Heteronuclear Rhodium, Palladium, Platinum, and Gold Organoimido Complexes from Dinuclear Organoamido Rhodium Precursors

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Dedicated to Professor José Vicente on the occasion of his 65th birthday

Abstract: Treatment of the organoamido complexes $[Rh_2(\mu\text{-}4\text{-}HNC_6H_4Me)_2(L_2)_2]$ (L_2 = 1,5-cyclooctadiene (cod), L = CO) with *n*BuLi gave solutions of the organoimido species $[Li_2Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2(L_2)_2]$. Further reaction of $[Li_2Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2(cod)_2]$ with $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ afforded the neutral tetranuclear complex $[Rh_4(\mu\text{-}4\text{-}NC_6H_4Me)_2(cod)_4]$ (**2**), which rationalizes the direct syntheses of **2** from $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ and $Li_2NC_6H_4Me$. Reactions of $[Li_2Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2(CO)_4]$ with chloro complexes such as $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$, $[MCl_2(cod)]$ (M = Pd, Pt), and $[Ru_2(\mu\text{-}Cl)_2Cl_2(p\text{-}cymene)_2]$ afforded the homo- and heterotrinuclear complexes $PPN[Rh_3(\mu\text{-}4\text{-}NC_6H_4Me)_2(CO)_6]$ (**5**; PPN = bis(triphenylphosphine)iminium), $[(CO)_4Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2M(cod)]$ (M = Pd (**6**), Pt(**7**)) and $[(CO)_4Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2Ru(p\text{-}cymene)]$ (**8**), while the reaction with $[AuCl(PPh_3)]$ gave the tetranuclear compound $[(CO)_4Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2\{Au(PPh_3)\}_2]$ (**9**). The structures of complexes **6**, **8**, and **9** were determined by X-ray diffraction studies. The anion of **5** reacts with $[AuCl(PPh_3)]$ to give the butterfly cluster $[\{Rh_3(\mu\text{-}4\text{-}NC_6H_4Me)_2(CO)_6\}Au(PPh_3)]$ (**10**), in which the Au atom is bonded to two rhodium atoms. Reaction of the anion of **5** with $[Rh(cod)(NCMe)_2](BF_4)$ gave the tetranuclear complex $[Rh_4(\mu\text{-}4\text{-}NC_6H_4Me)_2(CO)_6(cod)]$ (**11**) in which the Rh(cod) fragment is π-bonded to one of the arene rings, while the reaction of the anion of **5** with $[PdCl_2(cod)]$ afforded the heterotrinuclear complex **6** through a metal exchange process.

Keywords: gold · organoimido complexes · palladium · platinum · rhodium

Introduction

Transition-metal organoimido (nitrene, RN^{2-}) chemistry has experienced a remarkable growth in recent years, with these hard nitrogen donor ligands exhibiting diverse reactivities.[1] Terminal organoimido ligands are far more prevalent in complexes of high-valent, early and mid transition metals than in complexes of late transition elements.[2] Metal organoimido complexes have been used as catalysts for the metathesis of olefins[3] and imines,[4] and in C–H activation reactions.[5] In contrast, transition-metal organoimido complexes of the late transition metals are rare. For some time, the d^6 iridium,[6] ruthenium,[7] and osmium[8] organoimido complexes $[Cp^*Ir{\equiv}NR)]$ and $[(arene)M{\equiv}NR]$ (M = Ru, Os; R = alkyl, aryl) stood as the only examples of terminal organoimido complexes with d-electron counts greater than four, until the recent report of the d^8 nickel[9] and cobalt[10] compounds $[(dtbpe)Ni{=}NR]$ and $[(PhBP_3)Co{=}NR]$(R = aryl, dtbpe = $(tBu_2P)_2C_2H_4$, $PhBP_3$ = $[PhB(CH_2PPh_2)_3]^-$). This scarcity has been attributed to a π-electron conflict between filled metal dπ orbitals and lone electron pairs residing on the π-donating ligands, which increases the reactivity of the metal–N moieties.[11] Low-valent late transition metal organoimido complexes with electron counts greater than six, although unusual, are represented by the dinuclear complexes $[Rh_2(\mu\text{-}NR)(\mu\text{-}dppm)_2(CO)_2]$,[12] some ruthenium and osmium clusters,[13] the sole neutral palladium(II) complex $[Pd_3(\mu\text{-}NR)_2(\mu\text{-}NHR)(PEt_3)_3]Cl$,[14] and the tetranuclear rhodium(I) compounds $[Rh_4(\mu\text{-}NR)_2(diolefin)_4]$.[15] In these complexes the π-electron conflict is overcome by coordination of the hard nitrogen donor to several metal atoms. In fact, the noticeable stability of the Rh–N bonds in the tetranuclear complexes provides new reactivity patterns, which

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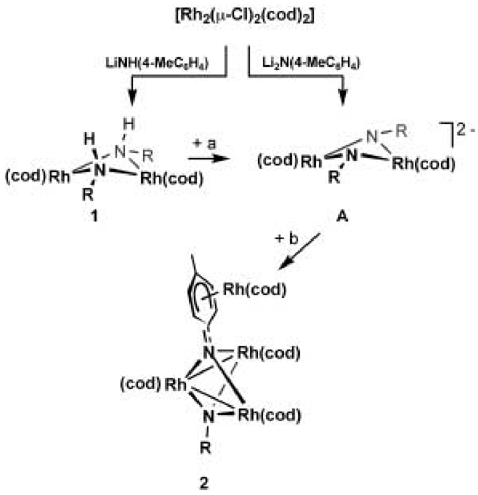
allow unusual transformations.[16] Furthermore, organoimido-bridged heterometallic complexes are almost unknown. The only examples include the reactive early-late complex $[Cp_2Zr(\mu\text{-}tBuN)IrCp^*]$[17] and related compounds.[18]

In the search of new types of heterometallic imido compounds of the platinum metals group, we report here the use of a general synthetic strategy for the formation of triangular heterometallic organoimido compounds starting from dinuclear organoamido rhodium complexes.[19] This approach has allowed the preparation of new organoimido complexes of the late transition metals in a low oxidation state, as well as providing a rationalization of the chemical pathway leading to previously reported tetranuclear rhodium organoimido complexes.

