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Unusual Structures and Reactivity of Mixed Metal Cluster Complexes Containing the Palladium/Platinum Tri-*t*-butylphosphine Grouping

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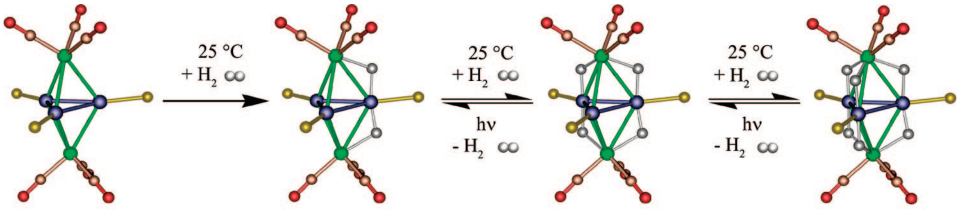


25 **26** **27** **28**

Polynuclear metal carbonyl complexes have a range of applications in chemical research: for example, they can serve as surface models to probe features of heterogeneous catalysis and can perform novel transformations of organic molecules in solutions. Mixed metal complexes can demonstrate bimetallic cooperativity and synergism and can also serve as precursors to multimetallic heterogeneous catalysts that have superior activities and selectivities.

This Account describes the results of our recent comprehensive study of the chemistry of mixed metal cluster complexes containing the sterically encumbered $M(PBu^t_3)$, M = Pd or Pt, group. This grouping readily adds to the metal−metal bonds of metal carbonyl cluster complexes and modifies their reactivity. We have prepared new, highly electronically unsaturated mixed metal complexes that exhibit unusually high reactivity toward hydrogen. The platinum atom of the $Pt(PBu^t_3)$ grouping can bond to as many as five metal atoms, and it can interconvert, sometimes rapidly, between the different bonding modes. The large steric effects of the PBu^t_3 ligand allowed us to prepare highly unsaturated, stable, mixed-metal complexes, and these complexes react with hydrogen, sometimes reversibly, under very mild conditions to yield polyhydride complexes. Strong evidence suggests that the $Pt(PBu^t_3)$ group can also activate metal−hydrogen bonds in other complexes. In the future, we expect that researchers will prepare a greater variety of mixed metal complexes containing the $Pd/Pt(PBu^t_3)$ group or other similar bulky groups, and that some of these complexes will exhibit even more unusual chemistry than what we have observed so far.

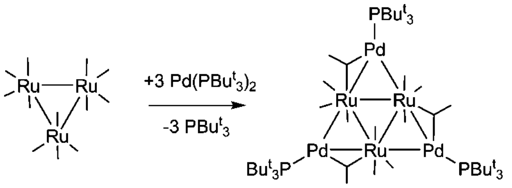
Introduction

Over the years, there has been considerable interest in trying to prepare polynuclear metal carbonyl cluster complexes having both high stability and high reactivity so that they can be more effective catalysts for chemical reactions such as hydrogenations, hydroformylations, and hydrosilylations.[1,2]Most stable metal carbonyl cluster complexes are relatively unreactive under mild conditions because they are electronically saturated. Reactivity of these complexes typically proceeds by cleavage of a metal−metal bond that often leads to fragmentation of the complexes or by the dissociation one or more of the CO ligands upon heating to produce the electronic and coordination unsaturation necessary to permit the addition of substrate molecules to the metal atoms.[3] It is well-known that bulky ligands can stabilize unsaturated mononuclear metal complexes that can also exhibit high reactivity toward hydrogen and other small molecules that are of interest to the chemical industry.[4] There have been a number of reports that have shown that the introduction of bulky phosphine ligands into the coordination sphere of polynuclear metal cluster complexes can lead to the formation of stable unsaturated complexes that also exhibit high reactivity toward hydrogen.[5]

Over the past few years, we have carried out a systematic investigation of the synthesis, structures, and reactivity of heteronuclear (mixed) metal cluster complexes containing the palladium or platinum tri-*t*-butylphosphine grouping, M(PBu$^t_3$), M = Pd or Pt. This grouping was chosen for study for the following reasons: (1) palladium and platinum are two of the most catalytically active metals in the periodic table; (2) the tri-*t*-butylphosphine ligand is probably the most sterically crowded of all of the common phosphine ligands; (3) the M(PBu$^t_3$) grouping is readily obtained by ligand dissociation from the readily available,[6] air-stable complexes Pd(PBu$^t_3$)$_2$ and Pt(PBu$^t_3$)$_2$; (4) bulky phosphine−palladium complexes have been shown to be an important family of catalysts for a variety of cross-coupling reactions;[7] and (5) mixed metal clusters containing platinum have been shown to exhibit superior properties as precursors to heterogeneous catalysts.[8] A summary of our studies of mixed metal cluster complexes containing the palladium/platinum tri-*t*-butylphosphine grouping is given in this Account.

Syntheses, Structures, and Bonding

One of the first reactions that we investigated was the reaction of Pd(PBu$^t_3$)$_2$ with Ru$_3$(CO)$_{12}$.[9] The product of this reaction was the six metal cluster complex Ru$_3$(CO)$_{12}$[Pd(PBu$^t_3$)]$_3$, **1**, eq (1); for clarity terminal CO ligands are represented in these equations as a single straight line from the symbol of the metal element to which they are attached; bridging CO ligands are represented as a line to the symbols of the two metals to which they are attached.



(1)

The central part of the cluster consists of a triangle of ruthenium atoms very similar to that of Ru$_3$(CO)$_{12}$ itself. A palladium atom with one appended phosphine ligand bridges each of the three Ru−Ru bonds, see Figure 1.

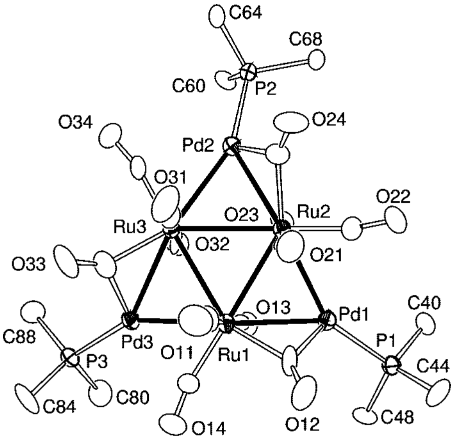
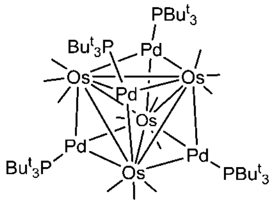


FIGURE 1. An ORTEP diagram of the molecular structure of **1**.

