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Platinum Promoted Insertion of an Alkyne into a Metal−Hydrogen Bond

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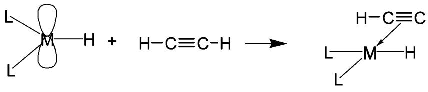
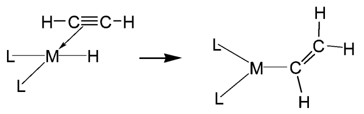
Bimetallic cooperativity or synergism is central to the function of some of today's most important heterogeneous catalysts.[1−4] For example, the combination of rhenium or iridium with platinum provides a petroleum reforming catalyst that is superior to that of platinum alone.[2] Adding ruthenium to palladium provides a superior catalyst for hydrogenating benzene.[3] Adding ruthenium to platinum provides a superior catalyst for the oxidation of methanol as used in the direct methanol fuel cell.[4] There are probably many different mechanisms for producing bimetallic synergism, but there are very few, if any, that are understood in detail. Herein we will provide a demonstration of a bimetallic cooperativity in unprecedented detail and clarity for the insertion of an alkyne into a metal−hydrogen bond, a key molecular transformation that has implications in the very important family of reactions known as catalytic hydrogenations.[5]

The insertion of alkynes and alkenes into a metal−hydrogen bond is one of the most basic steps in the process known as catalytic hydrogenation through which alkynes are converted to alkenes and alkenes are converted to alkanes.[5] In its most common form, the insertion of an alkyne into a metal−hydrogen bond involves first the coordination of the alkyne (e.g., C_2H_2) to a metal−hydride complex by using a low lying orbital that is available on the metal atom, eq 1a.[6] In most cases, the alkyne then "inserts" via a four-center transition state into the metal−hydrogen bond to form an alkenyl ligand, (e.g., C_2H_3) eq 1b.[7]

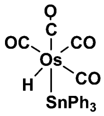


(1a)



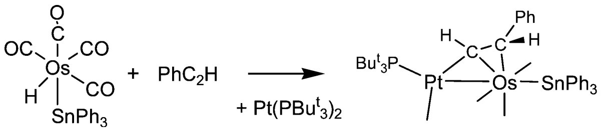
(1b)

In the absence of a low lying orbital on the metal atom, the reaction 1 does not proceed readily. For example, the saturated 18 electron complex $HOs(CO)_4SnPh_3$, **1**[8] does not react with phenylacetylene, PhC_2H, even when solutions of the two compounds are heated to reflux in toluene solvent (110 °C) for 1 h.



1

However, in the presence of $Pt(PBu^t_3)_2$, there is a rapid reaction (minutes) between **1** and PhC_2H at room temperature to yield the trimetallic complex $PtOs(CO)_4(SnPh_3)(PBu^t_3)[\mu\text{-}HC_2(H)Ph]$, **2**, eq 2.[9] The molecular structure of **2** as determined crystallographically is shown in Figure 1.[10] Compound **2** contains a $Pt(PBu^t_3)$ group bonded to the osmium atom by the platinum atom, Pt(1)−Os(1) = 2.7198(4) Å. A phenylalkenyl ligand, $HC_2(H)Ph$, was formed that bridges the Pt−Os bond. It is σ-bonded to the platinum atom and π-bonded to the osmium atom. The $HC_2(H)Ph$ ligand was formed by the insertion of the PhC_2H into the Os−H bond with transfer of the hydrogen atom to the phenyl-substituted carbon atom of the alkyne. Note the *E*-stereochemistry of the alkenyl ligand which is consistent with cis insertion of the alkyne via the classical four-center transition state.[6,7]



(2)

To understand the nature of the promotional effect of the platinum on this reaction, the reaction of **1** with $Pt(PBu^t_3)_2$ was investigated in the absence of added PhC_2H. In this case, the new compound $PtOs(CO)_4(SnPh_3)(PBu^t_3)(\mu\text{-}H)$, **3** was formed in 45% yield.[11] A diagram of the molecular structure of **3** as determined crystallographically is shown in Figure 2.[12] Compound **3** was formed by the direct addition of a $Pt(PBu^t_3)$ group to the Os−H bond of **1**. The hydrido ligand H(1) has assumed a bridging position between the osmium atom and the platinum atom and one CO ligand from the $Os(CO)_4$ group has been shifted into a bridging position between the two metal atoms. Notably, the Os−H bond is 0.28(6) Å longer and presumably weaker than the Os−H bond in **1**.[8] Compound **3** formally contains an unusual heteropolar metal−metal bond, Pt(1)−Os(1) = 2.7623(4) Å, formed by donation of a pair of electrons from the 18 electron osmium atom in **1** to the 12 electron platinum of the $Pt(PBu^t_3)$ group. Most importantly, when **3** was treated with PhC_2H, it was converted to **2** in 28% yield.