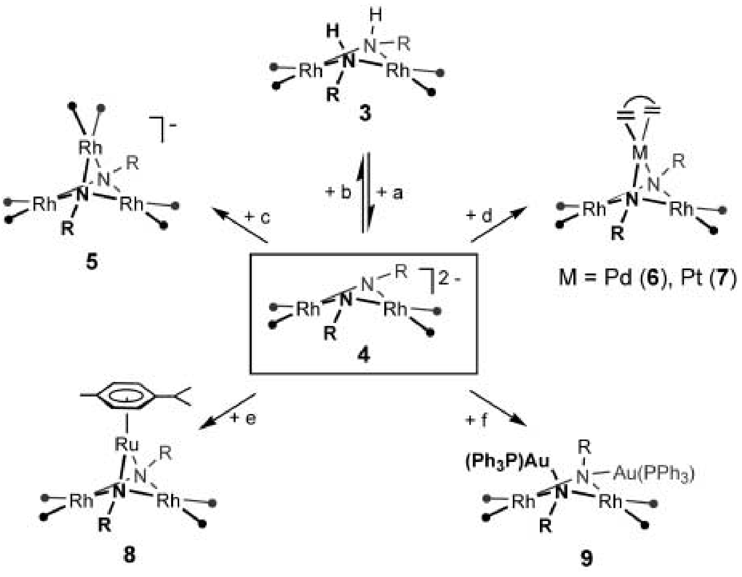
Results and Discussion

A typical approach to the synthesis of organoimido complexes of late transition metals such as ruthenium(II), osmium(II), and iridium(III) involves the reaction of a dichloro metal complex with an alkali amide (LiNHR) in a 1:2 molar ratio. Although this methodology seems more appropriate for the preparation of bis(organoamido) complexes, these undergo an internal acid–base disproportionation to give organoimido compounds and free amine. This disproportionation described for d^6 metal compounds is not observed for diolefin rhodium(I) complexes, allowing the preparation of organoamido rhodium(I) compounds. Thus, the reaction of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ with $LiNH(4\text{-}MeC_6H_4)$ in a 1:2 molar ratio gives the dinuclear[19] organoamido complex $[Rh_2(\mu\text{-}4\text{-}HNC_6H_4Me)_2(cod)_2]$ (**1**) (Scheme 1), which does not progress further to an organoimido complex and free amine, even on prolonged heating and with excess lithium amide. Nevertheless, the deprotonation of complex **1** could produce anionic organoimido compounds, as recently reported for some organoamido platinum, palladium, and iridium complexes with d^8 electron counts, derived from primary amines.[20] Thus, the treatment of **1** with *n*BuLi gave air- and thermally sensitive dark red solutions at low temperature. These solutions contain the organoimido species $[Li_2Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2(cod)_2]$ (**A**, Scheme 1), whose presence is confirmed by treatment with $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (Scheme 1) to afford the neutral organoimido tetranuclear compound $[Rh_4(\mu\text{-}4\text{-}NC_6H_4Me)_2(cod)_4]$ (**2**) in moderate yield. Complex **2** was straightforwardly prepared by the one-pot reaction of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ with $Li_2N(4\text{-}MeC_6H_4Me)$ in a 1:1 molar ratio (Scheme 1). The previously communicated[15] X-ray molecular structure of complex **2** shows two *p*-tolyl imido ligands capping either side of a trirhodium triangle through the nitrogen atoms, while the phenyl ring of one of these ligands coordinates an isolated Rh(cod) fragment in a η^5 fashion.



Scheme 1. Formation of organoamido and organoimido rhodium compounds. a) *n*BuLi; b) $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$.

The above described stepwise synthesis of **2** rationalizes the one-pot preparation of tetranuclear organoimido rhodium compounds,[15] which involves the intermediacy of deprotonated amido compounds such as **A** (Scheme 1), their reaction with the rhodium choro complex to incorporate one Rh(cod) fragment into the trimetallic core, and the binding of a second Rh(cod) fragment to the arene ring. Moreover, this explanation of the preparative approach strongly suggests that dinuclear organoamido complexes of rhodium(I) could be appropriate precursors for the synthesis of homometallic and heterometallic organoimido complexes of the late transition metals in low oxidation states. To extend this protocol to other metals, $[Rh_2(\mu\text{-}4\text{-}HNC_6H_4Me)_2(cod)_2]$ could be a candidate, but the analogous complex with π-acid carbonyl ligands would provide a more stable deprotonated amido species because of the decreased basicity of the rhodium centers. Indeed, thermally stable dark red solutions containing $[Li_2Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2(CO)_4]$ (**4**) were prepared by reacting the tetracarbonyl compound $[Rh_2(\mu\text{-}4\text{-}HNC_6H_4Me)_2(CO)_4]$ (**3**) with *n*BuLi in diethyl ether at low temperature (Scheme 2). Indirect evidence for the existence



Scheme 2. Homo- and heteronuclear complexes derived from $[Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2(CO)_4]^{2-}$. a) *n*BuLi; b) H_2O; c) $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$; d) $[MCl_2(cod)]$; e) $[Ru_2(\mu\text{-}Cl)_2Cl_2(p\text{-}cymene)_2]$; f) $[AuCl(PPh_3)]$. Carbonyl ligands are denoted by ●.

of such species was obtained from the addition of a stoichiometric amount of water to the dark red solutions, which regenerated the yellow starting material **3** almost immediately. Moreover, the high solubility of this species in diethyl ether seems to indicate the coordination of the lithium ions to the nitrogen atoms, as suggested for the related $[Li_2Ir_2(\mu\text{-}4\text{-}NC_6H_4Me)_2(CO)_4]$ compound.[20b] The ionic trinuclear compound $PPN[Rh_3(\mu\text{-}4\text{-}NC_6H_4Me)_2(CO)_6]$ (**5**) was isolated by successive additions of 0.5 molar equivalents of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ to **4**, and the salt of a bulky cation such as PPNCl (Scheme 2). The formation of **5** involves the bonding of the $Rh(CO)_2$ moiety to **4** through both nitrogen atoms to give the trimetallic core $Rh_3(\mu\text{-}4\text{-}NC_6H_4Me)_2$. Complex **5** was characterized by elemental analyses and spectroscopic data (see Experimental Section).

With experimental evidence for the presence of $[Li_2Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2(CO)_4]$ in the dark red solutions coming from the deprotonation of **3** and confirmation of its behavior as a good synthon for polynuclear compounds, our attention was focused on the preparation of heterometallic organoimido complexes. Thus, addition of one molar equivalent of $[MCl_2(cod)]$ (M = Pd, Pt) to solutions of **4** afforded the neutral trinuclear complexes $[(CO)_4Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2M(cod)]$ (M = Pd (**6**), Pt (**7**)) (Scheme 2). The new compounds **6** and **7** were isolated as red (**6**) and green (**7**) crystalline solids in good yields, and were characterized by analytical and spectroscopic methods as well as by a X-ray diffraction study on complex **6**. An ORTEP view of the molecular structure of **6** is shown in Figure 1, and selected bond lengths and angles are given in Table 1. Complex **6** has an imposed crystallographic C_2 symmetry, with the twofold axis passing through the Pd atom and the midpoint of the Rh1···Rh1′ line. In the open triangular Rh_2Pd core the Pd1···Rh1 and Rh1···Rh1′ separations are 2.885(1) and 2.836(1) Å, respectively. The triangle is capped on both sides by two *p*-tolylimido ligands, bound through the N atoms, the Rh1–N1, Rh1′–N1, and Pd1–N1 bond lengths being 2.077(7), 2.075(7,) and 2.055(7) Å, respectively. The carbon atoms of the two terminal carbonyl ligands complete a slightly distorted square plane around each Rh atom, indicating that metal–metal interactions are weak, even if the metal–metal separations are rather short. The cyclooctadiene molecule is coordinated to the Pd atom in the usual manner through the two double bonds. Taking into account the midpoints of the two double bonds, the coordination around the Pd atom is square planar as well.