One CO ligand from each ruthenium atom has adopted a bridging coordination across one of the two Ru−Pd bonds to each palladium atom. The six-metal cluster is not planar; the three palladium atoms are slightly displaced out of the Ru$_3$ plane, all to the same side. The molecule can be viewed as a tris-Pd(PBu$^t_3$) adduct of Ru$_3$(CO)$_{12}$ because no ligands were eliminated from the Ru$_3$(CO)$_{12}$ in its formation. The structure exhibited by **1** should contain 90 valence electrons on the metal atoms if each of the metal atoms contains the standard 18 electron configuration.[10] However, compound **1** contains only 84 cluster valence electrons and is, thus, formally electron deficient by the amount of six electrons. Note, however, that this electron counting dilemma is alleviated if one accepts a 16 electron configuration for each of the three palladium atoms in this complex, but even the 16 electron model would require each palladium atom to share both of the electrons in the associated Ru−Ru bond. In fact, the metal−metal bonding in this complex is considerably more complicated than that.[9] Suffice it to say here, the molecule undergoes a second-order Jahn−Teller distortion that lowers the symmetry and produces the nonplanarity of the six metal atoms in order to maximize the Pd−Ru bonding. The platinum homologue of **1**, which is not quite as stable, has recently been reported.[11] Similar products were obtained from the reactions of Os$_3$(CO)$_{12}$ with Pd(PBu$^t_3$)$_2$[12] and Pt(PBu$^t_3$)$_2$ under mild conditions,[13] but at higher temperatures, the Os$_3$ cluster grew to a tetrahedral Os$_4$ cluster that added four Pd(PBu$^t_3$) groups to yield the eight-metal cluster complex Os$_4$(CO)$_{12}$[μ_3-Pd(PBu$^t_3$)]$_4$, **2**, that contained four triply bridging Pd(PBu$^t_3$) groups, one on each of the four faces of the Os$_4$ tetrahedron.[14] Compound **2** is also electron deficient. The metal atoms in **2** obey neither the 18 electron rule nor the polyhedral skeletal electron pair (PSEP) theory.[10] The PSEP theory would require a total of 108 valence electrons on the eight metal atoms. Compound **2** has only 104 valence electrons. Fenske−Hall molecular orbital calculations showed that the lowest unoccupied molecular orbital (LUMO) in **2** is doubly degenerate and has very low energy, −3.09 eV, for an unoccupied orbital. As expected, **2** reacts readily with electron-donating reagents. For example, **2** reacts with hydrogen at room temperature to yield the hydride containing complex $H_4Os_4(CO)_{12}$,which has lost the palladium phosphine groupings.[14]



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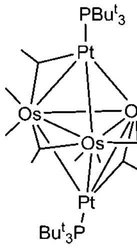

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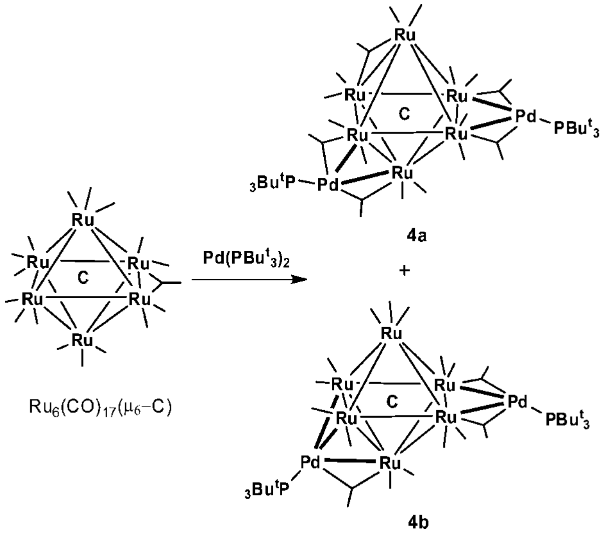
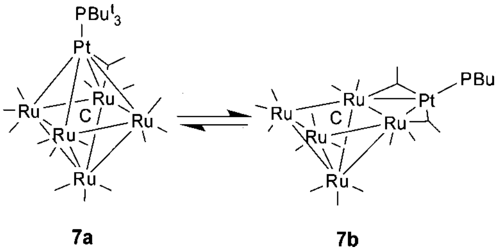
It was not possible to prepare the platinum homologue of **2** from the reaction of $Os_3(CO)_{12}$ with Pt(PBu$^t_3$)$_2$, but an interesting triosmium complex, $Os_3(CO)_{10}$[Pt(PBu$^t_3$)]$_2$ (**3**), with two triply bridging Pt(PBu$^t_3$) groups was obtained from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with Pt(PBu$^t_3$)$_2$.[15] Compound **3** also reacts with hydrogen under mild conditions, as described in the following section, Hydrogen Activation by Clusters Containing Pt(PBu$^t_3$) Groups, in this Account.

