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^{195}Pt NMR of Heteropolymetallic Complexes Containing Secondary Dithiooxamides as Binucleating Ligands

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Monometallic [Pt{*S*-$S_2C_2(NR)_2H$}$_2$] (*S*-$S_2C_2(NR)_2H$ = κ^2-*S,S*-$S_2C_2(NR)_2H$ = bis-dialkyl-dithioxamidate, R = methyl, isoamyl, benzyl) and binuclear and trinuclear heterobimetallic complexes [Pt{*S*-$S_2C_2(NR)_2H$}{μ-$S_2C_2(NR)_2$}ML_n] (μ-$S_2C_2(NR)_2$ = κ^2-*S,S*(Pt)-κ^2-*N,N*(M)-$S_2C_2(NR)_2$) and [Pt{{μ-$S_2C_2(NR)_2$}ML_n}$_2$] (ML_n^+ = [(η^3-allyl)palladium]$^+$, [bis-(2-phenylpyridine)rhodium]$^+$, [(η^6-p-cymene)(chloro)ruthenium]$^+$, [(1,4-cyclooctadiene)rhodium]$^+$, [(pentamethyl-cyclopentadienyl)(chloro)rhodium]$^+$) have been prepared and characterized. The progressive substitution of the residual amidic hydrogen in the [Pt{*S*-$S_2C_2(NR)_2H$}$_2$] complexes with a ML_n^+ metal fragment results in the deshielding of platinum nuclei, a red shift of the MLCT absorption maximum, and a decrease in the oxidation potential. Such behavior has been interpreted as a progressive electron shift from platinum to the binucleating ligands, the extent of which depends on the nature of ML_n^+ metal fragment.

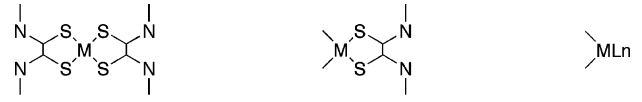
Introduction

Heteropolymetallic complexes, in which the electronic communication between metals is propagated via bridging atoms, are of special interest because they can display peculiar photoelectrochemical, electronic, and magnetic properties, and therefore they could be used for molecular-based devices.[1]

Synthetic strategies to achieve topologically and stereochemically controlled heteropolymetallic systems are based on the use of "metalloligands" (i.e., metal complexes used as ligands).[2] These procedures exploit heterotopic ligands already bound to one metal with free coordination sites that can bind a second metal (the same or a different kind of metal). Such ligands allow step-by-step syntheses because of the different reactivities of the various donor sites, which are generally chelating systems. In this context, the oxamato and oximato ligands have been extensively used to generate families of polymetallic compounds via a sequential strategy.[3]

Another binucleating ligand, 1,10-phenanthroline-5,6-dione, has been used as building block for polymetallic systems; it possesses a bifunctional character and exhibits different reactivities in its functionalities.[4]

Scheme 1



We have favored the strategy of using "metal dithiooxamidate" building blocks as ligands to synthesize various heterometal complexes.[5−7] Our objective was to build up linear heteropolymetallic chains of the type C−$(B)_n$−A−$(B)_m$−C′ (C may be equal to C′, $m \geq n \geq 0$) through a modular use of bischelate dithioxamide complexes of the type [M{*S*-$S_2C_2(NR)_2H$}$_2$] (M = divalent transition metal ions, R = alkyl groups) (A in the Scheme 1), monochelate [L_nM{*S*-$S_2C_2(NR)_2H$}] precursors (B), and nonligating fragments (C).

The present paper deals with different series of complexes of types [Pt{*S*-$S_2C_2(NR)_2H$}$_2$], [Pt{*S*-$S_2C_2(NR)_2H$}{μ-S_2C_2-

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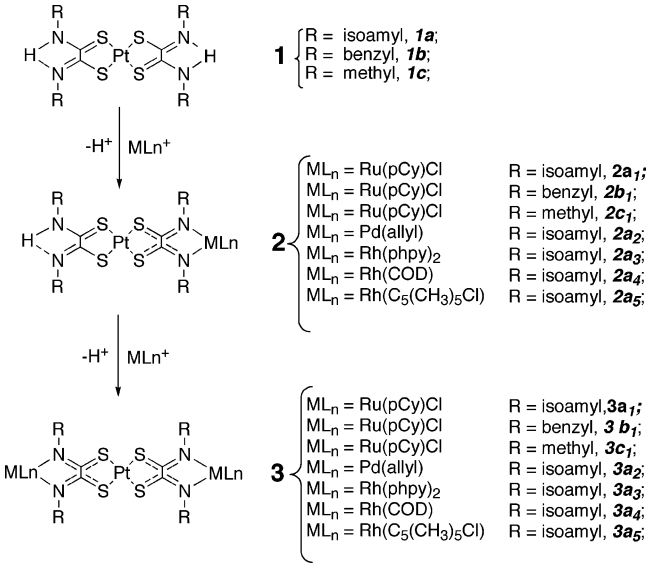
Scheme 2



$(NR)_2\}ML_n]$ and $[Pt\{\{\mu\text{-}S_2C_2(NR)_2\}ML_n\}_2]$ ($S\text{-}S_2C_2(NR)_2H^-$ = terminal dithiooxamidate; $S_2C_2(NR)_2$ = bridging dithiooxamidate; L_nM^+ = $[Ru(\eta^6\text{-}p\text{-Cymene})Cl]^+$, $[(\eta^3\text{-allyl})ClPd]^+$, $[Rh(2\text{-phenylpyridine})_2]^+$, $[Rh(cyclooctadiene)]^+$, $[Rh(pentamethylcyclopentadienyl)Cl]^+$), for which we have demonstrated that peripheral metal fragments $[ML_n]^+$ have a strong effect in modifying the electron density on the Pt(II) centers via the bridging dithioxamidate ligand. Even more interestingly, this effect seems to be highly controllable and tunable as a function of the nature of the peripheral metal fragments.

Results and Discussion

One of the complexes which appears in this paper, $[Pt\{\{\mu\text{-}S_2C_2(NR)_2\}Pd(\eta^3\text{-allyl})\}_2]$, has been already synthesized and its properties have been discussed.[7] In particular, it has been found that the synthesis of the quoted complex is stereoselective because this trimetallic complex has been prepared as one of the two possible isomers (the endo isomer).