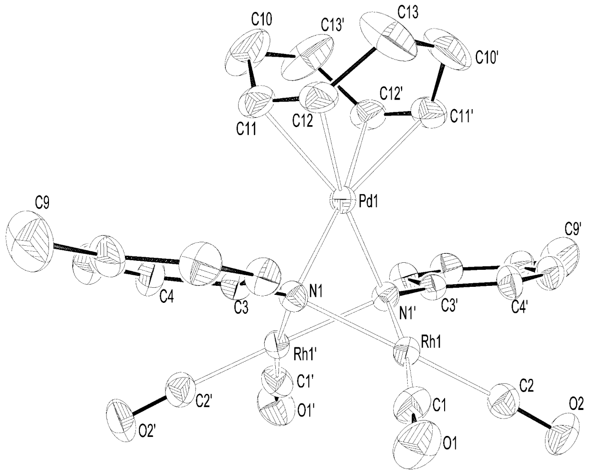


Figure 1. Structure of **6** (thermal ellipsoids are drawn at 30% probability level).

Table 1. Selected bond lengths [Å] and angles [°] of complex **6**.[a]

Pd1···Rh1′	2.885(1)	Rh1–C1	1.847(12)
Pd1···Rh1	2.885(1)	Rh1–C2	1.854(11)
Rh1···Rh1′	2.8361(15)	Rh1–N1	2.077(7)
Pd1–N1′	2.055(7)	Rh1–N1′	2.075(7)
Pd1–N1	2.055(7)	N1–C3	1.402(11)
Pd1–M1	2.144(5)	N1–Rh1′	2.075(7)
N1-Pd1-M1	100.2(3)	N1-Rh1-N1′	73.3(3)
N1-Pd1-M1′	174.3(3)	C3-N1-Pd1	120.2(6)
M1-Pd1-M1′	85.4(3)	C3-N1-Rh1	130.1(6)
N1′-Pd1-N1	74.2(4)	Pd1-N1-Rh1	88.6(3)
C1-Rh1-C2	87.8(5)	C3-N1-Rh1′	130.0(6)
C1-Rh1-N1	99.3(4)	Pd1-N1-Rh1′	88.6(3)
C2-Rh1-N1′	99.5(4)	Rh1-N1-Rh1′	86.2(3)

[a] M1 is the midpoint of the C11–C12 bond. Symmetry transformation used to generate equivalent atoms: $-x+1, y, -z+1/2$.

Complexes **6** and **7** were found to be single species in solution, and their structures corresponded to that described for **6** in the solid state. Thus, they show three ν(CO) bands in the IR spectra (see Experimental Section). These absorptions were found to be shifted to lower frequencies by about $25\,cm^{-1}$ relative to $[Rh_2(\mu\text{-}4\text{-}HNC_6H_4Me)_2(CO)_4]$ (**3**), suggesting an enhancement of the backbonding to the CO ligands owing to the incorporation of the M(cod) moiety into the core. In accordance with the C_{2v} symmetry of the complexes the *p*-tolyl rings were found to be equivalent and the ^1H NMR spectra of both complexes showed one signal each for the olefinic, methylenic *endo*, and methylenic *exo* cod protons. Coordination of cod to platinum was clearly detectable by the platinum satellites ($^3J(H,Pt) = 58.2$ Hz) of the signal for the olefinic protons in complex **7**.

The related compound $[(CO)_4Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2Ru(p\text{-cymene})]$ (**8**) (Scheme 2) was prepared by adding $[Ru_2(\mu\text{-}Cl)_2Cl_2(p\text{-cymene})_2]$ to **4** at low temperature. Complex **8** was obtained as a red crystalline solid, and an X-ray diffraction study confirmed the formation of the heterometallic $Rh_2Ru(\mu\text{-}4\text{-}NC_6H_4Me)_2$ core, even if the poor quality of the crystals prevented us from obtaining accurate structural parameters. This structure is also maintained in solution according to the NMR and IR data (see Experimental Section). An ORTEP view of the molecular structure of **8** is shown in Figure 2, and selected bond lengths and angles are given in Table 2. The structure of **8** is strictly comparable to that of complex **6**, if the Pd(cod) fragment is replaced by Ru(arene). In the open triangular Rh_2Ru core, the Ru1···Rh1, Ru1···Rh2, and Rh1···Rh2 separations are short (2.853(3), 2.869(4), and 2.802(7) Å, respectively). Two *p*-tolylimido ligands cap the metal triangular core, bonded through the N atoms. Two terminal carbonyl groups bonded to each Rh atom complete a slightly distorted square planar coordination, while the *p*-cymene molecule is coordinated to the Ru1 atom in a η^6 fashion.

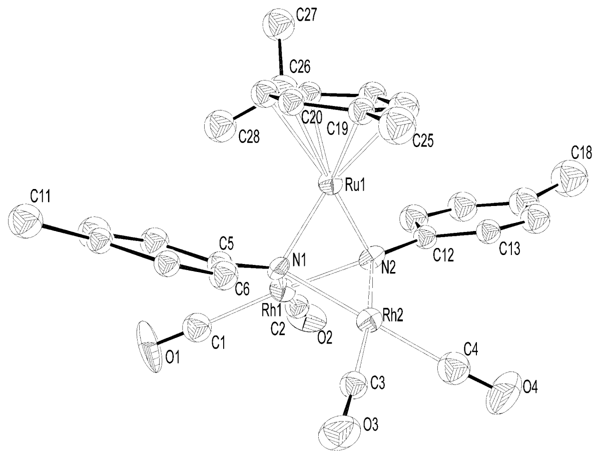


Figure 2. Strcture of **8** (thermal ellipsoids are drawn at 30% probability level).