Treatment of the octahedral cluster complex $Ru_6(CO)_{17}(\mu_6\text{-}C)$ with Pd(PBu$^t_3$)$_2$ yielded the bis-Pd(PBu$^t_3$) adduct, $Ru_6(CO)_{17}(\mu_6\text{-}C)$[Pd(PBu$^t_3$)]$_2$ (**4**), eq 2, which exists in two isomeric forms, **4a** and **4b**, in the solid state, one in which both of the Pd(PBu$^t_3$) groups bridge edges of the Ru_6 octahedron and one in which one of the Pd(PBu$^t_3$) groups bridges an edge and the other bridges a triangular Ru_3 face of the cluster.[9] The structure of the latter isomer demonstrates that the palladium atom can also bond simultaneously to three metal atoms. The reaction of $Ru_6(CO)_{17}(\mu_6\text{-}C)$ with Pt(PBu$^t_3$) provides both a mono-Pt(PBu$^t_3$) adduct, $Ru_6(CO)_{17}(\mu_6\text{-}C)$[Pt(PBu$^t_3$)] (**5**), and a bis-Pt(PBu$^t_3$) adduct of $Ru_6(CO)_{17}(\mu_6\text{-}C)$[Pt(PBu$^t_3$)]$_2$ (**6**). Compound **5** contains a triply bridging Pt(PBu$^t_3$) group, while **6** contains two edge-bridged Pt(PBu$^t_3$) groups like **4a**.[9]



(2)

The reaction of $Ru_5(CO)_{15}(\mu_5\text{-}C)$ with Pt(PBu$^t_3$)$_2$ yielded a mono-Pt(PBu$^t_3$) adduct, $Ru_5(CO)_{15}(\mu\text{-}C)$[Pt(PBu$^t_3$)] (**7**), that exists in two isomeric forms, **7a** and **7b**, in the solid state and in solution. In **7a**, the Pt(PBu$^t_3$) bridges the square base of the square pyramidal Ru_5 cluster and is bonded to all four metal atoms to form an octahedral Ru_5Pt cluster. In **7b**, the Pt(PBu$^t_3$) bridges only one edge of the square pyramidal Ru_5 cluster. Interestingly, the two isomers interconvert rapidly on the NMR time scale at room temperature in solution, eq 3.[16] The reaction of $Ru_5(CO)_{15}(\mu_5\text{-}C)$ with Pd(PBu$^t_3$)$_2$ produces a similar pair of interconverting isomers of a mono-Pd(PBu$^t_3$) adduct, $Ru_5(CO)_{15}(\mu_5\text{-}C)$[Pd(PBu$^t_3$)], but the most interesting product of this reaction is the bis-Pd(PBu$^t_3$) adduct $Ru_5(CO)_{15}(\mu_6\text{-}C)$[Pd(PBu$^t_3$)]$_2$ (**8**) that contains a quadruply bridging Pd(PBu$^t_3$) group and a triply bridging Pd(PBu$^t_3$) group. In this compound the two Pd(PBu$^t_3$) groups interchange their sites intramolecularly by a modification of the opening and closing process that is operative for compound **7**, eq 4.[16]



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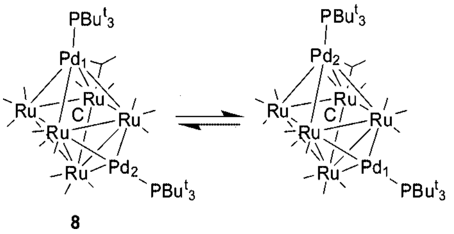

(4)

The tendency of the Pd(PBu$^t_3$) group to bridge metal−metal bonds is so strong that it even promotes the formation of metal−metal bonds. For example, Pd(PBu$^t_3$)$_2$ reacts with $Ru(CO)_5$ to yield the compound $Ru_2(CO)_9$[Pd(PBu$^t_3$)]$_2$ (**9**).[17] Compound **9** contains two ruthenium atoms that are joined by a Ru−Ru bond and two bridging Pd(PBu$^t_3$) groups, one on each side of the Ru−Ru bond. Compound **9** could be viewed as a bis-Pd(PBu$^t_3$) adduct of $Ru_2(CO)_9$. Although the complex $Ru_2(CO)_9$ is known,[18] it is unstable at room temperature and is unlikely to be the precursor to **9**. The metal−metal bonding in **9** is highly delocalized as shown by the highest occu-

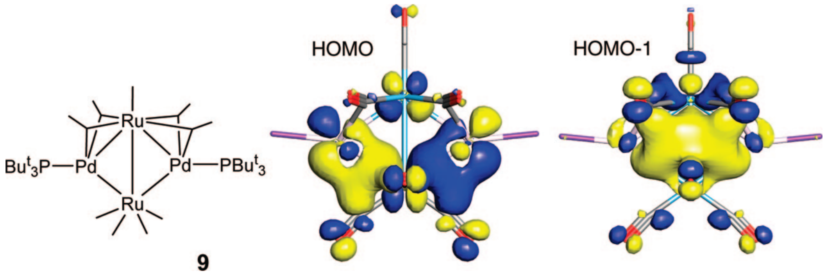

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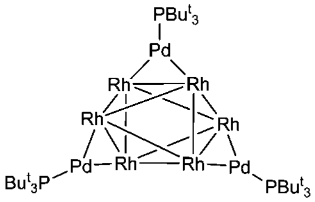
FIGURE 2. A line structure (left) and the HOMO and HOMO − 1 of the cluster complex **9**. These orbitals are three-center two-electron bonds; the HOMO shows the Ru(CO)$_4$ fragment interacting with the antisymmetric combination of the two Pd fragment LUMO orbitals, and the HOMO − 1 shows the Ru(CO)$_5$ fragment interacting with the symmetric combination of the two Pd fragment LUMO orbitals.

pied molecular orbitals, HOMO and HOMO − 1, shown in Figure 2. The Pt homologue of **9** has also been synthesized.[17]

To examine the versatility of the M(PBu$^t_3$), M = Pd or Pt, grouping to add across metal–metal bonds, we continued our reactivity studies to the group 9 metals, Rh and Ir. The reaction of $\mathrm{Rh_4(CO)_{12}}$ with Pd(PBu$^t_3$)$_2$ yielded two products, $\mathrm{Rh_6(CO)_{16}}$[Pd(PBu$^t_3$)]$_3$ (**10**) and $\mathrm{Rh_6(CO)_{16}}$[Pd(PBu$^t_3$)]$_4$ (**11**).[19] Both products contain hexarhodium clusters: compound **10** has three edge-bridging Pd(PBu$^t_3$) groups and **11** has four edge-bridging Pd(PBu$^t_3$) groups (for clarity, the CO ligands are not shown in the line structures of **10** and **11**). The Pt homologue of **11** was also prepared.