To understand the electronic structure in **3** and its possible role in the reaction of **3** with PhC_2H to yield **2**, Fenske−Hall molecular orbitals of **3** were calculated.[13] The lowest unoccupied molecular

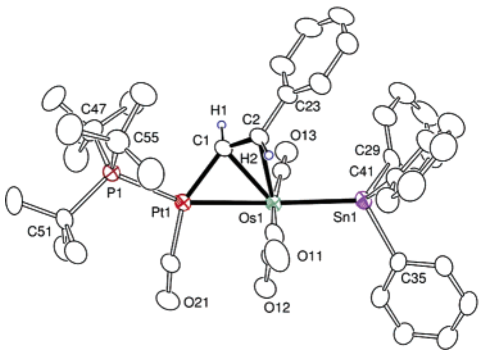


Figure 1. An ORTEP diagram of the molecular structure of **2** showing 30% probability thermal ellipsoids. Selected bond distances (in Å) are as follows: (molecule **1**) Pt(1)−Os(1) = 2.7198(4), Pt(1)−C(1) = 2.012(6), Os(1)−C(1) = 2.246(7), Os(1)−C(2) = 2.364(6), Pt(1)−P(1) = 2.3446(17), Os(1)−Sn(1) = 2.6921(5). (molecule 2) Pt(2)−Os(2) = 2.7177(4), Pt(2)−C(3) = 2.017(6), Os(2)−C(3) = 2.243(7), Os(2)−C(4) = 2.375(6), Pt(2)−P(2) = 2.3432(17), Os(2)−Sn(2) = 2.6840(5).

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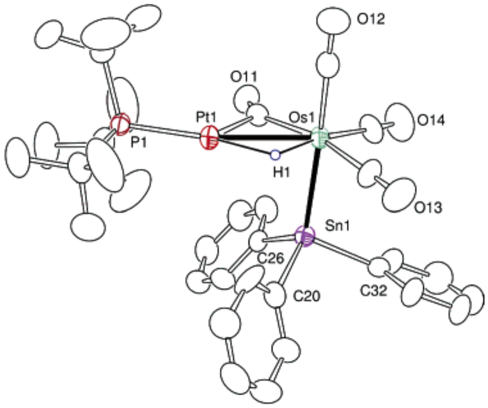


Figure 2. ORTEP diagram of the molecular structure of **3** showing 40% probability thermal ellipsoids. Selected bond distances (in Å) are as follows: Pt(1)−Os(1) = 2.7628(3), Pt(1)−P(1) = 2.2808(14), Pt(1)−C(11) = 1.982(6), Pt(1)−H(1) = 1.92(6), Os(1)−C(11) = 2.071(6), Os(1)−Sn(1) = 2.7281(5), Os(1)−H(1) = 1.95(6).

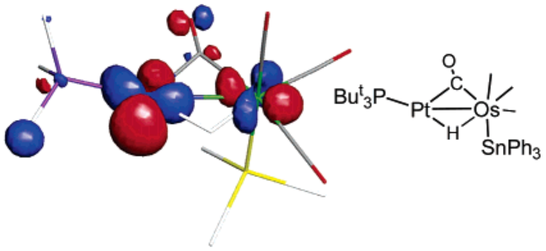
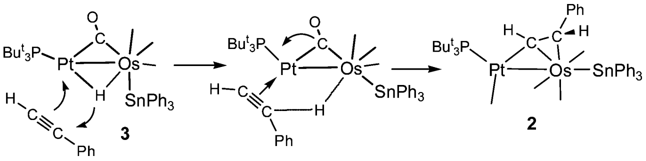


Figure 3. Lowest unoccupied molecular orbital (LUMO) of **3**.

Scheme 1



orbital (LUMO) of **3** is shown in Figure 3. Most interestingly, a major component of the LUMO is derived from an empty d-orbital on the platinum atom, see Figure 3.