Table 2. Selected bond lengths [Å] and angles [°] of complex **8**.[a]

Ru1···Rh1	2.853(3)	Rh2–C4	1.92(4)
Ru1···Rh2	2.869(4)	Rh2–N2	1.98(2)
Rh2···Rh1	2.802(4)	Rh2–N1	2.05(2)
Ru1–CE	1.66(6)	Rh1–C2	1.83(3)
Ru1–N2	1.99(2)	Rh1–C1	1.98(4)
Ru1–N1	2.03(3)	Rh1–N2	2.04(2)
Rh2–C3	1.83(4)	Rh1–N1	2.12(3)
N1-Ru1-CE	140.76	C5-N1-Ru1	119.2(16)
N2-Ru1-CE	145.76	Rh2-N1-Ru1	89.5(9)
N2-Ru1-N1	73.5(9)	C5-N1-Rh1	128.8(16)
C3-Rh2-C4	81.4(16)	Rh2-N1-Rh1	84.6(9)
C4-Rh2-N2	104.6(14)	Ru1-N1-Rh1	87.0(10)
C3-Rh2-N1	100.8(13)	C12-N2-Ru1	113.2(16)
N2-Rh2-N1	73.1(10)	C12-N2-Rh2	132.2(16)
C2-Rh1-C1	89.4(14)	Ru1-N2-Rh2	92.6(9)
C2-Rh1-N2	102.0(12)	C12-N2-Rh1	128.9(15)
C1-Rh1-N1	97.8(12)	Ru1-N2-Rh1	90.1(9)
N2-Rh1-N1	70.5(9)	Rh2-N2-Rh1	88.1(9)
C5-N1-Rh2	133.7(18)		

[a] CE is the centroid of the C19–C24 ring

Reaction of **4** with two molar equivalents of $[AuCl(PPh_3)]$ gave the heterotetranuclear rhodium/gold imido-bridged complex $[(CO)_4Rh_2(\mu\text{-}4\text{-}NC_6H_4Me)_2\{Au(PPh_3)\}_2]$ (**9**). Complex **9** was isolated as an orange crystalline solid that was found to be thermally unstable in solution. Solutions of **9** in [D$_6$]benzene decompose to a mixture of unidentified compounds with a half-life of 2 h at room temperature under an argon atmosphere. The incorporation of two gold atoms to **4** was evident from the 1:1 molar ratio between the signals of the equivalent *p*-tolyl rings and the multiplet corresponding to the PPh_3 ligands in the ^1H NMR spectrum. Moreover, an interaction between the rhodium and phosphorus nuclei was detected because of the coupling of the phosphorus with two equivalent rhodium nuclei to give a triplet ($^2J(P,Rh) = 1.3$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum. The presence of only two strong ν(CO) bands (2031, 1969 cm^{-1}) in the IR spectrum of **9** indicated that the species has a different symmetry from that shown by complexes **6**–**8**. Complex **9** has been fully characterized as a tetranuclear complex by an X-ray study. An ORTEP view of the structure of **9** is shown in Figure 3, and selected bond lengths and angles are given in Table 3. Complex **9** has an imposed crystallographic C_i symmetry so that the Au_2Rh_2 metal core has a perfectly planar raftlike structure with the two open Rh_2Au triangles sharing a common Rh–Rh′ side. The Rh1···Rh1′, Rh1···Au1, and Rh1···Au1′ separations are 3.198(2), 3.115(2), and 3.110(2) Å, respectively. The two Rh_2Au triangles are capped on opposite sides by an N atom from the *p*-tolylimido ligand with Rh1–N1, Rh1′–N1, and Au1–N1 bond lengths of 2.058(8), 2.103(8), and 2.072(8) Å respectively. Two carbonyl groups are bonded to each Rh atom, while a triphenylphosphane ligand is coordinated to the Au atom. The coordination around each Rh atom, involving the two carbon atoms of the carbonyl groups and the two N atoms of the *p*-tolylimido ligands, is nearly square planar. The Au atom is nearly linearly bonded to the P atom of the PPh_3 ligand (N1–Au1–P1 174.2(3)°), indicating that metal–metal interactions are weak, even if the metal–metal separations are rather short. It is notable that the $Au(PPh_3)$ fragments are located at the *anti* positions of the four-membered

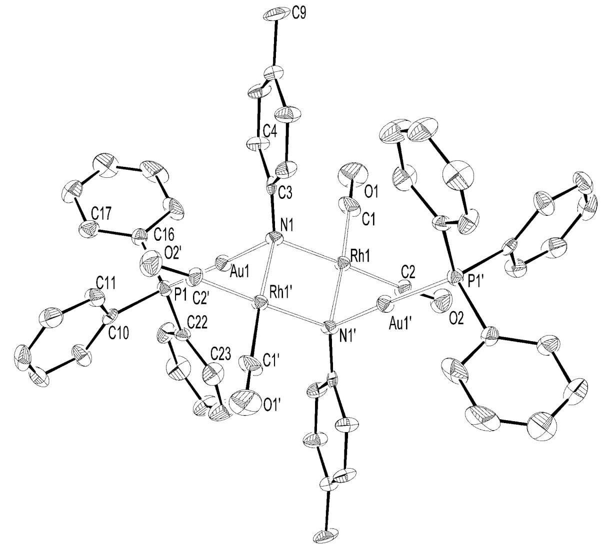


Figure 3. Structure of **9** (thermal ellipsoids are drawn at 30% probability level).

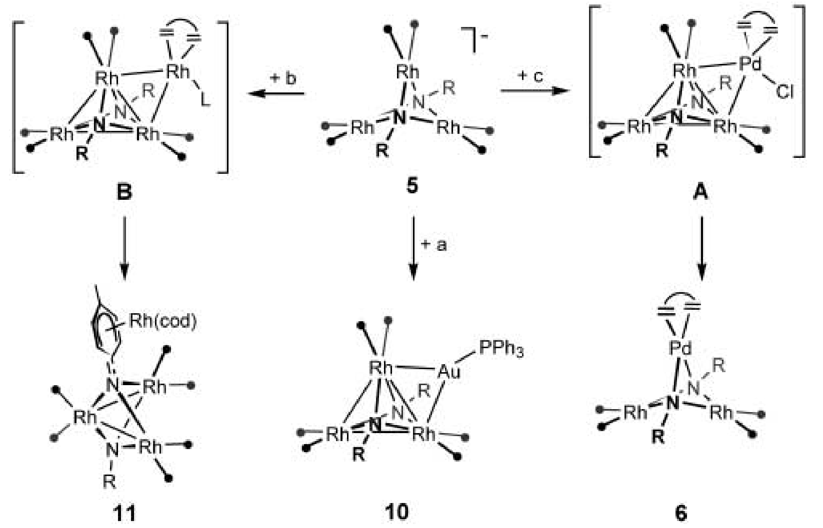
Table 3. Selected bond lengths [Å] and angles [°] of complex **9**.[a]

Rh1···Au1′	3.1102(16)	Rh1–N1′	2.103(8)
Rh1···Au1	3.1151(17)	Au1–N1	2.072(8)
Rh1···Rh1′	3.198(2)	Au1–P1	2.245(3)
Rh1–C2	1.839(12)	N1–C3	1.392(12)
Rh1–C1	1.856(13)	N1–Rh1′	2.103(8)
Rh1–N1	2.058(8)		
C2-Rh1-C1	87.9(5)	C3-N1-Au1	118.2(7)
C1-Rh1-N1	95.8(5)	Rh1-N1-Au1	97.9(3)
C2-Rh1-N1′	96.7(4)	C3-N1-Rh1′	120.9(7)
N1-Rh1-N1′	79.6(4)	Rh1-N1-Rh1′	100.4(4)
N1-Au1-P1	174.2(3)	Au1-N1-Rh1′	96.3(3)
C3-N1-Rh1	118.4(6)		

[a] Symmetry transformation used to generate equivalent atoms: $-x+1$, $-y$, $-z$.