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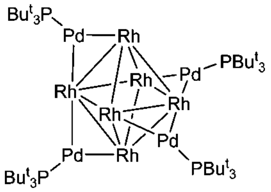

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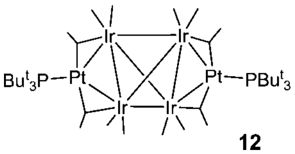
The metal–metal bonds in $\mathrm{Ir_4(CO)_{12}}$ are stronger than those in $\mathrm{Rh_4(CO)_{12}}$,[20] and it was found that $\mathrm{Ir_4(CO)_{12}}$ reacts with Pt(PBu$^t_3$)$_2$ without expansion of the Ir$_4$ cluster to yield the bis-Pt(PBu$^t_3$) adduct, $\mathrm{Ir_4(CO)_{12}}$[Pt(PBu$^t_3$)]$_2$ (**12**), where the two Pt(PBu$^t_3$) groups bridge opposite edges of an Ir$_4$ tetrahedron.[21]



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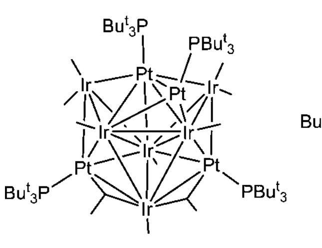
However, reactions of $\mathrm{Ir_4(CO)_{12}}$ with Pt(PBu$^t_3$)$_2$ at elevated temperatures yielded higher nuclearity Ir$_6$ and Ir$_8$ species, $\mathrm{Ir_6(CO)_{10}}$[Pt(PBu$^t_3$)]$_4$ (**13**) and $\mathrm{Ir_8(CO)_{12}}$[Pt(PBu$^t_3$)]$_4$ (**14**), that contained quadruply bridging and quintuply bridging Pt(PBu$^t_3$) groups.[21]



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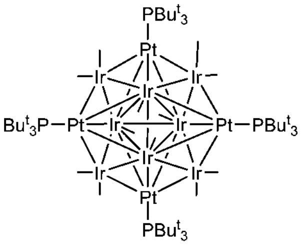

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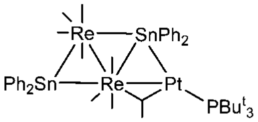
It was found that it is even possible to add Pd(PBu$^t_3$) and Pt(PBu$^t_3$) groups to certain transition metal–main group metal–metal bonds. For example, the reaction of the compound $\mathrm{Re_2(CO)_8}$(μ-$\mathrm{SnPh_2}$)$_2$ with Pt(PBu$^t_3$)$_2$ yielded the compounds $\mathrm{Re_2(CO)_8}$(μ-$\mathrm{SnPh_2}$)$_2$[Pt(PBu$^t_3$)]$_n$ (**15**, $n = 1$, and **16**, $n = 2$) where the Pt(PBu$^t_3$) groups bridge one and two of the Re–Sn bonds, respectively.[22] The addition of the Pt resulted in the formation of an unusual triply bridging $\mathrm{SnPh_2}$ ligand. It was also possible to prepare a mono-Pt(PBu$^t_3$) adduct of the related compound $\mathrm{Re_2(CO)_8}$(μ-$\mathrm{GePh_2}$)$_2$ where the Pt(PBu$^t_3$) group bridged a Re–Ge bond.[22]



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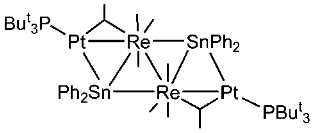

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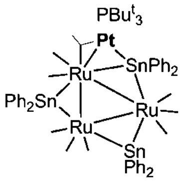
It was also found that mono-, bis- and tris-Pt(PBu$^t_3$) adducts, $\mathrm{Ru_3(CO)_9}$(μ-$\mathrm{SnPh_2}$)$_3$[Pt(PBu$^t_3$)]$_n$ (**17**–**19**, n = 1–3), could be obtained from the reaction of the planar cluster complex $\mathrm{Ru_3(CO)_9}$(μ-$\mathrm{SnPh_2}$)$_3$ with Pt(PBu$^t_3$)$_2$.[23] Compounds **17**–**19** are planar and are formed by the progressive addition of one to three Pt(PBu$^t_3$) groups to Ru–Sn bonds around the periphery of the central $\mathrm{Ru_3Sn_3}$ cluster. Each addition of a Pt(PBu$^t_3$) group destabilized the HOMO of the $\mathrm{Ru_3(CO)_9}$(μ-$\mathrm{SnPh_2}$)$_3$ cluster, which resulted in a progressively smaller HOMO–LUMO gap and an increasing red shift of the principal absorption in the UV–vis absorption spectrum.

To compare the relative affinity of the Pt(PBu$^t_3$) group for a Ru–Ru bond versus a Ru–Sn bond, the reaction of $\mathrm{Ru_2(CO)_8}$(μ-$\mathrm{SnPh_2}$) (**20**) with Pt(PBu$^t_3$)$_2$ was investigated.[24] Both mono- and bis-Pt(PBu$^t_3$) adducts, $\mathrm{Ru_2(CO)_8}$(μ-$\mathrm{SnPh_2}$)[Pt(PBu$^t_3$)]



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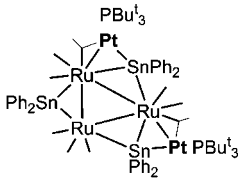

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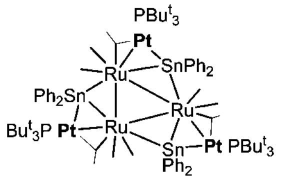