It has been proposed that, once the first allylpalladium moiety enters the platinum precursor $[Pt\{S\text{-}S_2C_2(NR)_2H\}_2]$ (R = isoamyl), **1a** (Scheme 2), a back-donation mechanism correlates both the palladium and platinum d orbitals through the NCS system of the binucleating ligand. Thus, the second allylpalladium fragment will be forced to interact with the set of platinum d orbitals in a preferred orientation. One could expect the reactivity of the nitrogen-chelating systems in the precursor $[Pt\{S\text{-}S_2C_2(NR)_2H\}_2]$ (R = isoamyl) (**1a** in the Scheme 2) to be different from the reactivity of the residual chelating system in bimetallic $[Pt\{S\text{-}S_2C_2(NR)_2H\}\{\mu\text{-}S_2C_2(NR)_2\}Pd(\eta^3\text{-allyl})$ $\kappa\text{-}N,N\text{-Pd}$, $\kappa\text{-}S,S\text{-Pt}]$, (**2a$_2$**). Actually, we have successfully synthesized the heterobimetallic compound **2a$_2$** according to Scheme 2, taking advantage of the difference in reactivity between the nitrogen-chelating sites, =N−H···N= of **1a** and **2a$_2$**.

The addition of another allyl palladium fragment to **2a$_2$** produces the trinuclear heterobimetallic species **3a$_2$** (Scheme 2).

We have observed that the ^{195}Pt resonances are progressively shifted toward lower fields on going from **1a** to **3a$_2$**. The deshielding of the platinum nucleus, caused by the progressive substitution of a proton in **1a** with a metal fragment having total charge +1, indicates that electron density is transferred from the platinum center to peripheral sites in the **2a$_2$** and **3a$_2$** complexes. In other words, such a deshielding may be considered to be a result of the electronic influence exerted by the $[Pd(\eta^3\text{-allyl})]^+$ fragment on the Pt(II) centers, mediated by the binucleating dithiooxamidate. Therefore, we thought it would be interesting to study ^{195}Pt resonance shifts in several families of bi- and trimetallic complexes synthesized as shown in Scheme 2.

For the sake of simplicity, we labeled the mononuclear complexes **1**, the binuclear compounds **2**, and the trinuclear species **3**. Letters and subscript numbers indicate the alkyl substituents of the dithiooxamides and the heterometallic fragments, respectively.

The type **1** complexes were synthesized following known procedures[8] and characterized by elemental and NMR spectral analysis. The type **2** compounds are new. The NMR data are consistent with their molecular formula. In fact, proton spectra of **2a$_n$** complexes (n = 1, 2, 3, 5) show two sets of signals for the N−CH_2− protons; those belonging to the alkyl arms near the ML_n^+ fragment are diastereotopic because of the close proximity of the dissymmetrizing ML_n^+ group and appear as the AB part of an ABX_2 system, while the N−CH_2− protons belonging to the alkyl arms far from the ML_n^+ fragments appear in the spectrum as a triplet. When ML_n^+ is $Rh(COD)^+$ (**2a$_4$**), it is possible to distinguish between the near and far N−CH_2− protons because the signal of the near group is split by coupling with Rh nucleus. Furthermore, the NOESY TP spectra show cross-peaks between the the AB part of the ABX_2 system in **2a$_n$** (n = 1, 2, 3, 5) or the split triplet in **2a$_4$** and the signals of the proper protons of the L_n ligands in ML_n^+ fragments (cymene ring protons, terminal CH_2 allyl protons, low field COD protons, pyridine H^6 in phenylpyridine groups, and methyl protons in C_5Me_5 rings).

All type **3** compounds have the same topology as the known **3a$_2$** complex (i.e., they consist of two ML_n^+ metal fragments linked to the nitrogen-chelating systems of a platinum(II)-bis-(dialkyl-dithioxamidate) core). Complexes **3a$_n$** (n = 1, 2, 3, 5), **3b$_1$** and **3c$_1$** could exist in two isomeric forms: endo/eso (**3a$_2$**), meso/rac (**3a$_3$**), cis/trans (**3a$_1$**, **3b$_1$**, **3c$_1$**, and **3a$_5$**). As described above, **3a$_2$** can be synthesized only as the endo isomer; **3a$_3$** was prepared as an equimolar meso/rac mixture which could not be resolved, and **3a$_1$**, **3b$_1$**, **3c$_1$**, and **3a$_5$** were obtained as cis/trans mixtures in which one of the two isomers appeared to be present as a minor component. Further column chromatography of the isomeric mixtures provided the major isomer in a pure form for **3a$_1$**, **3b$_1$**, **3c$_1$**, and **3a$_5$**. We did not obtain X-ray quality crystals of these latter compounds, and as a consequence, their geometry remains uncertain.

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Table 1. [195]Pt NMR (δ), Absorption Maxima (λ) and Oxidation Potential (E) for a Variety of Mononuclear, Binuclear, and Trinuclear Platinum Complexes

complex	δ (ppm)	λ (nm)	E (V vs SCE)
1a	110	452	1.04
1b	120	457	
1c	110	447	
2a$_1$	316	484	0.97
2b$_1$	303	493	
2c$_1$	328	479	
2a$_2$	254	465	0.97
2a$_3$	269	460	0.95
2a$_4$	247	483	0.88
2a$_5$	301	472	0.98
3a$_1$	510	511	0.90
3b$_1$	520	530	
3c$_1$	530	503	
3a	380	476	0.96
3a$_3$	413	466	*a*
3a$_4$	364	504	0.88
3a$_5$	481	489	0.99

[a] Adsorbed on the electrode.

It is important to point out that there was very little differences (about 2 ppm) between the platinum shifts of the two isomers and no significant difference between the absorption spectra of the isomeric mixtures and those of the corresponding pure compounds.

[195]Pt NMR. We have registered [195]Pt NMR spectra for all of the complexes. The observed chemical shifts, expressed in absolute frequency (TMS = 100 MHz), occur over a range of about 400 ppm, which is large enough to consider [195]Pt NMR a sensitive probe of the electronic structure of our mono, bi, and trimetallic complexes. There are several extensive papers on [195]Pt chemical shifts. [9−12] Other reports are concerned with [195]Pt NMR of platinum complexes containing sulfur ligands,[13−15] but to our knowledge, there are no reports which ones refer to dithioxamides either chelated to platinum or bridged between platinum and another metal. The [195]Pt NMR results are reported in Table 1.

