A Way to Novel Heterometallic Raft-like Clusters from Neutral Precursors

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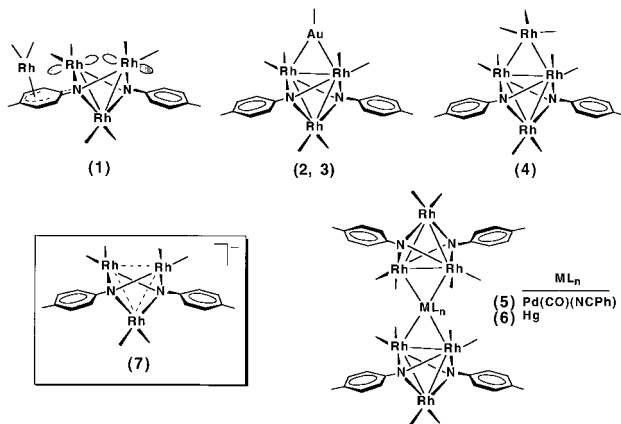Zaragoza-C.S.I.C., E-50009 Zaragoza, Spain*

While the basic concept of a ligand in coordination and organometallic chemistry is that of a species containing main-group nonmetal donor atoms, the fact that metal atoms are able to act as donors in polar dative metal–metal bonds[1] enables one to envisage metal clusters playing the role of classical ligands. We report here the use of a novel, general synthetic strategy based on this concept. The use of an imido-bridged cluster capable of changing from neutral to anionic character with a concomitant increase of basicity at a dimetal site has led to the facile preparation of an unprecedented PdRh$_6$ moiety and other planar raftlike clusters. These results may signal a breakthrough in the synthesis of metal clusters.

Inspection of the recently reported[2] compound [Rh$_4$(μ-*p*-MeC$_6$H$_4$N)$_2$(tfb)$_4$] (**1**) (tfb = tetrafluorobenzobarrelene), which possesses a triangular metal core with one nonbonded edge and a fourth metal atom η^5-coordinated to one anionic arene ring (Chart 1), reveals the presence of electron density–available

Chart 1

(1)   (2, 3)   (4)

(7)

(5) Pd(CO)(NCPh)
(6) Hg

for donation–between the metals at the open edge. A positive test for the functionality of this edge is the reaction of the neutral species **1** with AuCl(PPh$_3$) in THF to give the yellow cluster [Rh$_3$(μ-*p*-MeC$_6$H$_4$N)$_2$(tfb)$_3$Au(PPh$_3$)] (**2**) in 61% isolated yield. Moreover, a yellow compound, structurally identical to **2** but containing carbonyl ligands, [Rh$_3$(μ-*p*-MeC$_6$H$_4$N)$_2$(CO)$_6$Au(PPh$_3$)] (**3**), results from a reaction of the neutral planar butterfly cluster[3] [Rh$_4$(μ-*p*-MeC$_6$H$_4$N)$_2$(CO)$_7$(cod)] (cod = 1,5-cyclooctadiene) (**4**) with AuCl(PPh$_3$) in dichloromethane. According to the spectroscopic data, the structures of **2** and **3** are similar to that found for complex **4**, where the "Rh(CO)(cod)" vertex

Figure 1. Structure of [{Rh$_3$(μ-*p*-MeC$_6$H$_4$N)$_2$(CO)$_6$}$_2$Pd(CO)(NCPh)] (**5**). Selected bond distances (Å) and angles (deg): Pd–Rh(2) 2.834-(1), Pd–Rh(3) 2.829(1), Pd–Rh(4) 2.840(1), Pd–Rh(5) 2.803(1), Rh-(1)–Rh(2) 2.862(1), Rh(1)–Rh(3) 2.796(1), Rh(2)–Rh(3) 2.834(1), Rh(4)–Rh(5) 2.818(1), Rh(4)–Rh(6) 2.839(1), Rh(5)–Rh(6) 2.840-(1), Pd–N(5) 2.015(7), Pd–C(100) 1.824(10), C(100)–Pd–N(5) 177.7-(3), C(100)–Pd–Rh(2) 87.5(3), C(100)–Pd–Rh(3) 84.7(3), C(100)–Pd–Rh(4) 86.1(3), C(100)–Pd–Rh(5) 85.3(3).

of **4**, which is unsupported by bridging ligands, has been formally substituted by the "AuPPh$_3$" moiety.