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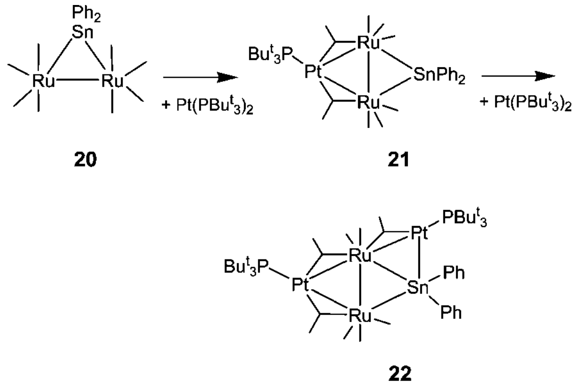
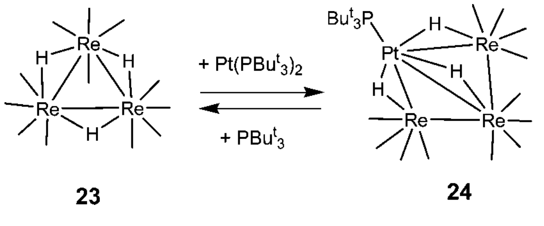
(**21**) and $Ru_2(CO)_8(\mu\text{-}SnPh_2)[Pt(PBu^t_3)]_2$ (**22**), were obtained eq 5. The structural analysis of the monoadduct showed that the first $Pt(PBu^t_3)$ group was added to the Ru−Ru bond of **20**. The second $Pt(PBu^t_3)$ addition then occurred at one of the Ru−Sn bonds to yield **22**. A molecular orbital analysis of **20** provided an explanation for the preference of the $Pt(PBu^t_3)$ for the Ru−Ru bond in **20** by showing that the orbital representing the Ru−Ru bond is energetically more accessible than the Ru−Sn orbitals.



(5)

An interesting result was obtained when we investigated the reaction of $Pt(PBu^t_3)_2$ with the hydride-containing complex $Re_3(CO)_{12}(\mu\text{-}H)_3$ (**23**). This reaction yielded the mono-Pt(PBu^t_3) adduct, $Re_3(CO)_{12}(\mu\text{-}H)_3[Pt(PBu^t_3)]$ (**24**), but instead of simply adding across a Re−Re bond, the $Pt(PBu^t_3)$ group was inserted into an Re−Re bond, eq 6.[25]



(6)

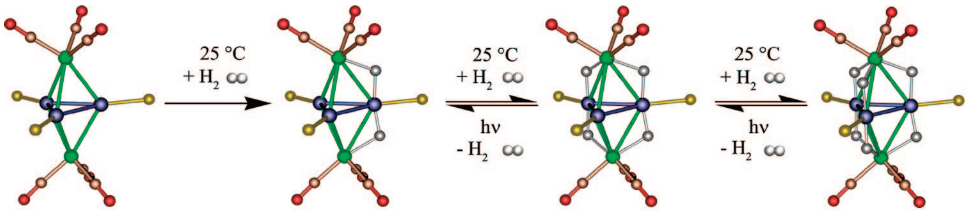
This may be a result of the fact that each Re−Re bond in **23** contains a bridging hydrido ligand. Interestingly, the platinum atom in **24** is bonded to all three rhenium atoms and the hydrido ligands have been repositioned so that each Pt−Re bond contains one bridging hydrido ligand. When **24** was treated with PBu^t_3, the $Pt(PBu^t_3)$ group was eliminated and compound **23** was regenerated.

Hydrogen Activation by Clusters Containing Pt(PBu$^t_3$) Groups

It was not possible to prepare any $Pd(PBu^t_3)$ or $Pt(PBu^t_3)$ adducts of $Re_2(CO)_{10}$, but $Re_2(CO)_{10}$ does react with $Pt(PBu^t_3)_2$ at 125 °C with loss of CO to yield the remarkable, highly electronically unsaturated cluster complex $Pt_3Re_2(CO)_6(PBu^t_3)_3$, **25**.[25] The structure of **25** consists of a trigonal bipyramidal cluster of three platinum atoms and two rhenium atoms. The three platinum atoms, each with one pendant PBu^t_3 ligand, define the equatorial plane. The apical sites are occupied by the two $Re(CO)_3$ groups. It is as if a $[Pt(PBu^t_3)]_3$ trimer has been inserted between two $Re(CO)_3$ groups. There is no bond between the rhenium atoms. Compound **25** contains a total of 62 valence electrons, ten less than the 72 expected if the five metal atoms were to contain formal 18 electron configurations.[10] The platinum−rhenium bonds are quite short. The average Re−Pt bond distance was 2.6483(7) Å. The shortness is probably a consequence of the electronic unsaturation. Molecular orbital calculations revealed five low-lying empty orbitals delocalized across the metal cluster. Anticipating reactivity to sources of electrons, the reaction of **25** with hydrogen was investigated. Indeed, compound **25** reacts with hydrogen at room temperature to form a series of new hydride-containing complexes, $Pt_3Re_2(CO)_6(PBu^t_3)_3(\mu\text{-}H)_n$ (**26**−**28**; $n = 2$, 4, and 6) formed by the sequential addition of 1, 2, and 3 equiv of H_2 to **25**, Figure 3.[25]

Each of the products **26**−**28** have been isolated and structurally characterized. The compounds are all structurally similar to **25** and differ only in the number of hydrido ligands. In all of the compounds, the hydrido ligands bridge the Pt−Re bonds. In **28**, each of the six Pt−Re bonds contains one bridging hydrido ligand. In **27**, two of the hydrido ligands, a symmetric pair on each side of the Pt_3 plane, are missing, and in **26** four of the hydrido ligands, two symmetric pairs on each side of the Pt_3 plane, are missing.

Experiments have indicated that the hydrogen addition occurs, mechanistically, without the dissociation of a phosphine ligand. Space filling models of the structure indicate that there is sufficient space for the H_2 molecule to access the metal atoms by passing between the *t*-butyl groups of Pt(P-Bu$^t_3$) ligands on neighboring platinum atoms. A computational analysis of the reaction suggests that the H_2 is activated first

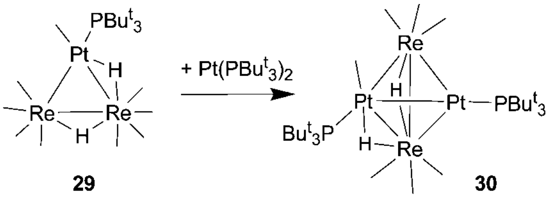


25 **26** **27** **28**

FIGURE 3. Schematic of reversible addition of hydrogen to the Pt_3Re_2 cluster complex **25**: platinum (blue), rhenium (green), phosphorus (gold), oxygen (red), carbon (pink), hydrogen (gray).

by addition to a single metal atom.[25] Cleavage of the H−H bond is assisted by a neighboring metal atom. Cleavage by a platinum-based mechanism is preferred only slightly over a possible rhenium-based mechanism. Most interestingly, it was found that hydrogen was eliminated from **28**, as H_2, upon exposure to UV−vis irradiation. Compounds **27** and **26** were regenerated in this way, but not **25**. Some **25** was formed when the irradiation of **28** was conducted in quartz glassware, but considerable decomposition of all of the compounds occurred under these conditions.