Platinum chemical shifts both in mono- and polynuclear metal complexes depend very little on the nature of alkyl substituent R for a given ML_n^+ (Table 1). Figure 1 shows [195]Pt chemical shifts versus nuclearity for complexes containing the same alkyl substituent (R = isoamyl) but different heterometallic fragments; it can be seen that each ML_n^+ fragment shows a specific capacity to attract electrons from platinum.

The linear relationships shown in Figure 1 imply that the difference in chemical shift, $\Delta\delta$, caused by the linkage of the first ML_n^+ fragment to one nitrogen-chelating system of the precursor [Pt{*S*-$S_2C_2(NR)_2H$}$_2$] has the same value

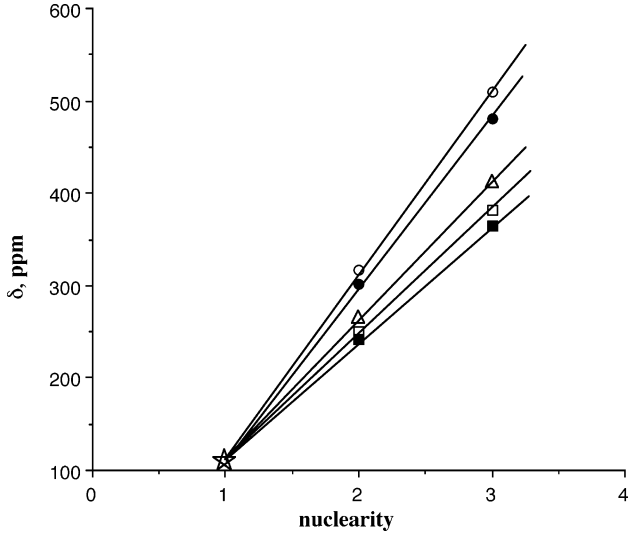

Figure 1. [195]Pt chemical shifts vs nuclearity in [Pt{*S*-$S_2C_2(NR)_2H$}$_2$] (**1a**), [Pt{*S*-$S_2C_2(NR)_2H$}{μ-$S_2C_2(NR)_2$}ML_n] (**2a$_n$**, n = 1, 2, 3, 4, 5) and [Pt-{{μ-$S_2C_2(NR)_2$}ML_n}$_2$] (**3a$_n$**, n = 1, 2, 3, 4, 5). Each straight line correlates the mononuclear species (★) with the bi- and trinuclear heterobimetallic complexes in which the alkyl substituent R is the isoamyl group and the heterometallic fragment ML_n^+ is [Ru(p-cymene)Cl]$^+$(○), [Rh(C_5Me_5)Cl]$^+$ (●), [Rh(2-phenylpyridine)$_2$]$^+$ (△), [Pd(η^3-allyl)]$^+$ (□), or [Rh(COD)]$^+$ (■).

as that observed by linking a second ML_n^+ fragment to the residual nitrogen-chelating system of the bimetallic species [Pt{*S*-$S_2C_2(NR)_2H$}{μ-$S_2C_2(NR)_2$}ML_n]. In other words, upon coordination of a ML_n^+ fragment there is an electronic removal from platinum toward ML_n^+ via the π^* systems of the NCS frames in the binucleating dithiooxamide. The observed electronic removal could have been balanced by a π donation from the π system of the dithiooxamide ligand to the empty platinum d orbitals. In such a case, we should have expected the $\Delta\delta$ value related to the first metalation of precursor **1** to be different from the $\Delta\delta$ value related to the metalation of the corresponding binuclear complex, **2**. Actually, the possibility of a π donation from the bridging dithioxamide to the platinum d orbitals would require a C═C double bond connecting the two NCS frames, as has already been observed in some dithiolene−platinum(II) complexes.[15] A number of X-ray measurements performed on uncoordinated dithioxamides[16−18] and their metal complexes [5−8,19,20] have shown that the central C−C bond is always a single bond. The unique exception deals with a tertiary dithioxamide-chelated to an electron-rich metal fragment, in which the ligand is reduced in the dithiolenic form.[21] Thus, the *S*,*S*-platinum-chelated dithioxamidate cannot behave as a π donor ligand; consequently, each ML_n^+ fragment produces the same [195]Pt $\Delta\delta$ because the two dithioxamidate ligands do not transmit any electronic effect to each other. As a consequence, the linkage of the ML_n^+ fragment to the nitrogen-chelating system of the platinum-

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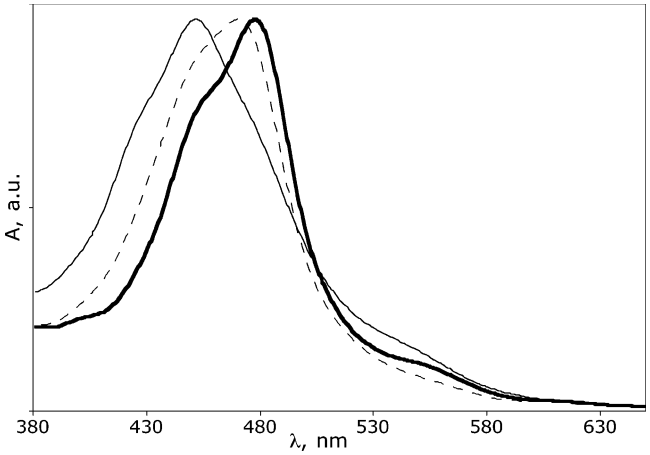

Figure 2. Normalized room-temperature absorption spectra of [Pt{*S*-S_2C_2-$(NR)_2H$}$_2$] (R = isoamyl) (plain line, ***1a***), [Pt{*S*-$S_2C_2(NR)_2H$}{μ-S_2C_2-$(NR)_2$}Pd(η^3-allyl)] (R = isoamyl) (dashed line, ***2a*$_2$**), and [Pt{{μ-S_2C_2-$(NR)_2$}Pd(η^3-allyl)}$_2$] (R = isoamyl), (bold line, ***3a*$_2$**).

chelated dithioxamidate produces a downfield shift of the ^{195}Pt resonance which is independent of the other chelated dithioxamidates linking a further ML_n^+ fragment.