Rh_2N_2 metallacycle, whereas complexes **5**–**8** could be considered as derived from the *syn* configuration.

We have also investigated the reactions of the ionic compound PPN[$Rh_3(\mu\text{-}4\text{-}NC_6H_4Me)_2(CO)_6$] (**5**) with electrophilic metal complexes, which gave distinct results depending on the nature of metal complex added. Thus, the reaction of **5** with [AuCl(PPh_3)] gave the complex [{$Rh_3(\mu\text{-}4\text{-}NC_6H_4Me)_2(CO)_6$}Au($PPh_3$)] (**10**) (Scheme 3), in which the Au(PPh_3) fragment was found to be bonded to two rhodium atoms, forming a planar butterfly heterometallic cluster. This bonding scheme, with the Au atom acting as a wing of the butterfly, was supported by the observation of a large coupling between the phosphorus and two equivalent rhodium nuclei (^2J(P,Rh) = 17 Hz) and a small coupling (^3J(P,Rh) = 5 Hz) with the third ^{103}Rh active nucleus to give a triplet of doublets in the ^{31}P{^{1}H} NMR spectrum of **10**. Moreover, the two equivalent rhodium atoms involved in the bonding with the gold atom were detected at $\delta = -125$ ppm, while the third rhodium atom resonated at $\delta = 50$ ppm in the ^{31}P,^{103}Rh{^{1}H} hetcorr spectrum.



Scheme 3. Some reactions of the anion [$Rh_3(\mu\text{-}4\text{-}NC_6H_4Me)_2(CO)_6$]$^-$ with chlorocomplexes. a) [AuCl(PPh_3)]; b) [Rh(cod)(NCMe)$_2$](BF$_4$); c) [PdCl$_2$(cod)]. Carbonyl ligands are denoted by ●.

The formation of **10** from **5** can be rationalized by assuming that a Rh–Rh edge in the anion **5** is able to engage a new metal fragment through two unsupported metal–metal bonds. Alternatively, the Rh–Rh edge can be considered as an anionic two-electron donor ligand that binds the gold atom.

Quite surprisingly, the reaction of **5** with [PdCl$_2$(cod)] gave the above described complex [(CO)$_4$Rh$_2$(μ-4-NC$_6$H$_4$Me)$_2$Pd(cod)] (**6**), while the addition of [Rh(cod)(NCMe)$_2$](BF$_4$) to **5** afforded the tetranuclear complex [Rh$_4$(μ-4-NC$_6$H$_4$Me)$_2$(CO)$_6$(cod)] (**11**) (Scheme 3). Although no intermediates were detected in these reactions, the rationalization of the bonding in the gold compound **10** suggests these reactions start by the coordination of the metals to the active rhodium–rhodium edge in **5** to give the intermediates **A** and **B** (Scheme 3). At this stage, these species transform following different pathways. The heteronuclear palladium complex (**A**) undergoes a metal exchange of the Rh(CO)$_2$ moiety, which is extruded as [Rh$_2$(μ-Cl)$_2$(CO)$_4$], by Pd(cod), which is incorporated into the trinuclear core (Scheme 3). Most probably, the transfer of the chloride ligand from the Pd to the Rh atom in the intermediate **A** initiates the metal exchange process, with coordination of the Pd center to the nitrogen atoms. It is interesting to note the preference of the imido ligand for the Pd(cod) moiety over the Rh(CO)$_2$ fragment. In contrast, the formation of **11** from the proposed species **B** (Scheme 3) is accomplished by the migration of the electron-poor fragment Rh(cod) from the active edge to the arene ring without changes in the trinuclear core.

Conclusion

Homo- and hetero-nuclear organoimido complexes of late transition metals in low oxidation states are accessible from appropriate organoamido rhodium(I) compounds. The new complexes reported here were found to be reasonably stable in spite of the unfavorable predictions about the stability of this type of complex. In our case, the possible π-conflict between filled metal dπ orbitals and lone electron pairs residing on the organoimido ligand[11] was avoided by removing the cause, that is, by using all the electrons of the organoimido moiety for coordination to three metal atoms. This decreases the reactivity of the nitrogen moiety,[2b] which remains as a triply bridging ligand. Moreover, we have found an unpredictable preference of the imido ligand for the Pd(cod) moiety over the Rh(CO)$_2$ fragment in metal exchange reactions. The engagement of Pt(cod) and Pd(cod) moieties in bonding with the organoimido ligand in the heterometallic complexes suggests that unknown imido complexes of these metals could be stable and possible to isolate.

Experimental Section

Starting materials and physical methods: All reactions were carried out under argon using standard Schlenk techniques. The complexes [Rh$_2$(μ-4-HNC$_6$H$_4$Me)$_2$(cod)$_2$][19] [PdCl$_2$(cod)],[21] [PtCl$_2$(cod)],[21] and [AuCl(PPh$_3$)][22] were prepared according to literature methods. Solvents were dried and distilled under argon before use by standard methods. Carbon, hydrogen, and nitrogen analyses were performed by using a Perkin–Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet 550 spectrophotometer. Mass spectra were recorded with a VG Autospec double-focusing mass spectrometer operating in the FAB$^+$ mode. Ions were produced with the standard Cs$^+$ gun at about 30 KV, 3-nitrobenzyl alcohol (NBA) was used as matrix. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker ARX 300 and on a Varian UNITY 300 spectrometers operating at 300.13 and 299.95 MHz for ^{1}H, respectively. Chemical shifts are reported in parts per million relative to $SiMe_4$, using the signal of the deuterated solvent as reference and H_3PO_4 as external reference (for ^{31}P).

[Rh$_2$(μ-4-HNC$_6$H$_4$Me)$_2$(CO)$_4$] (3): Carbon monoxide was slowly bubbled through a suspension of [Rh$_2$(μ-4-HNC$_6$H$_4$Me)$_2$(cod)$_2$] (**1**) (635.0 mg, 1.00 mmol) in diethyl ether (20 mL) to give a yellow solution in about 30 min. The solution was concentrated to a volume of about 3 mL. Hexane (10 mL) was added and the CO bubbling was continued for a further 30 min. The resulting solution was left under a carbon monoxide atmosphere in a freezer at −30 °C for two days to render yellow crystals of **3**. The solid was separated by filtration, washed with cold pentane, and dried under vacuum (yield: 371.1 mg; 70 %). ^{1}H NMR ([D$_6$]benzene, 25 °C): $\delta = 7.05$ (δ_{A}, 4H), 6.85 (δ_{B}, J(A,B) = 8.4 Hz, 4H; *p*-MeC$_6$*H*$_4$), 2.07 (s, 6H; *p*-*Me*C$_6$H$_4$), 1.73 ppm (s, 2H; NH); ^{13}C{^{1}H} NMR ([D$_6$]benzene, 25 °C): $\delta = 185.1$ (d, ^{1}J(C,Rh) = 69 Hz; CO), 157.5 (C^{i}), 131.5(C^{p}), 129.2 (C^{m}), and 120.4 (C^{o}) (*p*-Me*C*$_6$H$_4$), 20.4 ppm (*p*-*Me*C$_6$H$_4$); IR (diethyl ether): $\tilde{\nu} = 2077$ (s), 2058 (s), 2004 cm^{-1} (s) (CO); MS: *m*/*z* (%): 530 (35) [*M*]$^{+}$, 474 (100) [*M*−2CO]$^{+}$; elemental analysis calcd (%) for $C_{18}H_{16}N_2O_4Rh_2$ (530.1): C 40.78, H 3.04, N 5.28; found: C 40.75, H 2.94, N 5.21.