With experimental confirmation of this method of synthesis in hand, it seemed feasible to extend this protocol to allow the flexible construction of higher nuclearity clusters. Thus, reaction of **4** with dihalogenocomplexes such as [PdCl$_2$(NCPh)$_2$] in dichloromethane gives the novel dark green heterometallic cluster [{Rh$_3$(μ-*p*-MeC$_6$H$_4$N)$_2$(CO)$_6$}$_2$Pd(CO)(NCPh)] (**5**). Complex **4** also reacts with HgI$_2$ to give [{Rh$_3$(μ-*p*-MeC$_6$H$_4$N)$_2$(CO)$_6$}$_2$Hg] (**6**), where mercury, a well-known metal glue for metal clusters,[4] links two trirhodium units.

The X-ray structure of **5** (Figure 1) shows a novel unprecedented planar raftlike arrangement of the seven metal atoms, in which two trirhodium units are linked by a palladium atom to form a central heterometallic bowtie, which has its opposite extrema edge-bridged by one rhodium atom each. The central palladium atom links two identical trirhodium cores, each supported by two face-capping tolylimido ligands, through a total of four unbridged Rh–Pd bonds. (The metal–metal separations are within the range appropriate for metal-metal bonds). A carbonyl and a benzonitrile group, *trans* to each other, complete a pseudo-octahedral coordination around the Pd. Within the trirhodium core each Rh is bonded to two nitrogen atoms and two carbonyl groups; however, the rhodium atoms present two distinct geometries, since two of them are bound additionally to the palladium atom.

The formation of **2** from **1** involves the release of the Rh-(diolefin) fragment, originally η^5-bonded to the arene ring, as [RhCl(diolefin)]$_2$. This causes a transfer of the negative charge of the arene ring into the trimetal core, which binds the AuPPh$_3$ fragment to the rhodium atoms at the open edge, forming two new Au–Rh bonds and a Rh–Rh bond. In contrast, the formation of **3** from **4** resembles a formal substitution of the Rh(CO)(cod) fragment by Au(PPh$_3$). These reactions, which involve neutral clusters and complexes, can best be understood by viewing the moiety [Rh$_3$(μ-*p*-MeC$_6$H$_4$N)$_2$(L)$_6$]$^-$, as a synthon that behaves as an anionic ligand with two electronically connected coordination sites, namely the two metal–donor atoms in the trimetal core and the arene ring. We have shown

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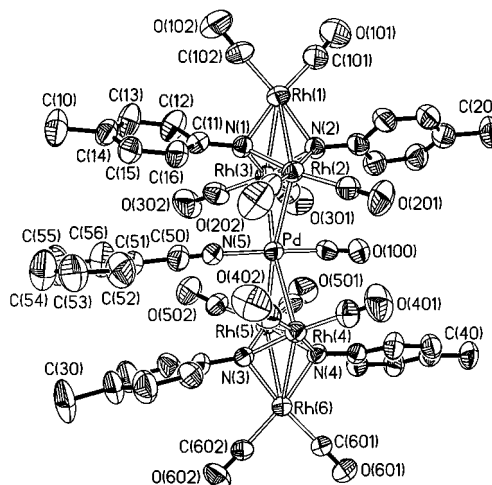
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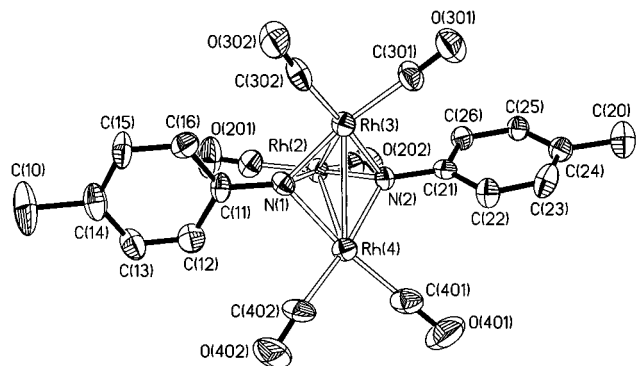**Figure 2.** Structure of the anion $[Rh_3(\mu\text{-}p\text{-MeC}_6H_4N)_2(CO)_6]^-$ in **7**. Selected bond distances (Å): Rh(2)−Rh(3) 2.887(1), Rh(2)−Rh(4) 2.840(2), Rh(3)−Rh(4) 2.898(2), Rh(2)−N(1) 2.076(9), Rh(3)−N(1) 2.055(10), Rh(4)−N(1) 2.080(10), Rh(2)−N(2) 2.052(9), Rh(3)−N(2) 2.056(9), Rh(4)−N(2) 2.036(9)
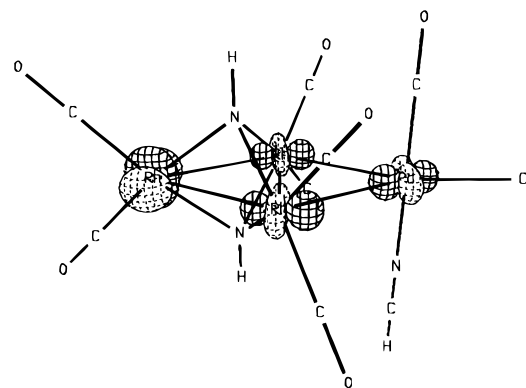
that metal fragments can migrate from one site to the other depending on the reaction conditions in neutral clusters.[3] Seen in this light, the formation of the novel palladium complex **5** from **4** and $[PdCl_2(NCPh)_2]$ represents an unusual "duplication" of the reaction with $AuCl(PPh_3)$, with the formation of two Rh−Rh and four Rh−Pd bonds. Alternatively, the formation of **5** can be viewed as the result of the formal addition of two anionic ligands $[Rh_3(\mu\text{-}p\text{-MeC}_6H_4N)_2(L)_6]^-$ to the palladium-carbonyl fragment $[Pd(CO)(NCPh)]^{2+}$.