Electronic spectroscopy. The strong absorption bands in the visible region exhibited by all of the type **1** mononuclear complexes (Table 1, Figure 2) have already been assigned to the Pt(dπ)/S(p) → dithiooxamide (π*) CT transition[22] on the basis of both the experimental evidence and the structural and electronic similarities between the Pt(II)−dithiooxamide compounds and the Pt(II)−dithiolate complexes.[23,24]

In all of the type **1** complexes, the visible absorption maximum is accompanied by a shoulder at a slightly higher energy. This higher-energy shoulder could be attributed to the vibrational progression of the main band. The Pt(dπ)/S(p) → dithiooxamide (π*) CT transitions in mononuclear complexes warrant further comments: the Pt(II) metal ion provides a large electronic coupling between the two chelating sulfur-containing ligands, as demonstrated in the square-planar d^8 complexes of Ni(II), Pd(II), and Pt(II).[25,26]

The HOMO in the type **1** complexes is therefore probably well described as being delocalized on both ligands, receiving a contribution from the Pt(dπ) and all the S(p) orbitals. On the other hand, the ^{195}Pt NMR evidence rules out the possibility of an extended electronic coupling between ligands, and therefore, the molecular LUMO will be centered on the amidic moiety of a single DTO ligand and will not be delocalized on the entire molecule. The lower-energy spectrum in Figure 2 (bold line) refers to a typical symmetrical trinuclear heterobimetallic complex (type **3** compounds). Also, in this case, the absorption bands can be assigned to the Pt(dπ)/S(p) → dithiooxamide (π*) CT transition, and the shoulder can be attributed to the vibrational progression of the main band; the lower energy of the transition is probably the result of the destabilization of the HOMO and the stabilization of LUMO caused by the electron redistribution between the metal and the ligands following the progressive metalation of species **1**. The dashed spectrum in Figure 2 refers to the bimetallic complex ***2a*$_2$**; it looks like an unresolved broad band. This absorption band can be attributed to two Pt(dπ)/S(p) → dithiooxamide (π*) CT transitions: one with energy similar to that of the mononuclear species and the other one with energy similar to that of the trinuclear species. As a result, maxima and shoulders overlap and an unresolved band appears in the spectrum.

In essence, the value of λ_{max} in the electronic spectra of the type **1**, **2**, and **3** complexes can be considered to be an estimate of the HOMO−LUMO separation. It is known that the main contribution to the shielding of a heavy metal nucleus, such as ^{195}Pt, should be the paramagnetic term defined by Ramsey,[27] which was evaluated for d^8 platinum complexes by Dean and Green[28] who obtained the following expression

$$\sigma_p = -\frac{16}{3}\beta^2 <r^{-3}> C_{a_{1g}}{}^2 [2C_{a_{2g}}{}^2 \Delta E_A{}^{-1} + C_{e_g}{}^2 \Delta_E{}^{-1}] \quad (1)$$

where

$$\Delta E_A = E(^1A_{2g} - {}^1A_{1g})$$
$$\Delta E_E = E(^1A_g - {}^1A_{1g}) \quad (2)$$

and $C_{a_{1g}}$, $C_{a_{2g}}$, and C_{e_g} are the coefficients of the platinum d orbitals. If we make the approximation that $C_{a_{1g}} \approx C_{e_g}$, then the observed chemical shifts should follow the equation

$$\delta_{Pt} = m\lambda + c \quad (3)$$

where λ is the weighted mean of the reciprocal transition energies (i.e., $^1/_3(2E_A{}^{-1} + E_E{}^{-1})$) and c allows for the arbitrary zero used for our shifts. The whole set of data in our hands (i.e., δ vs λ_{max} for all the complexes) fits the significant straight line $\delta_{Pt} = 4.84\lambda - 2010$ ($R^2 = 0.647$, $p < 0.00001$, Figure 3). In this graph, one can see several

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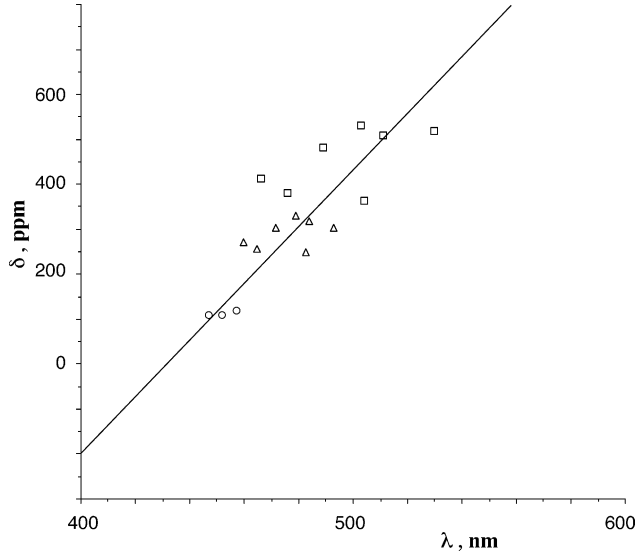

Figure 3. Plot of ^{195}Pt chemical shift vs $\lambda = 1/3(2\Delta E_A^{-1} + \Delta E_E^{-1})$ for mononuclear (○), binuclear (△), and trinuclear complexes (□).