Inspection of the molecular structure of **3** and its LUMO allows us to understand not only how the Os−H bond is activated by the platinum atom, but also how that Pt atom facilitates the addition and insertion of the PhC_2H into the OsH bond (see Scheme 1).

First of all, the interaction of the Pt atom with the hydrido ligand weakens the Os−H bond relative to that in **1**. Second, the empty d-orbital on the platinum atom in the LUMO of **3** provides a readily accessible bonding site for the complexation of the alkyne ligand which then inserts into the Pt−H and Os−H bonds resulting in the transfer of the hydrido ligand to the Ph-substituted carbon atom. The $HC_2(H)Ph$ ligand then adopts the $\sigma,\pi-$bonding mode as observed in **2**. The overall mechanism may involve more than one multicenter transition state. Details regarding possible intermediates are not available at this time.

Our studies have shown how the addition of the electronically unsaturated metal-containing molecular fragment, $Pt(PBu^t_3)$, promotes an important reaction both by activating a selected bond (Os−H) of one metal complex and then by facilitating the addition and transformation of a selected reagent (PhC_2H) at that bond. The two metals working together are able to accomplish what the one metal atom, osmium, could not do alone. The form of this platinum promoted insertion reaction should be completely general. It should also apply to other types of insertion reactions and quite possibly other related metal−ligand fragments, such as $Pd(PBu^t_3)$.[14]

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Supporting Information Available: Crystallographic data of **2**−**4** (CIF) and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Adams, R. D. *J. Organomet. Chem.* **2000**, *600*, 1. (b) Hermans, S.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Sankar, G.; Gleeson, D. *Angew. Chem. Int. Ed.* **2001**, *40*, 1211. (c) Hidai, M. Fukuoka, A.; Koyasu, Y.; Uchida, Y. *J. Mol. Catal.* **1986**, *35*, 29. (d) Guczi, L.; Schay, Z.; Stefler, G.; Mizukami, *J. Mol. Catal.* **1999**, *141*, 177.

(2) (a) Sinfelt, J. H. *Bimetallic Catalysts. Discoveries, Concepts and Applications*; Wiley: New York, 1983. (b) Sinfelt, J. H. *Adv. Chem. Eng.* **1964**, *5*, 37. (c) Sinfelt, J. H. *Acc. Chem. Res.* **1977**, *10*, 15.

(3) Thomas, J. M.; Johnson, B. F. G.; Raja, R.; Sankar, G.; Midgley, P. A. *Acc. Chem. Res.* **2003**, *36*, 20.

(4) (a) Hogarth, M. P.; Ralph T. R. *Platinum Met. Rev.* **2002**, *46*, 146. (b) Hogarth, M. P.; Hards, G. A. *Platinum Met. Rev.* **1996**, *40*, 150.

(5) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry;* University Science Books: Mill Valley, CA, 1987; Chapter 10.

(6) Li, X.; Vogel, T.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2005**, *24*, 62.

(7) Selmeczy, A. D.; Jones, W. D. *Inorg. Chim. Acta* **2000**, *300−302*, 138.

(8) Adams, R. D.; Captain, B.; Zhu, L. *Organometallics* **2006**, *25*, 4183.