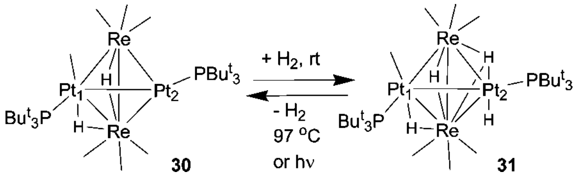
The reaction of $PtRe_2(CO)_9(PBu^t_3)(\mu\text{-}H)_2$ (**29**) with $Pt(PBu^t_3)_2$ provided the electronically unsaturated diplatinum−dirhenium cluster complex $Pt_2Re_2(CO)_7(PBu^t_3)_2(\mu\text{-}H)_2$ (**30**), eq 7.[26]



(7)

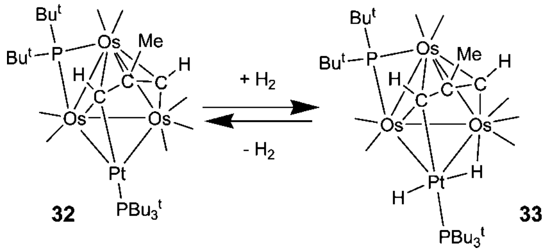
Compound **30** contains four metal atoms in a tetrahedral-like arrangement. There are two hydrido ligands; one bridges the Re−Re bond, and the second bridges one of the Pt−Re bonds. Compound **30** contains only 54 valence electrons on the metal atoms, which is six less than the number of 60 expected for an electronically saturated tetrahedral cluster complex.[10] Anticipating unusual reactivity, the reaction of **30** with hydrogen was also investigated, and as expected, **30** reacted readily with H_2 to yield the tetrahydrido complex $Pt_2Re_2(CO)_7(PBu^t_3)_2(\mu\text{-}H)_2(\mu_3\text{-}H)(H)$ (**31**), eq 8.[26]

Compound **31** is unusual because it contains three types of hydrido ligands, one triple bridge, two edge bridges, and one terminal hydride, all in the same molecule. Compound **31** eliminated 1 equiv of H_2 when heated to 97 °C or when exposed to UV−vis irradiation to regenerate **30** in good yield. The mechanism of the addition of H_2 to **30** was also investigated computationally.[26] These calculations have indicated that the H_2 molecule adds to the platinum atom labeled as Pt_2 in eq 8 and the H−H bond cleavage occurs at that atom as well. This is reasonable because the platinum atoms in **30** have different coordinations; that is, Pt_1 contains one PBu$^t_3$ ligand and one CO ligand, while Pt_2 contains only a PBu$^t_3$ ligand; therefore, Pt_2 is coordinationally unsaturated compared with Pt_1.



(8)

Another interesting unsaturated mixed metal cluster complex is the compound $PtOs_3(CO)_7(PBu^t_3)(\mu\text{-}PBu^t_2)(\mu_4\text{-}CHCMeCH)$ (**32**), which was obtained from the reaction of $Os_3(CO)_{12}$ with $Pt(PBu^t_3)_2$ at 125 °C.[27] Compound **32** contains a Pt(PBu$^t_3$) group, but also contains a bridging PBu$^t_2$ ligand and quadruply bridging CHC(Me)CH ligand that was formed by the cleavage of a *t*-butyl group from a PBu$^t_3$ ligand. Compound **32** contains a total of 58 cluster valence electrons. In an electronically saturated form, it would have 62 electrons. Although its unsaturation is not high, compound **32** readily reacts with hydrogen at room temperature to yield the dihydrido complex $PtOs_3(CO)_7(PBu^t_3)(\mu\text{-}PBu^t_2)(\mu_4\text{-}CHCMeCH)(\mu\text{-}H)(H)$ (**33**), eq 9.[28]



(9)

Compound **33** is structurally similar to **32**, but it contains one hydrido ligand that bridges a bond to one of the osmium atoms and one hydrido ligand that is terminally coordinated to the platinum atom. The addition of hydrogen to **32** is reversible at room temperature. When nitrogen is purged through solutions of **33**, it eliminates hydrogen and regenerates **32**. A molecular orbital analysis of **32** showed that the lowest unoccupied molecular orbital (LUMO) is concentrated on the platinum atom. A computational analysis of the hydro-

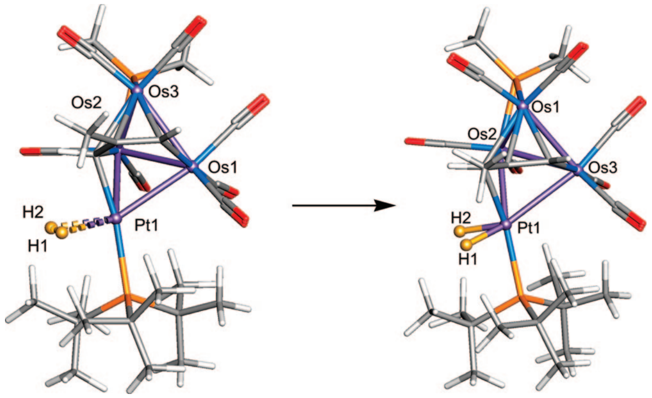
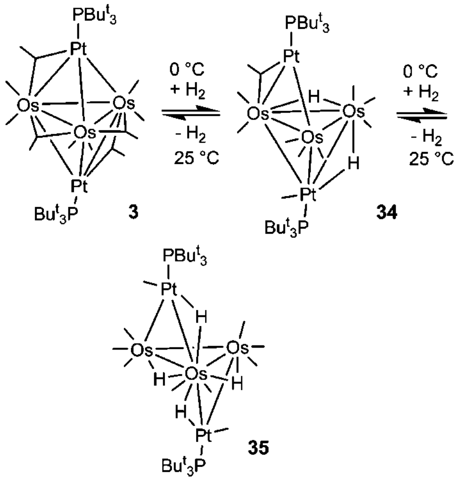


FIGURE 4. A computational simulation of the activation of hydrogen on the platinum atom of **32**. The structure on the left shows an η-H_2 ligand coordinated to the platinum atom. The H−H bond has been cleaved in the structure on the right.

gen addition reaction showed, as expected, that the hydrogen molecule is added to the complex at the platinum atom and the H−H cleavage occurs by an oxidative addition mechanism, see Figure 4.