PPN[Rh$_3$(μ-4-NC$_6$H$_4$Me)$_2$(CO)$_6$] (5): The addition of *n*BuLi (200.0 μL; 1.6 M, 0.32 mmol) to a yellow solution of [Rh$_2$(μ-4-HNC$_6$H$_4$Me)$_2$(CO)$_4$] (**3**) (84.8 mg, 0.16 mmol) in diethyl ether (8 mL) at −78 °C immediately produced a dark red solution. After stirring for 15 min, solid [Rh$_2$(μ-Cl)$_2$(CO)$_4$] (31.1 mg; 0.08 mmol) was added and the reaction mixture was allowed to reach room temperature for 1 h. The solution was evaporated to dryness and the residue was dissolved in dichloromethane (10 mL) and treated with solid PPNCl (92.0 mg, 0.16 mmol). The resulting suspension was filtered over kieselgühr and the filtrate was concentrated to about 3 mL and layered with diethyl ether (15 mL) to render yellow microcrystals in two days. The mother liquor was decanted and the crystals were dried under vacuum (yield: 147.1 mg; 75 %). ^{1}H NMR (CDCl$_3$, 25 °C): $\delta = 7.59$ (m, 6H; PPN), 7.39 (m, 28H; PPN + δ_{A}), 6.72 (δ_{B}, J(A,B) = 7.8 Hz, 4H; *p*-MeC$_6$*H*$_4$), 2.14 ppm (s, 6H; *p*-*Me*C$_6$H$_4$); ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): $\delta = 190.5$ (d, ^{1}J(C,Rh) = 68 Hz; CO), 167.6 (C^{i}), 129.4 (C^{p}), 127.3 (C^{m}), and 123.3 (C^{o}) (*p*-Me*C*$_6$H$_4$), 134.0 (C^{p}), 132.0 (d, ^{3}J(C,P) = 11 Hz; C^{m}), 129.5 (d, ^{2}J(C,P) = 28 Hz; C^{o}), and 126.8 (d, ^{1}J(C,P) = 110 Hz; C^{i}) (PPN), 20.3 ppm (*p*-*Me*C$_6$H$_4$); IR (dichloromethane): $\tilde{\nu} = 2015$ (s), 1960 cm^{-1} (s) (CO); MS: *m*/*z* (%): 687 (100) [*M*]$^{-}$, 659 (55) [*M*−CO]$^{-}$; elemental analysis calcd (%) for $C_{56}H_{44}N_3O_6P_2Rh_3$ (1225.6): C 54.88, H 3.62, N 3.43; found: C 55.12, H 3.71, N 3.28.

[(CO)$_4$Rh$_2$(μ-4-NC$_6$H$_4$Me)$_2$Pd(cod)] (6): Solid [PdCl$_2$(cod)] (42.8 mg, 0.15 mmol) was added to a solution of [Li$_2$Rh$_2$(μ-4-NC$_6$H$_4$Me)$_2$(CO)$_4$] in diethyl ether, prepared as described for **5** starting from **3** (80.6 mg, 0.15 mmol), and *n*BuLi (187.4 μL; 1.6 M, 0.30 mmol) at −78 °C. The resulting suspension was stirred for 2 h at low temperature and then for 12 h more at room temperature to give a red suspension. This was evaporated to dryness to give a red microcrystalline solid, which was washed with methanol (2×10 mL at −80 °C), and pentane (5 mL), and dried under vacuum (yield: 85.8 mg; 71 %). Crystals suitable for X-ray diffraction studies were obtained from the slow diffusion of hexane into a dichloromethane solution of **6**. ^{1}H NMR (CDCl$_3$, 25 °C): $\delta = 7.22$ (δ_{A}, 4H), 6.92 (δ_{B}, J(A,B) = 8.1 Hz, 4H; *p*-MeC$_6$*H*$_4$), 4.33 (s, 4H; =CH), 2.60 (m, 4H; CH$_2^{exo}$), 2.25 (m, 4H; CH$_2^{endo}$), 2.19 ppm (s, 6H; *p*-*Me*C$_6$H$_4$); ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): $\delta = 189.3$ (d, ^{1}J(C,Rh) = 68 Hz; CO), 159.6 (C^{i}), 133.4 (C^{p}), 128.7 (C^{m}), and 125.6 (C^{o}) (*p*-Me*C*$_6$H$_4$), 111.9 (=CH), 29.1 (CH$_2$), 20.5 ppm (*p*-*Me*C$_6$H$_4$); IR (dichloromethane): $\tilde{\nu} = 2050$ (s), 2031 (s), 1977 cm^{-1} (s) (CO); elemental analysis calcd (%) for $C_{26}H_{26}N_2O_4Rh_2Pd$ (742.7): C 42.04, H 3.53, N 3.77; found: C 41.60, H 3.71, N 3.60.

[(CO)$_4$Rh$_2$(μ-4-NC$_6$H$_4$Me)$_2$Pt(cod)] (7): Compound **7** was prepared and isolated as described for **6** starting from **3** (80.6 mg, 0.15 mmol), *n*BuLi (187.4 μL; 1.6 M, 0.30 mmol), and [PtCl$_2$(cod)] (56.2 mg, 0.15 mmol) to give green microcrystals of **7**. Yield: 87.8 mg (70 %). ^{1}H NMR (CDCl$_3$, 25 °C): $\delta = 7.04$ (δ_{A}, 4H), 6.94 (δ_{B}, J(A,B) = 7.5 Hz, 4H; *p*-MeC$_6$*H*$_4$), 3.99 (m, ^{3}J(H,Pt) = 58.2 Hz, 4H; =CH), 2.51 (m, 4H; CH$_2^{exo}$), 2.28 (s, 6H; *p*-*Me*C$_6$H$_4$), 2.16 ppm (m, 4H; CH$_2^{endo}$); ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): $\delta = 188.6$ (d, ^{1}J(C,Rh) = 70 Hz; CO), 157.3 (C^{i}), 133.3 (C^{p}), 128.3 (C^{m}), and 125.3 (t, ^{3}J(C,Rh) = 1.5 Hz; C^{o}) (*p*-MeC$_6$H$_4$), 92.2 (=CH), 29.9 (CH$_2$), 20.3 ppm (*p*-*Me*C$_6$H$_4$); IR (dichloromethane): $\tilde{\nu} = 2052$ (s), 2033 (s), 1981 cm^{-1} (s) (CO); elemental analysis calcd (%) for $C_{26}H_{26}N_2O_4Rh_2Pt$ (831.4): C 37.56, H 3.15, N 3.37; found: C 36.93, H 3.61, N 3.12.