(9) Compound **2** was obtained in 31% yield from the reaction of **1** with PhC_2H, in the presence of $Pt(PBu^t_3)_2$ in CH_2Cl_2 solvent at room temperature for 10 min, separated on 0.25 mm silica gel plates, crystallized from CH_2Cl_2/hexane solvent. Spectral data: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2049 (m), 2015 (m), 1977 (s). ^1H NMR (toluene-d_8 in ppm) at −65 °C: $\delta = 9.25$ (d, 1H, CH, $^3J_{H-H} = 14$ Hz), 9.01 (d, 2H, CH, $^3J_{H-H} = 13$ Hz), 8.89 (d, 1H, CH, $^3J_{H-H} = 13$ Hz, $^3J_{Pt-H} = 51$ Hz), 6.02 (d, 1H, CH, $^3J_{H-H} = 13$ Hz), 5.87 (d, 1H, CH, $^3J_{H-H} = 13$ Hz), 5.73 (d, 1H, CH, $^3J_{H-H} = 13$ Hz), 4.82 (d, 1H, CH, $^3J_{H-H} = 14$ Hz); at +60 °C, $\delta = 1.12$ (d, 27H, CH_3, $^3J_{P-H} = 13$ Hz). $^{31}P\{^1H\}$ NMR (toluene-d_8 in ppm) at −50 °C: $\delta = 93.0$ (s, 1P, $^1J_{Pt-P} = 2952$ Hz), 90.8 (s, 1P, $^1J_{Pt-P} = 2942$ Hz, $^3J_{Sn-P} = 39$ Hz), 90.1(s, 1P, $^1J_{Pt-P} = 3226$ Hz, $^3J_{Sn-P} = 20$ Hz), 88.0 (s, 1P, $^1J_{Pt-P} = 2910$ Hz, $^3J_{Sn-P} = 20$ Hz). Compound **2** exists in solution as a mixture of four interconverting isomers. Variable temperature ^1H NMR spectra clearly shows the dynamical exchange of all four isomers over the range −65 to +110 °C (see Supporting Information). A structurally similar isomer **4** formed by alkyne insertion with transfer of the hydrido ligand to the hydrogen substituted carbon atom of the alkyne was also obtained from this reaction in 19% yield. It was also characterized crystallographically (see Supporting Information). Satisfactory elemental analyses have been received.

(10) Crystal data for **2**: $PtOsSnPO_4C_{42}H_{49}$, $M_r = 1152.76$, triclinic, space group $P\bar{1}$, $a = 15.2610(15)$ Å, $b = 15.4146(15)$ Å, $c = 21.044(2)$ Å, $\alpha = 76.544(2)°$, $\beta = 73.541(2)°$, $\gamma = 76.415(2)°$, $V = 4540.8(8)$ Å^3, $Z = 4$, $T = 294$ K, Mo Kα = 0.71073 Å. The final $R1(F^2)$ was 0.0405 for 16059 reflections $I > 2\sigma(I)$.

(11) Compound **3** was obtained in 45% yield from the reaction of **1** with $Pt(PBu^t_3)_2$ in CH_2Cl_2 solvent at room temperature for 30 min, separated by TLC on silica, and crystallized from hexane solvent. Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2124 (w), 2076 (vs), 2038 (w, sh), 2010 (vs), 1809 (m). ^1H NMR (CD_2Cl_2 in ppm): $\delta = 1.34$ (d, 27H, CH_3,$^3J_{P-H} = 13$ Hz), −5.99 (d, H, hydride, $^2J_{P-H} = 46$ Hz, $^1J_{Pt-H} = 566$ Hz, $^2J_{119Sn-H} = 46$ Hz, $^2J_{117Sn-H} = 44$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 in ppm): $\delta = 101.8$ (s, 1P, $^1J_{Pt-P} = 6437$ Hz). Satisfactory elemental analyses have been received.

(12) Crystal data for **3**: $PtOsSnPO_4C_{34}H_{43}$, $M_r = 1050.63$, monoclinic, space group $P2_1/n$, $a = 15.3785(8)$ Å, $b = 12.0732(6)$ Å, $c = 20.6568(10)$ Å, $\beta = 108.841(1)°$, $V = 3629.2(3)$ Å^3, $Z = 4$, $T = 294$ K, Mo Kα = 0.71073 Å. The final $R1(F^2)$ was 0.0376 for 6971 reflections $I > 2\sigma(I)$.

(13) (a) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768. (b) Manson, J.; Webster, C. E.; Hall, M. B. *JIMP Development*, version 0.1.v117; Department of Chemistry, Texas A&M University: College Station, TX, July 2004; http://www.chem.tamu.edu/jimp/. (c) Lichtenberger, D. L. *MOPLOT2: for orbital and density plots from linear combinations of Slater or Gaussian type orbitals*, version 2.0; Department of Chemistry, University of Arizona: Tucson, AZ, June 1993.

(14) (a) Adams, R. D.; Captain, B.; Fu, W.; Hall, M. B.; Manson, J.; Smith, M. D.; Webster, C. E. *J. Am. Chem. Soc.* **2004**, *126*, 5253. (b) Adams, R. D.; Captain, B.; Smith, M. D. *J. Cluster Sci.* **2004**, *15*, 139. (c) Adams, R. D.; Captain, B.; Zhu, L. *J. Cluster Sci.* **2006**, *17*, 87.

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