The final hydrogen activation reaction to be described here involves the complex $Os_3(CO)_{10}[Pt(PBu^t_3)]_2$ (**3**). Compound **3** was found to react with hydrogen even at 0 °C. Two products were formed in a sequence of two H_2 additions to yield the compounds $Os_3(CO)_{10}[Pt(PBu^t_3)]_2(\mu\text{-}H)_2$ (**34**) and $Os_3(CO)_{10}[Pt(PBu^t_3)]_2(\mu\text{-}H)_4$ (**35**), eq. (10).[15]

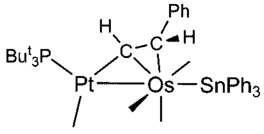


(10)

With each addition of H_2, one Pt−Os bond was cleaved and one of the triply bridging Pt(PBu^t_3) groups was converted to an edge-bridging group and a CO ligand was shifted to a terminal position on the platinum atom. Each molecule of hydrogen was converted into hydrido ligands that bridge metal−metal bonds. The product **35** thus contains two bridging Pt(PBu^t_3)(CO) groups and four bridging hydrido ligands. The H_2 activation process of compound **3** is fundamentally different from that of the previously described compounds because metal−metal bond cleavages are involved. The reason for this can be attributed to its electronic configuration. Compound **3** is only slightly electron deficient, 68 valence electrons versus the expected 72 electron count.[10] In fact, one could argue that **3** is not unsaturated at all if one accepts 16 electron configurations for the two platinum atoms as the norm. Thus, the electrons that are added to the cluster of **3** by the addition of H_2 do not enter empty molecular orbitals but instead go into antibonding orbitals that ultimately lead to the cleavages of metal−metal bonds and the subsequent structural rearrangements. Interestingly, the addition of hydrogen to **3** is readily reversible; simple purging solutions of **34** and **35** with nitrogen regenerates **3**. One problem with this reaction is that **35** continues to react with hydrogen over time, and this results in irreversible degradation of the complex by loss of a platinum-containing group.[15a]

Activation of Metal Complexes by the Pt(PBu^t_3) Group

Perhaps one of the more intriguing examples of bond activation by the Pt(PBu^t_3) group is the activation of the M−H bond in the complexes $HM(CO)_4(SnPh_3)$ (**36** and **37**, M = Ru and Os) toward alkyne insertion. For example, complex **37** does not react with PhC_2H even in a toluene solution at reflux (110 °C).[29] However, solutions of **37** and PhC_2H containing $Pt(PBu^t_3)_2$ react rapidly to yield the mixed metal complex $PtOs(CO)_4(SnPh_3)(PBu^t_3)[\mu\text{-}HCC(H)Ph]$ (**38**), which contains a HCC(H)Ph ligand bridging the Pt−Os bond in this dinuclear metal complex. The HCC(H)Ph ligand was formed by insertion of the PhC_2H into the Os−H bond and transfer of the hydrogen atom to the phenyl-substituted carbon atom. To understand this complex reaction, the reaction of $Pt(PBu^t_3)_2$ with **37** was investigated in the absence of PhC_2H. This reaction produced the platinum−osmium complex, $PtOs(CO)_4(SnPh_3)(PBu^t_3)(\mu\text{-}H)$ (**39**), which was subsequently shown to react with PhC_2H to yield **38**. The molecular structure of **39** is shown in Figure 5.



38

Although it contains a metal−metal bond, a bridging hydrido ligand, and a bridging carbonyl ligand, compound **39** can still be viewed as a Pt(PBu^t_3) adduct of **37**. From the structure of **39**, one can immediately see how the platinum atom activates the Os−H bond. It has formed a bonding interaction to both the osmium and the hydrogen atom. The Os−H

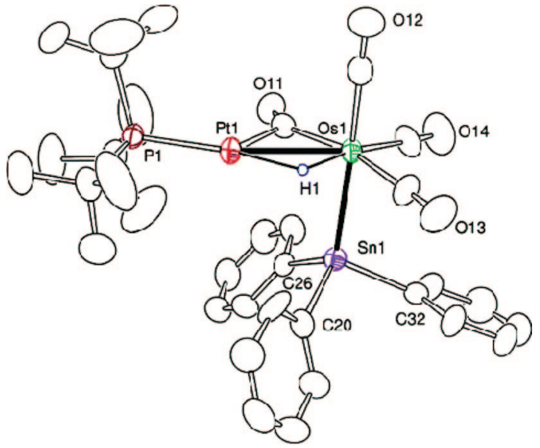


FIGURE 5. An ORTEP diagram of the molecular structure of **39**.

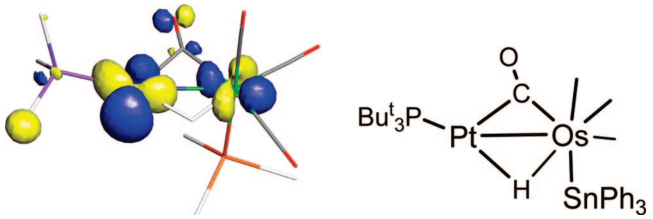


FIGURE 6. A contour diagram of the Fenske–Hall LUMO of **39** and a line structure (right) showing the orientation of the atoms.

bond length in **39**, Os(1)–H(1) = 1.95(6) Å, is substantially longer than that in **37**, 1.67(4) Å.[30]

A Fenske–Hall molecular orbital analysis of **39** provided some additional insight into the nature of the reaction of the **39** with PhC$_2$H and the role of the platinum atom in that. A contour diagram of the lowest unoccupied molecular orbital (LUMO) of **39** is shown in Figure 6. An obvious feature of this orbital is that it contains a large component on the platinum atom. It is believed that this frontier orbital is the one that facilitates the addition of the PhC$_2$H molecule to **39** via formation of a bonding interaction between the platinum atom and the π-bond of the PhC$_2$H molecule, and in turn, because of its proximity and interaction with the hydrido ligand, it also promotes the insertion of the PhC$_2$H ligand into the Pt–H and Os–H bonds.