[(CO)$_4$Rh$_2$(μ-4-NC$_6$H$_4$Me)$_2$Ru(*p*-cymene)] (8): Compound **8** was prepared and isolated as described for **6** starting from **3** (80.6 mg, 0.15 mmol), *n*BuLi (187.4 μL; 1.6 M, 0.30 mmol), and [Ru$_2$(μ-Cl)$_2$(Cl)$_2$(*p*-cymene)$_2$] (49.1 mg, 0.08 mmol) to give red microcrystals of **8**. Yield: 68.7 mg (60 %). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): $\delta = 7.27$ (δ_{A}, 4H), 6.99 (δ_{B}, J(A,B) = 8.4 Hz, 4H; *p*-MeC$_6$*H*$_4$), 4.79 (δ_{A}, 2H), 4.76 (δ_{B}, J(A,B) = 6.1 Hz, 2H; *p*-MeC$_6$*H*$_4$-CHMe$_2$), 2.33 (s, 6H; *p*-*Me*C$_6$H$_4$), 2.30 (hp, ^{3}J(H,H) = 6.6 Hz, 1H; *p*-MeC$_6$H$_4$-C*H*Me$_2$), 2.17 (s, 3H; *p*-*Me*C$_6$H$_4$-CHMe$_2$), 1.31 ppm (d, ^{3}J(H,H) = 6.6 Hz, 6H; *p*-MeC$_6$H$_4$-CH*Me*$_2$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): $\delta = 190.4$ (d, ^{1}J(C,Rh) = 71 Hz; CO), 167.5 (C^{i}), 132.9 (C^{p}), 128.4 (C^{m}), and 122.1 (C^{o}) (*p*-MeC$_6$H$_4$), 101.9, 90.6, 83.3, and 80.3 (*p*-Me*C*$_6$H$_4$-CHMe$_2$), 31.9 (*p*-MeC$_6$H$_4$-*C*HMe$_2$), 24.0 (*p*-MeC$_6$H$_4$-CH*Me*$_2$), 21.1 (*p*-*Me*C$_6$H$_4$-CHMe$_2$), 20.8 ppm (*p*-*Me*C$_6$H$_4$); IR (dichloromethane): $\tilde{\nu} = 2048$ (s), 2029 (s), 1979 cm^{-1} (s) (CO); MS: *m*/*z* (%): 763 (35) [*M*]$^{+}$, 650 (100) [*M*−4CO]$^{+}$; elemental analysis calcd (%) for $C_{28}H_{28}N_2O_4Rh_2Ru$ (763.4): C 44.05, H 3.70, N 3.67; found: C 43.50, H 3.60, N 3.53.

[(CO)$_4$Rh$_2$(μ-4-NC$_6$H$_4$Me)$_2${Au(PPh$_3$)}$_2$] (9): Solid [AuCl(PPh$_3$)] (148.4 mg, 0.30 mmol) was added to a solution of [Li$_2$Rh$_2$(μ-4-NC$_6$H$_4$Me)$_2$(CO)$_4$] (**4**) (0.15 mmol) prepared as described for **6**. After stirring for a few seconds, just to dissolve the gold compound, the yellow solution was maintained undisturbed in the dry ice/acetone bath overnight to give orange-yellow microcrystals suitable for X-ray diffraction studies. The mother liquor was decanted and the crystals were washed with cold methanol and dried under vacuum (yield: 141.0 mg; 65 %). ^{1}H NMR ([D$_6$]benzene, 25 °C): $\delta = 8.15$ (δ_{A}, 4H), 6.68 (δ_{B}, J(A,B) = 8.1 Hz, 4H; *p*-MeC$_6$*H*$_4$), 7.75 (m, 12H; H^{o}PPh$_3$), 7.02 (m, 18H; H^{m+p}PPh$_3$), 2.08 ppm (s, 6H; *p*-*Me*C$_6$H$_4$); ^{31}P{^{1}H} NMR ([D$_6$]benzene, 25 °C): $\delta = 32.5$ ppm (t, J(P,Rh) = 1.3 Hz); IR (THF): $\tilde{\nu} = 2031$ (s), 1969 cm^{-1} (s) (CO); MS: *m*/*z* (%): 1418 (5) [*M*−CO]$^{+}$, 459 (100) [AuPPh$_3$]; elemental analysis calcd (%) for $C_{54}H_{44}N_2O_4P_2Rh_2Au_2$ (1446.6): C 44.83, H 3.06, N 1.93; found: C 45.20, H 3.19, N 2.08.

[{Rh$_3$(μ-4-NC$_6$H$_4$Me)$_2$(CO)$_6$}Au(PPh$_3$)] (10): Solid [AuCl(PPh$_3$)] (39.6 mg 0.08 mmol) was added to a dichloromethane (10 mL) solution of PPN[Rh$_3$(μ-4-NC$_6$H$_4$Me)$_2$(CO)$_6$] (**5**) (98.0 mg, 0.08 mmol) at room temperature. After stirring for 1 h, the solution was evaporated to dryness, the residue extracted with diethyl ether (2×10 mL) and filtered through Celite. The resulting yellow solution was concentrated to about 5 mL, layered with hexane (5 mL), and kept undisturbed in the fridge for two days. The mother liquor was decanted and the yellow crystals were dried under vacuum (yield: 73.4 mg; 75 %). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): $\delta = 7.67$–7.49 (m, 15H; PPh$_3$), 7.26 (δ_{A}, 4H), 6.85 (δ_{B}, J(A,B) = 8.0 Hz, 4H; *p*-MeC$_6$*H*$_4$), 2.27 ppm (s, 6H; *p*-*Me*C$_6$H$_4$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): $\delta = 35.7$ ppm (td, ^{2}J(P,Rh) = 17 Hz, ^{3}J(P,Rh) = 5 Hz); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): $\delta = 188.8$ (d, ^{1}J(C,Rh) = 70 Hz, 2C; CO), 187.3 (d, ^{1}J(C,Rh) = 65 Hz, 4C; CO), 165.4 (q, ^{2}J(C,Rh) = ^{4}J(C,P) = 1 Hz; C^{i}), 133.1 (C^{p}), 128.2 (C^{m}), and 123.1 (q, ^{3}J(C,Rh) = ^{5}J(C,P) = 1 Hz; C^{o}) (*p*-Me*C*$_6$H$_4$), 134.3 (d, ^{2}J(C,P) = 14 Hz; C^{o}), 132.2 (d, ^{4}J(C,P) = 3 Hz; C^{p}), 130.6 (d, ^{1}J(C,P) = 54 Hz; C^{i}), and 129.7 (d, ^{3}J(C,P) = 12 Hz; C^{m}) (PPh$_3$), 20.6 ppm (*p*-*Me*C$_6$H$_4$); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2044$ (s), 2000 (s), 1983 cm^{-1} (w) (CO); MS(FAB^{+}): *m*/*z* (%): 1146 (33) [*M*]$^{+}$, 1118 (100) [*M*−CO]$^{+}$; elemental analysis calcd (%) for $C_{38}H_{29}N_2O_6PRh_3Au$ (1146.3): C 39.82, H 2.55, N 2.44; found: C 40.13, H 2.92, N 2.18.