However one views its reactivity, the novel anionic complex $[Rh_3(\mu\text{-}p\text{-MeC}_6H_4N)_2(CO)_6]^-$ can be liberated by reaction of **4** with nucleophiles. Thus, the yellow compound [Rh(CO)-(dppm)_2][Rh_3(\mu\text{-}p\text{-MeC}_6H_4N)_2(CO)_6] (**7**) is isolated by the addition of dppm to **4** in CH_2Cl_2.

The X-ray structure of **7** (Figure 2) shows an anion with a trinuclear core of rhodium atoms, doubly capped by two *p*-tolylimido ligands. Meanwhile, the cation is the known[5a] mononuclear rhodium complex $[Rh(CO)(dppm)_2]^+$ contaminated with a further known[5b] complex $[Rh(O_2)(dppm)_2]^+$. The metal−metal separations within the anion, in the range 2.840-(2)−2.898(2) Å, can be considered to be metal−metal bonds. Preliminary EHMO calculations accord with this idea, showing positive overlap population between the three metals. In addition, the trimetal core is an electron-rich zone, which indeed acts as a σ-donor ligand coordinating a further metal through two rhodium atoms. Thus, the bonding scheme of the metallic framework in **5** can be described as the result of the donation of σ-electrons from two trimetal cores to a vacant metal orbital on the palladium center (Figure 3). Since the electron density from the trimetal core is required for coordination to a further metal, the overall stability of the cluster increases. This results in slightly shorter metal−metal separations and also in the shift of $\nu(CO)$ to higher frequencies relative to the anion **7**.

Figure 3. Plot of the main interaction between the fragments $[Rh_3\text{-}(\mu\text{-HN})_2(CO)_6]^-$ and $[PdCl(CO)(NCH)]^+$ as an idealized model for **5**.

No π-interactions are likely to be involved in the bonding between the trirhodium cores and palladium. Indeed, complex **5** is fluxional, showing a low-energy intramolecular process, which can be described as free rotation of the trinuclear cores $[Rh_3(\mu\text{-}p\text{-MeC}_6H_4N)_2(CO)_6]^-$ around the Pd−Rh_2 vectors in accordance with the values of the activation entropy and activation enthalpy.[6]

In conclusion, the use of neutral clusters as precursors for metal−donor ligands is clearly open to exploitation, with the synthesis of complexes **2**−**6** demonstrating the potential of this methodology in the construction of both homo- and heteronuclear metal clusters.

Supporting Information Available: A listing of analytical and spectroscopic data of the new compounds, a plot of the variable temperature ^{1}H NMR data and Eyring equation for **5**, and crystallographic data for complexes **5** and **7** (64 pages). See any current masthead page for ordering and Internet access instructions.

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(6) The ^{1}H NMR spectrum in the low-exchange region corresponds to the structure found in the solid state, i.e., two pairs of equivalent *p*-tolylimido ligands, but in the fast-exchange region, at room temperature, corresponds to a symmetrical molecule having four equivalent *p*-tolylimido ligands. The thermodynamic data for the fluxional process were calculated from the variable temperature ^{1}H NMR spectra using the gNMR 3.6 Program (Budzelaar, P. H. M.; Cherwell Scientific Publ. Ltd.: Oxford OX4 4GA, U.K., 1995) for the two AB systems of the *p*-tolylamido ligands to give $\Delta H^{\ddagger} = 9.24$ kcal·mol^{-1}; $\Delta S^{\ddagger} = -8.4$ eu.