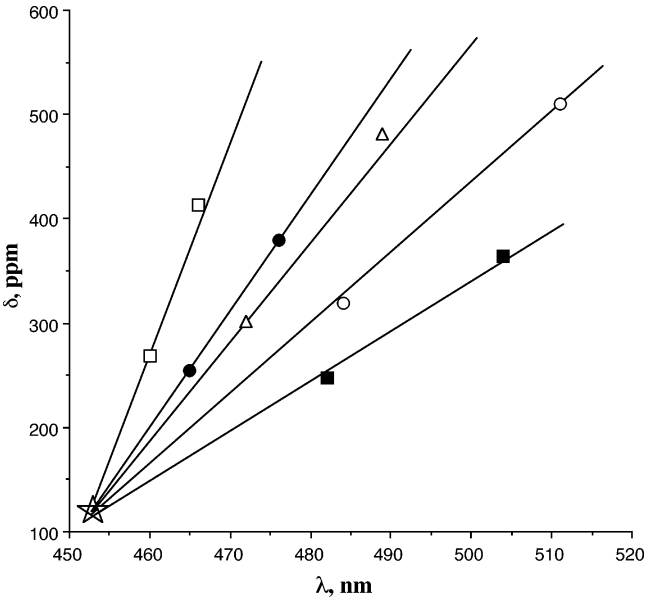

Figure 4. Plot of ^{195}Pt chemical shifts vs $\lambda = {}^1/_3(2\Delta E_A^{-1} + \Delta E_E^{-1})$ in [Pt{*S*-$S_2C_2(NR)_2H$}$_2$] (R = isoamyl) (**1a**), [Pt{*S*-$S_2C_2(NR)_2H$}{μ-$S_2C_2(NR)_2$}ML_n] (R = isoamyl) (**2a$_n$**, n = 1, 2, 3, 4, 5), and [Pt{{μ-$S_2C_2(NR)_2$}ML_n}$_2$] (R = isoamyl) (**3a$_n$**, n = 1, 2, 3, 4, 5). Each straight line correlates the mononuclear species (★) with bi- and trinuclear heterobimetallic complexes in which the heterometallic fragment ML_n^+ is [Pd(η^3-allyl)]$^+$ (□), [Ru(p-cymene)Cl]$^+$(●), [Rh(2-phenylpyridine)$_2$]$^+$ (△), [Rh(COD)]$^+$ (○), and [Rh(C_5Me_5)Cl]$^+$ (■).

groups of three points, each group representing complexes with the same alkyl substituent (R = isoamyl) and different ML_n^+ metal fragments (Figure 4) or complexes with the same metal fragment, [Ru(*p*-cymene)Cl]$^+$, and different alkyl substituents (Figure 5). In other words, significant straight lines correlate the ^{195}Pt chemical shift versus the weighted mean of the reciprocal transition energies in each family of complexes (**1**, **2**, and **3**). The slope of such lines depends on the nature of the ML_n^+ subunit and shows the redistribution of electrons between the metal and the ligands via the progressive and specific metalation of species **1**. In Figure 5, one can see three straight lines with similar slopes

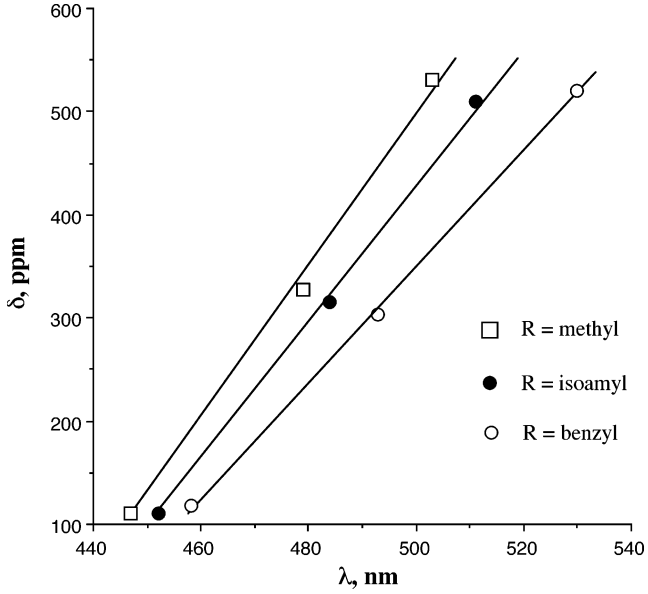

Figure 5. Plot of ^{195}Pt chemical shifts vs $\lambda = {}^1/_3(2\Delta E_A^{-1} + \Delta E_E^{-1})$ in [Pt{*S*-$S_2C_2(NR)_2H$}$_2$] (**1a**, **1b**, **1c**), [Pt{*S*-$S_2C_2(NR)_2H$}{μ-$S_2C_2(NR)_2$}ML_n] (**2a$_1$**, **2b$_1$**, **2c$_1$**), and [Pt{{μ-$S_2C_2(NR)_2$}ML_n}$_2$] (**3a$_1$**, **3b$_1$**, **3c$_1$**). Each straight line correlates mono, bi-, and trimetallic complexes in which the heterometallic fragment ML_n^+ is [Ru(p-cymene)Cl]$^+$ and R is methyl (□), isoamyl (●), and benzyl (○).

because they all refer to the progressive linking of the [Ru(*p*-cymene)Cl]$^+$ frame to three type **1** precursors, [Pt{*S*-$S_2C_2(NR)_2H$}$_2$] where R is a methyl, benzyl, or isoamyl group. The plot confirms that the chemical shift is independent of the nature of the R substituent and shows that λ_{max} is dependent on R. The sensitivity of the absorption band energy to the substituents of the dithioxamide moiety is in accordance with the MLCT nature of the measured transition.

Electrochemistry. Cyclic voltammetry experiments have shown irreversible processes. The oxidation potentials in the type **2** and **3** compounds were less positive, about 70 mV, than the potential of the monometallic precursor **1a** (Table 1). These oxidation processes could be the removal of one electron from the HOMO which, in type **2** and **3** compounds, is less stable than the HOMO of the monometallic precursor. Somewhat lower values (0.88 V) were detected in ***2*a$_4$** and ***3*a$_4$**, where ML_n^+ is [Rh(COD)]$^+$. According to the coordinated cyclooctadiene behavior,[15] the COD π orbitals in [Rh(COD)]$^+$ can overlap the π^* system in the NCS fragments of the bridging dithioxamide, in such a way that a further destabilization of the HOMO occurs, and as a consequence, the electron can be removed more easily.

The pattern of electrochemical behavior of our mono-, bi-, and trimetallic complexes is in accordance with both the NMR and absorption spectroscopy results. In fact, the metalation of the nitrogen-chelating systems in the binucleating dithioxamides causes an electronic shift from platinum to the SCN system. Such a shift produces destabilization of the HOMO, mainly centered on the sulfur atoms. As a consequence, deshielding of the ^{195}Pt nuclei, lowering of the HOMO−LUMO transition energies, and eventually, lowering of the oxidation potentials will occur.

Experimental Section

Dithioxamide ligands $S_2C_2(NR)_2H_2$ (R = methyl, isoamyl, benzyl) were synthesized according to the method of Hurd,[29] and the complex *cis*-Pt$(Me_2SO)_2Cl_2$ was prepared according to the method of Kukushkin.[30] Other reagents were commercially available products used as received.

^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{195}Pt{^{1}H} NMR spectra were recorded at 298 K on a Bruker ARX-300, equipped with a broad-band probe operating at 300.13, 75.48, and 64. 23 MHz, respectively. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm (relative to TMS) and are referenced to the residual solvent peak. The ^{195}Pt chemical shifts are reported by use of the absolute frequency (TMS = 100 MHz).