[Rh$_4$(μ-4-NC$_6$H$_4$Me)$_2$(CO)$_6$(cod)] (11): Compound **11** was prepared as described for **10** starting from **5** (98.0 mg, 0.08 mmol) and [Rh(cod)(NCMe)$_2$](BF$_4$) (30.4 mg, 0.08 mmol) to render 57.5 mg of dark microcrystals (80 %). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): $\delta = 7.27$ (δ_{A}, 4H), 6.85 (δ_{B}, J(A,B) = 8.5 Hz, 4H; *p*-MeC$_6$*H*$_4$), 2.27 (s, 6H; *p*-*Me*C$_6$H$_4$); 6.52 (δ_{A}, 4H), 6.18 (δ_{B}, J(A,B) = 7.0 Hz, 4H; *p*-MeC$_6$*H*$_4'$), 4.29 (brs, 4H; =CH), 2.44 (m, 4H; CH$_2^{exo}$), 2.13 (m, 4H; CH$_2^{endo}$), 2.25 (s, 6H; *p*-*Me*C$_6$H$_4$), 2.13 ppm (s, 6H; *p*-*Me*C$_6$H$_4'$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): $\delta = 189.4$ (d, ^{1}J(C,Rh) = 66 Hz; CO), 189.1 (d, ^{1}J(C,Rh) = 73 Hz; CO), 166.5 (q, ^{2}J(Rh,C) = 1 Hz; C^{i}), 131.4 (C^{p}), 127.9 (C^{p}), and 123.1 (q, ^{3}J(Rh,C) = 1 Hz; C^{o}) (*p*-Me*C*$_6$H$_4$), 156.6 (C^{i}), 111.3 (d, ^{1}J(Rh,C) = 3 Hz; C^{p}), 103.8 (d, ^{1}J(Rh,C) = 3 Hz; C^{m}), and 99.2 (dq, ^{1}J(Rh,C) = 3 Hz, ^{3}J(Rh,C) = 1 Hz; C^{o}) (*p*-Me*C*$_6$H$_4'$), 81.3 (d, J(Rh,C) = 13 Hz; =CH), 31.8 (CH$_2$), 20.5 (*p*-

MeC_6H_4), 20.5 ppm (*p*-*Me*C_6H_4'); MS(FAB$^+$): *m*/*z* (%): 898 (50) [*M*]$^+$, 870 (75) [*M*−2CO]$^+$; elemental analysis calcd (%) for $C_{28}H_{26}N_2O_6Rh_4$ (898.15): C 37.44, H 2.92, N 3.12; found: C 37.28, H 2.85, N 3.18.

X-ray data collection, structure solution, and refinement for compounds 6, 8, and 9: The intensity data of compounds **6**, **8**, and **9** were collected at room temperature on ENRAF Nonius CAD 4 (**6**) and a Philips PW 1100 (**8** and **9**) diffractometers. All crystals of **8** were of poor quality so that the structural data that resulted were not particularly accurate. Crystallographic and experimental details for the structures are summarized in Table 4.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2)[23] with anisotropic thermal parameters for all the non-hydrogen atoms, except the carbon atoms in **8**. In the last cycles of the refinement the phenyl rings of **8** were treated as rigid groups. When necessary the data were corrected by absorption effect.[24]

Table 4. Crystal data and structure refinement for compounds **6**, **8**, and **9**.

Compound	**6**	**8**	**9**
formula	$C_{26}H_{26}N_2O_4PdRh_2$	$C_{28}H_{28}N_2O_4Rh_2Ru$	$C_{54}H_{44}Au_2N_2O_4P_2Rh_2$
form. weight	742.71	763.41	1446.60
λ [Å]	1.54184 ($Cu_{K\alpha}$)	0.71073 ($Mo_{K\alpha}$)	0.71073 ($Mo_{K\alpha}$)
temperature [K]	298(1)	298(1)	298(1)
crystal system	monoclinic	tetragonal	triclinic
space group	$C2/c$	$P4_1$	$P\bar{1}$
unit cell dimensions			
a [Å]	16.970(5)	8.672(3)	10.831(4)
b [Å]	9.415 (3)	8.672(3)	11.562 (5)
c [Å]	16.873(5)	38.589(5)	10.792(4)
α [°]			88.70(3)
β [°]	97.87(3)		69.11(2)
γ [°]			85.02 (3)
V [Å^3]	2670(1)	2902(1)	1258(1)
Z	4	4	1
ρ(calcd) [Mg m^{-3}]	1.847	1.747	1.910
μ [cm^{-1}]	155.35	16.72	65.68
max and min trans. factor	1.000, 0.549	1.000, 0.733	1.000, 0.730
F(000)	1456	1504	692
crystal size [mm]	0.13 × 0.11 × 0.21	0.22 × 0.15 × 0.20	0.22 × 0.12 × 0.31
θ range [°]	5.26–70.01	3.16–21.00	3.33–24.98
reflns. collct.	2620	1832	3175
indep reflns	2535 [R(int) = 0.0946]	1586 [R(int) = 0.0497]	3175
obs. reflns [$I > 2\sigma(I)$]	1867	1208	2012
data/restr./param.	2535/0/164	1586/8/166	3175/0/303
final R indices[a] [$I > 2\sigma(I)$]			
$R1$	0.0635	0.0533	0.0348,
$wR2$	0.1722	0.1411	0.0560
R indices (all data)			
$R1$	0.0791	0.0857	0.0816
$wR2$	0.1824	0.1635	0.0659

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma[w(F_c^2-F_o^2)^2]/\Sigma\,[w(F_o^2)^2]]$.

The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. In the final cycles of refinement a weighting scheme, $w = 1/[\sigma^2F_o^2+(0.1209P)^2+21.2628P]$ (**6**), $w = 1/[\sigma^2F_o^2+(0.0649P)^2+51.768402P]$ (**8**), $w = 1/[\sigma^2F_o^2+(0.012100P)^2]$ (**9**), where $P = (F_o^2+2F_c^2)/3$, was used.

CCDC-215800 (**6**), CCDC-215801 (**8**), and CCDC-215802 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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