It has also been shown that the Pt(PBu$^t_3$) group can promote CO ligand substitution reactions in certain carbonyl complexes. For example, it is known that Os$_3$(CO)$_{12}$ reacts with PPh$_3$ to yield the mono- and bis-PPh$_3$ derivatives, Os$_3$(CO)$_{11}$(PPh$_3$) and Os$_3$(CO)$_{10}$(PPh$_3$)$_2$. However, this reaction requires heating to temperatures as high as 140 °C. However, when the bis-Pt(PBu$^t_3$) adduct of Os$_3$(CO)$_{12}$, Os$_3$(CO)$_{12}$[Pt(PBu$^t_3$)]$_2$ (**40**), is treated with PPh$_3$, Os$_3$(CO)$_{11}$(PPh$_3$) and Os$_3$(CO)$_{10}$(PPh$_3$)$_2$ are formed at room temperature.[13] Clearly, the Pt(PBu$^t_3$) groups are facilitating the removal of the CO ligands from the osmium atoms. The reason for this can be seen in the structure of **40**; some of CO ligands on the osmium atoms have formed bridging coordination across some of the Pt–Os bonds making it easier for the platinum atom to remove them from the osmium atoms, see Figure 7.

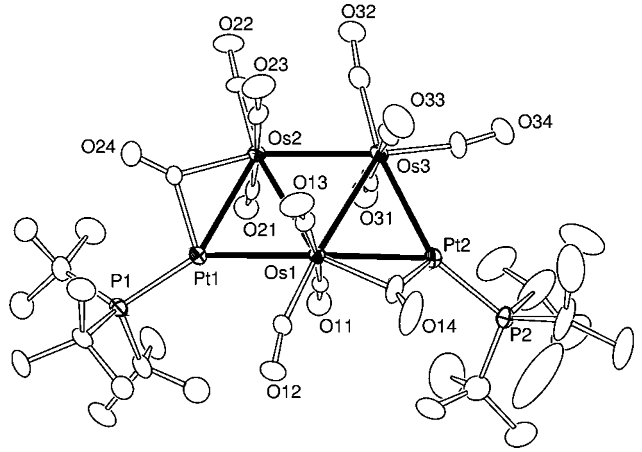


FIGURE 7. An ORTEP diagram of the molecular structure of **40**.

It seems that suitable mixed metal complexes containing the Pt(PBu$^t_3$) group will find applications in homogeneous catalysis. While this seems likely, one must be aware that the association of the Pt(PBu$^t_3$) group to the metal–metal bonds in the clusters that we have studied is not a strong one. Many donor substrates that might be the object of catalytic reactions can also function as ligands and react at the Pt(PBu$^t_3$) group and cleave it from the mixed metal complex. The Pt(PBu$^t_3$) fragment itself may then serve as an effective agent for certain types of catalysis.[31] Pd(PBu$^t_3$) is a well-established catalyst for C–C coupling reactions.[32]

Summary and Prospects

The Pd/Pt(PBu$^t_3$) group has been shown to be a versatile component in mixed metal cluster complexes. It can add to the metal–metal bonds of polynuclear metal complexes with only minor perturbations in the structure of the original complex. It has been shown that the platinum atom of the Pt(PBu$^t_3$) group can bond to two, three, four, and even five metal atoms and it can interconvert between these bonding modes, sometimes rapidly on the NMR time scale. Because of the huge steric effects of the PBu$^t_3$ ligand, highly unsaturated, stable, mixed-metal complexes can be prepared. These complexes have been shown to react with hydrogen, sometimes reversibly, under very mild conditions to yield polyhydride complexes. The platinum atom appears to play a key role in the hydrogen activation reactions. There is strong evidence that the Pt(PBu$^t_3$) group can also activate metal–hydrogen bonds in other complexes.

It seems likely that it should be possible to prepare an even greater variety of mixed metal complexes containing the Pt(P-

Bu^t_3) group and that some of these complexes will exhibit even more unusual chemistry than has been uncovered to date. The chemistry of the Pd/Pt(PBu^t_3) group could be simulated and modified by the utilization of other bulky phosphine ligands such as P(cyclo-C_6H_{11})$_3$ and P(iso-C_3H_7)$_3$. It seems likely that the Pt(PBu^t_3) group and mixed metal complexes of it will have applications in some areas of homogeneous catalysis, particularly those where hydrogen activation is involved. It is certain that transition metal catalysts will play an important role in the emerging hydrogen economy,[33] and complexes that can activate hydrogen under mild conditions will almost certainly find applications there too.

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BIOGRAPHICAL INFORMATION

Richard D. Adams received his B.S. degree from the Pennsylvania State University in 1969 and a Ph.D. in chemistry from the Massachusetts Institute of Technology in 1973. He was Assistant Professor of Chemistry at SUNY, Buffalo, 1973−1975, and Assistant and Associate Professor at Yale, 1975−1984. He was appointed Professor of Chemistry at the University of South Carolina in 1984, Arthur S. Williams Professor of Chemistry in 1995−2005, and Carolina Distinguished Professor in 2006. He was the recipient of the 1999 American Chemical Society award for Inorganic Chemistry. He is the American Regional Editor for the *Journal of Organometallic Chemistry* and a coeditor of the *Journal of Cluster Science*.

Burjor Captain received a B.A. in chemistry from Ohio Wesleyan University in 1998 and completed his Ph.D. in 2002 with Professor Richard D. Adams at the University of South Carolina. He continued his postdoctoral studies with Prof. Adams at the University of South Carolina investigating polynuclear metal cluster complexes. In August of 2007, he joined the faculty as an assistant professor in the Chemistry Department at the University of Miami, Coral Gables. His research interests include metal cluster chemistry, organometallic synthesis, and catalysis. He is the coauthor of over 70 publications.

FOOTNOTES

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