General Procedure for the Synthesis of Bis-dithioxamidato Complexes [Pt{*S*-$S_2C_2(NR)_2H$}$_2$] (R = isoamyl (1a), benzyl (1b), methyl (1c)). $S_2C_2(NR)_2H_2$ (1 mmol) was added to a stirred suspension of *cis*-Pt$(Me_2SO)_2Cl_2$ (211 mg, 0.5 mmol) in chloroform (60 mL). The reaction went to completion within 0.5 h at room temperature, and the solution turned purple. Sodium bicarbonate (200 mg) was added, and the solution turned yellow. After the mixture was stirred for 0.5 h, the solution was filtered and concentrated to a small volume (~10 mL). The solid obtained by addition of petroleum ether 40−60 (~100 mL) was collected and washed with diethyl ether.

1a. ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp): δ 3.16 (t, 8H, $^3J_{HH}$ = 6.20 Hz, N−CH_2−), 1.65 (m, 12H, N−CH_2−CH_2−CH−$(CH_3)_2$), 0.92 (d, 24H, $^3J_{HH}$ = 6.20 Hz, N−CH_2−CH_2−CH−$(CH_3)_2$).^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$, room temp): δ 179.43 (*C*S), 47.78 (N−*C*H_2−), 37.50 (N−CH_2−*C*H_2−), 26.25 (N−CH_2−CH_2−*C*H−), 22.40 (N−CH_2−CH_2−CH−(*C*H_3)$_2$). ^{195}Pt{^{1}H} NMR (64.23 MHz, $CDCl_3$, room temp): δ 110. Anal. Calcd for $C_{24}H_{46}N_4PtS_4$ (MW 713.99): C, 40.37; H, 6.49; N, 7.85. Found: C, 40.45; H, 6.60; N, 7.80. Yield: 90%.

1b. ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp): δ 7.33 (m, 20H, phenyl protons), 4.81 (s, 8H, N−CH_2−).^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$, room temp): δ 184.60 (*C*S), 135.03 (*q*-Ph), 128.91 (*o*-Ph), 128.32 (*p*-Ph), 128.15 (*m*-Ph), 51.53 (N−*C*H_2−). ^{195}Pt{^{1}H} NMR (64.23 MHz, $CDCl_3$, room temp): δ 120. Anal. Calcd for $C_{32}H_{30}N_4PtS_4$ (MW 793.95): C, 48.41; H, 3.81; N, 7.06. Found: C, 48.45; H, 3.70; N, 7.26. Yield: 87.

1c. ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp): δ 3.35 (s, 12H, N−CH_3). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$, room temp): δ 183.02 (*C*S), 47.78 (N−*C*H_3). ^{195}Pt{^{1}H} NMR (64.23 MHz, $CDCl_3$, room temp): δ 110. Anal. Calcd for $C_8H_{14}N_4PtS_4$ (MW 489.56): C, 19.63; H, 2.88; N, 11.44. Found: C, 19.71; H, 2.99; N, 11.39. Yield: 89%.

General Procedure for the Synthesis of the Binuclear Heterobimetallic Complexes [Pt{*S*-$S_2C_2(NR)_2H$}{μ-$S_2C_2(NR)_2$}-ML_n] (ML_n^+ = [Ru(*p*-cymene)Cl]$^+$, R = isoamyl (2a$_1$), benzyl (2b$_1$), methyl (2c$_1$); ML_n^+ = [(η^3-allyl)Pd]$^+$, R = isoamyl (2a$_2$); ML_n^+ = [Rh(phpy)$_2$]$^+$, R = isoamyl (2a$_3$); ML_n^+ = [Rh(COD)]$^+$, R = isoamyl (2a$_4$); ML_n^+ = [Rh(C_5Me_5)Cl]$^+$ (2a$_5$)). [Pt{*S*-$S_2C_2(NR)_2H$}$_2$] (1 mmol) was added to a solution of [ML_nCl]$_2$ (0.5 mmol) in chloroform−methanol (10/1 v/v) (40 mL), and the mixture was allowed to stand for 0.5 h under reflux. After this, the solution was concentrated to 10 mL and purified by column chromatography on alumina with a mixture chloroform−petroleum ether (4/1, v/v) as eluent. The pure product was finally obtained by precipitation from the addition of petroleum ether 40/60 (about 100 mL) to a concentrated portion (about 10 mL) of the eluate.

2a$_1$. ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp): δ 5.37, 5.12 (2d, unresolved AA′XX′ spin system, 4H, cymene ring protons), 4.40, 3.89 (two double triplets, 4H, ABX_2 spin system, $^2J_{HH}$ = 11.00 Hz, $^3J_{HH}$ = 6.40 Hz, N−CH_2 near ruthenium), 3.58 (t, 4H,$^3J_{HH}$ = 6.40 Hz, N−CH_2− far from ruthenium), 2.76 (sl, 1H, $^3J_{HH}$ = 6.40 Hz, cymene −CH−$(CH_3)_2$), 2.32 (s, 3H, cymene CH_3), 1.92−1.64 (m, 12H, N−CH_2−CH_2−CH−$(CH_3)_2$), 1.17 (d, 6H, $^3J_{HH}$ = 6.40 Hz, cymene −CH−(CH_3)$_2$), 0.99, 0.98 (2d, 12H, N−CH_2−CH_2−CH−(CH_3)$_2$ near ruthenium), 0.91 (d, 12H, N−CH_2−CH_2−CH−(CH_3)$_2$ far from ruthenium). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$, room temp): δ 189.19, 179.81 (*C*S), 103.64, 100.80 (cymene quaternary carbons), 84.45, 83.53 (other cymene ring carbons), 61.19, 47.69 (N−*C*H_2−), 37.64, 34.98 (N−CH_2−*C*H_2−), 31.25 (cymene *C*H−$(CH_3)_2$), 27.01, 26.30 (N−CH_2−CH_2−*C*H−), 22.63 (cymene CH−(*C*H_3)$_2$), 22.55, 22.46 (N−CH_2−CH_2−CH−(*C*H_3)$_2$), 18.99 (cymene *C*H_3). ^{195}Pt{^{1}H} NMR (64.23 MHz, $CDCl_3$, room temp): δ 316. Anal. Calcd for $C_{34}H_{59}ClN_4PtRuS_4$ (MW 983.73): C, 41.51; H, 6.05; N, 5.70. Found: C, 41.60; H, 6.13; N, 5.63. Yield: 80%.

