selected molecular orbitals HOMO-29, HOMO-30, and HOMO-44 for **7** that show important bonding between the central palladium atom and atoms in the heterocycle.

reintroduced into the ring of **5** although as yet we have not been able to drive this conversion back to **7** to completion. The Pd readdition will, of course, depend on the nature of the Pd reagent and the ligands that are bonded to it. When a solution of **7/5** (4%/96%) in CD_2Cl_2 solvent in an NMR tube was treated with $\text{Pd}(\text{dba})_2$ at -20°C , the **7/5** ratio increased to 43%/57% over a period of 24 h as determined by the increase in the hydride resonance of **7** at $\delta = -17.89$ relative to that of **5** at $\delta = -14.94$.¹⁵

The mechanisms of the palladium-catalyzed cyclo-dimerization of **3** to **5**, the addition of Pd to **5**, and its removal from **7** have not yet been fully established. However, it seems most likely that the cyclo-dimerization begins with the insertion of a Pd-containing grouping into one of the Re-Sb bonds in **3** as was observed in the reaction of **3** with $\text{Pt}(\text{P}-t\text{-Bu}_3)_2$, Scheme 1.⁹ This process may even involve **7** as an intermediate. More interestingly, however, is the observation that the palladium atom not only can be removed from **7** but also can be reinserted back into the metallocycle **5**. The heterocycle **5** can thus be viewed as a host for the complexation of a single, uncharged palladium atom; see Scheme 2.

Scheme 2. Schematic of the Partially Reversible Removal of Pd from **7**



Efforts to introduce other metal atoms into the heterocycle **5** are in progress.

■ ASSOCIATED CONTENT

S Supporting Information. Details of the syntheses and characterizations of the new compounds, computational details and CIF files for each of the structural analyses are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ REFERENCES

- (1) (a) Cram, D. J.; Cram, J. M. *Science* **1974**, *183*, 803–809. (b) Gokel, G. W.; Leevy, W. M.; Weber, M. E. *Chem. Rev.* **2004**, *104*, 2723–2750. (c) Schneider, H. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1417–1436. (d) Lagona, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844–4870. (e) Lee, J. W.; Samal, S.; Selvapalam, N.; Kim, H.-J.; Kim, K. *Acc. Chem. Res.* **2003**, *36*, 621–630.
- (2) Crooks, R. M.; Zhao, M. Q.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 181–190.
- (3) (a) Leininger, S.; Olenyuk, Stang, P. J. *Chem. Rev.* **2000**, *100*, 853–908. (b) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2009**, *42*, 1650–1659. (c) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Res.* **2005**, *38*, 351–360. (d) McKinlay, R. M.; Cave, G. W. V.; Atwood, J. L. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 5944–5948. (e) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509–518. (f) Koblenz, T. S.; Wassenaar, J.; Reek, J. N. H. *Chem. Soc. Rev.* **2008**, *37*, 247–262. (g) Andrikopoulos, P. C.; Armstrong, D. R.; Clegg, W.; Gilfillan, C. J.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Parkinson, J. A.; Tooke, D. M. *J. Am. Chem. Soc.* **2004**, *126*, 11612–11620. (h) Kennedy, A. R.; Klett, J.; Mulvey, R. E.; Newton, S.; Wright, D. S. *Chem. Commun.* **2008**, 308–310.

(4) (a) Conn, M. M.; Rebek, J. *Chem. Rev.* **1997**, *97*, 1647–1668. (b) Atwood, J. L.; Barbour, L. J.; Jerga, A. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4837–4841.

(5) (a) Houk, K. N.; Leach, A. G.; Kim, S. P.; Zhang, X. *Angew. Chem., Int. Ed.* **2003**, *42*, 4872–4897. (b) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893–4012.

(6) Adams, R. D.; Pearl, W. C., Jr. *Organometallics* **2010**, *29*, 3887–3895.

(7) Adams, R. D.; Pearl, W. C., Jr. *Organometallics* **2009**, *48*, 9519–9525.

(8) Adams, R. D.; Captain, B.; Pearl, W. C., Jr. *J. Organomet. Chem.* **2008**, *693*, 1636–1644.

(9) Adams, R. D.; Hall, M. B.; Pearl, W. C., Jr.; Yang, X. *Inorg. Chem.* **2009**, *48*, 652–662.

(10) The amount of **7** in any particular crystal can only be determined by a complete single-crystal X-ray diffraction analysis and an occupancy refinement of the site of the palladium atom. The ratio of **5**:**7** in samples containing enough material for a ^1H NMR spectroscopic analysis is easily determined by the intensity ratio of their hydride resonances, $\delta = -14.94$ for **5** and -17.89 for **7**. Compound **6** is also formed in this reaction.

(11) The numbers given in the Figure 4 caption are the observed numbers from the crystallographic analysis. Since this crystal contains 51% **7** and 49% **5**, the observed numbers are really an average of the distances in **5** and **7**. One can obtain a better estimate of the true distances in **7** by recalculating using an expression that accounts for the partial occupancy, e.g. $(0.49x + 0.51y = z)$, where x = the bond distance observed in **5**, z = bond distance observed in this mixed crystal of **5** and **7**, and y is the unknown and would be the bond distance expected for **7** in a crystal that contains 100% of **7**. By using this calculation, the estimated interatomic distances in **7** would be: Re(1)–Re(2) = 3.5789(7), Re(3)–Re(4) = 3.4538(6), Pd(1)–Re(1) = 2.9348(18), Pd(1)–Re(2) = 2.9455(19), Pd(1)–Re(3) = 2.9820(18), Pd(1)–Re(4) = 2.9823(19), Re(1)–Sb(1) = 2.7696(10), Re(2)–Sb(2) = 2.8012(10), Pd(1)–Sb(1) = 2.6306(18), Pd(1)–Sb(2) = 2.6351(18), Pd(1)–H(1) = 1.90(10), Pd(1)–H(2) = 1.76(10), Re(1)–H(1) = 1.82(10), Re(2)–H(1) = 1.68(10), Re(3)–H(2) = 2.07(9), Re(4)–H(2) = 1.84(10).

(12) Masciocchi, N.; Sironi, A.; D'Alfonso, G. *J. Am. Chem. Soc.* **1990**, *112*, 9395–9397.

(13) Mendes, A.; Kemmit, R. D. W.; Fawcett, J.; Russell, D. R. *J. Organomet. Chem.* **1997**, *528*, 59–63.

(14) Computational Details: Calculations on compound **7** were performed by using the Gaussain09 and Amsterdam Density Functional (ADF) program packages. See Supporting Information.

(15) Compounds **5** and **7** are unstable in solution over extended periods, and therefore it was not possible to increase the conversion of **5** to **7** further by extending the reaction period of **5** with $\text{Pd}(\text{dba})_2$.