2b$_1$. ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp): δ 7.55−7.28 (m, 20H, phenyl protons), 5.75, 5.07 (2d, 4H, AB spin system, N−CH_2−, near ruthenium), 4.82, 4.67 (2d, 4H, unresolved AA′XX′ spin system, cymene ring protons), 3.46 (s, 4H, N−CH_2−, far from ruthenium), 2.07 (sl, 1H, $^3J_{HH}$ = 6.16 Hz, cymene −CH-$(CH_3)_2$), 1.90 (s, 3H, cymene −CH_3), 0.84 (d, 6H, $^3J_{HH}$ = 6.16 Hz, cymene −CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$, room temp): δ 192.78, 180.88 (*C*S), 136.77 (*q*-Ph), 128.76−127.60 (*o*,*m*,*p*-Ph), 100.08, 97.82 (cymene quaternary carbons), 82.01, 81.80 (other cymene ring carbons), 65.63, 53.34(N−*C*H_2−), 30.78 (cymene *C*H−$(CH_3)_2$), 22.50 (cymene CH−(*C*H_3)$_2$), 19.05 (cymene *C*H_3). ^{195}Pt{^{1}H} NMR (64.23 MHz, $CDCl_3$, room temp): δ 303. Anal. Calcd for $C_{42}H_{43}ClN_4PtRuS_4$ (MW 1063.69): C, 47.43; H, 4.07; N, 5.27. Found: C, 47.39; H, 4.10; N, 5.38. Yield: 72%.

2c$_1$. ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp): δ 5.45, 5.12 (2d, 4H, unresolved AA′XX′ spin system, cymene ring protons), 3.78 (s, 6H, N−CH_3, near ruthenium), 3.30 (s, 6H, N−CH_3, far from ruthenium), 2.71 (sl, 1H, $^3J_{HH}$ = 6.60 Hz, cymene CH−$(CH_3)_2$), 2.23 (s, 3H, cymene CH_3), 1.17 (d, 6H, $^3J_{HH}$ = 6.60 Hz, cymene CH−(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$, room temp): δ 189.28, 181.83 (*C*S), 102.82, 102.34 (cymene quaternary carbons), 84.95, 82.33 (other cymene ring carbons), 48.81, 36.12 (N−*C*H_3), 31.37 (cymene *C*H−$(CH_3)_2$), 22.46 (cymene CH−(*C*H_3)$_2$), 19.10 (cymene *C*H_3). ^{195}Pt{^{1}H} NMR (64.23 MHz, $CDCl_3$, room temp): δ 328. Anal. Calcd for $C_{18}H_{27}ClN_4PtRuS_4$ (MW 759.30): C, 28.47; H, 3.58; N, 7.38. Found: C, 28.31; H, 3.70; N, 7.25. Yield: 75%.

2a$_2$. ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp): δ 5.41, (m, 1H, CH allyl), 3.86−3.69 (m, 4H, N−CH_2−, near palladium), 3.61−3.46 (m, 6H, N−CH_2−, far from palladium + CH_2 allyl syn), 2.92, 2.89 (2d, 2H, $^2J_{HH}$ = 12.50 Hz, CH_2 allyl anti), 1.72−1.38 (m, 12H, N−CH_2−CH_2−CH−$(CH_3)_2$), 0.89−0.87 (m, 24H, $^3J_{HH}$ = 6.20 Hz, N−CH_2−CH_2−CH−(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.48, $CDCl_3$, room temp): δ 190.94 (*C*S), 115.31 (*C*H allyl), 57.69 (*C*H_2 allyl), 57.19, 47.74 (N−*C*H_2−), 37.63, 36.87 (N−CH_2−*C*H_2−), 26.59, 26.30 (N−CH_2−CH_2−*C*H), 22.77, 22.40 (N−CH_2−CH_2−CH−(*C*H_3)$_2$). ^{195}Pt{^{1}H} NMR (64.23 MHz, $CDCl_3$, room temp): δ 250. Anal. Calcd for $C_{27}H_{50}N_4PdPtS_4$ (MW 860.46): C, 37.69; H, 5.86; N, 6.51. Found: C, 37.73; H, 5.92; N, 6.43. Yield: 76%.

2a$_3$. ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp): δ 8.10 (d, 2H, J_o = 5.70 Hz, pyridyl *H*^{6}), 7.80 (m, 2H, pyridyl *H*^{4}), 7.78 (m, 2H, pyridyl *H*^{3}), 7.51 (d, 2H, J_o = 7.20 Hz, phenyl *H*$^{3'}$), 7.12 (m,

(29) Hurd, R. N.; De La Mater, J.; McEleheny, G. C.; Tuner, R. J.; Wallingford, W. H. *Org. Chem.* **1961**, *26*, 3980−3987.
(30) Kukushkin, Y. N.; Viaz'menskii, Y. E.; Zorina, L. I. *Russ. J. Inorg. Chem.* **1968**, 835−838.

2H, pyridyl H^5), 6.84 (t, 2H, J_o = 7.20 Hz, phenyl $H^{4'}$), 6.73 (t, 2H, J_o = 7.20 Hz, phenyl $H^{5'}$), 6.09 (d, 2H, J_o = 7.20 Hz, phenyl $H^{6'}$), 3.55 (t, 4H, N−CH_2−, far from rhodium), 3.50−3.39 (m, 4H, N−CH_2−, near to rhodium), 1.67−1.13 (m, 8H, N−CH$_2$−CH_2−), 1.07−0.95 (m, 4H, N−CH$_2$−CH$_2$−CH−), 0.88 (d, 12H, $^3J_{HH}$ = 6.70 Hz, N−CH$_2$−CH$_2$−CH−(CH_3)$_2$, far from rhodium), 0.41, 0.37 (2d, 12H, $^3J_{HH}$ = 6.70 Hz, N−CH$_2$−CH$_2$−CH−(CH_3)$_2$, near rhodium). ^{13}C{^{1}H} NMR (75.48 MHz, CDCl$_3$, room temp): δ 185.09, 180.16 (*C*S), 170.63 (phenyl $C^{1'}$), 165.58 (pyridyl C^2), 150.17 (pyridyl C^6), 143.29 (phenyl $C^{2'}$), 137.08 (pyridyl C^4), 132.24 (phenyl $C^{6'}$), 129.56 (phenyl $C^{5'}$), 123.50 (phenyl $C^{3'}$), 122.50 (pyridyl C^5), 122.35 (phenyl $C^{4'}$), 118.73 (pyridylC^3), 53.37, 47.74 (N−*C*H$_2$−), 37.70, 34.65 (N−CH$_2$−*C*H$_2$−), 26.37 (N−CH$_2$−CH$_2$−*C*H−), 22.48, 22.00 (N−CH$_2$−CH$_2$−CH−(*C*H$_3$)$_2$). ^{195}Pt{^{1}H} NMR (64.23 MHz, CDCl$_3$, room temp): δ 266. Anal. Calcd for $C_{46}H_{61}N_6PtRhS_4$ (MW 1124.27): C, 49.14; H, 5.47; N, 7.48. Found: C, 48.93; H, 5.52; N, 7.43. Yield: 72%.

2a$_4$. ^{1}H NMR (300.13 MHz, CDCl$_3$, room temp): δ 3.93 (bs, 4H, COD C*H*), 3.58 (t, 4H, N−CH_2−, far from rhodium), 3.06 (m, 4H, N−CH_2−, near rhodium), 2.43 (m, 4H, COD CH_2), 1.86 (m, 4H, COD CH_2), 1.65−1.50 (m, 12H, N−CH$_2$−CH_2−CH−), 0.91−089 (m, 24H, N−CH$_2$−CH$_2$−CH−(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.48, CDCl$_3$, room temp): δ 192.35, 179.85 (*C*S), 82.88 (d, J_{RhC} = 12.08 Hz, *C*H COD), 50.54, 47.76 (N−*C*H$_2$−), 37.68, 35.63 (N−CH$_2$−*C*H$_2$−), 30.68 (*C*H$_2$ COD), 27.04, 26.31 (N−CH$_2$−CH$_2$−*C*H−), 22.53, 22.49 (N−CH$_2$−CH$_2$−CH−(*C*H$_3$)$_2$). ^{195}Pt{^{1}H} NMR (64.23 MHz, CDCl$_3$, room temp): δ 243. Anal. Calcd for $C_{32}H_{57}N_4PtRhS_4$ (MW 924.07): C, 41.59; H, 6.22; N, 6.06. Found: C, 41.70; H, 6.23; N, 5.99. Yield: 71%.

2a$_5$. ^{1}H NMR (300.13 MHz, CDCl$_3$, room temp): δ 4.33, 3.69 (two double triplets, 4H, ABX$_2$ spin system, $^2J_{HH}$ = 13.79 Hz, $^3J_{HH}$ = 6.60 Hz, N−CH_2, near rhodium), 3.54 (t, 4H, $^3J_{HH}$ = 6.60 Hz, N−CH_2−, far from rhodium), 1.67 (m, 12H, N−CH$_2$−CH_2−CH−), 1.56 (s, 15H, cyclopentadienyl CH_3), 0.91, 0.88 (2d, 24H, $^3J_{HH}$ = 6.62 Hz, N−CH$_2$−CH$_2$−CH−(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.48, CDCl$_3$, room temp): δ 191.06, 179.90 (*C*S), 94.81 (d, J_{RhC} = 7.40 Hz, cyclopentadienyl ring carbons), 57.02, 47.70 (N−*C*H$_2$−), 37.70, 34.72 (N−CH$_2$−*C*H$_2$−), 27.15, 26.31 (N−CH$_2$−CH$_2$−*C*H−), 22.65, 22.54 (2s, N−CH$_2$−CH$_2$−CH−(*C*H$_3$)$_2$, near rhodium), 22.48 (N−CH$_2$−CH$_2$−CH−(*C*H$_3$)$_2$, far from rhodium), 9.01 (C$_5$(*C*H$_3$)$_5$). ^{195}Pt{^{1}H} NMR (64.23 MHz, CDCl$_3$, room temp): δ 295. Anal. Calcd for $C_{34}H_{60}ClN_4PtRhS_4$ (MW 986.57): C, 41.39; H, 6.13; N, 5.68. Found: C, 41.50; H, 6.19; N, 5.57. Yield: 78%.

General Procedure for the Synthesis of the Trinuclear Heterobimetallic Complexes [Pt{{μ-S$_2$C$_2$(NR)$_2$}ML$_n$}$_2$] (ML$_n^+$ = [Ru(p-cymene)Cl]$^+$, R = isoamyl (3a$_1$), benzyl (3b$_1$), methyl (3c$_1$); ML$_n^+$ =[(η^3-allyl)Pd]$^+$, R = isoamyl (3a$_2$); ML$_n^+$ = [Rh(phpy)$_2$]$^+$, R = isoamyl (3a$_3$); ML$_n^+$ = [Rh(COD)]$^+$, R = isoamyl (3a$_4$); ML$_n^+$ = [Rh(C$_5$Me$_5$)Cl]$^+$ (3a$_5$)). [Pt{*S*-S$_2$C$_2$(NR)$_2$H}$_2$] (1 mmol) was added to a solution of [ML$_n$Cl]$_2$ (1 mmol) in chloroform−methanol (10/1 v/v, 40 mL). After the mixture was refluxed for 0.5 h, the solution was concentrated to 10 mL and purified by chromatography on alumina with a mixture chloroform−petroleum ether (4/1, v/v) as eluent. The products was obtained by precipitation from the addition of petroleum ether 40/60 (about 100 mL) to a concentrated portion (about 10 mL) of eluates.

3a$_1$, **3b$_1$**, **3c$_1$**, and **3a$_5$** were isomeric mixtures in which one of the two isomers (cis or trans) appeared as a major component. For these compounds, a further column chromatography in which only the first fraction of the eluate was collected to give a pure isomer.

3a$_1$. ^{1}H NMR (300.13 MHz, CDCl$_3$, room temp): δ 5.33, 5.09 (2d, 8H, unresolved AA′XX′ spin system, cymene ring protons), 4.37, 3.85 (2m, 8H, ABX$_2$ spin system, $^2J_{HH}$ = 11.28 Hz, $^3J_{HH}$ = 5.20 Hz), 2.72 (seven lines, 2H, $^3J_{HH}$ = 5.20 Hz, cymene C*H*−(CH$_3$)$_2$), 2.20 (s, 6H, cymene CH_3), 1.90, 1.66 (2m, 12H, N−CH$_2$−CH_2−CH−), 1.16 (d, 12H, $^3J_{HH}$ = 5.20, cymene CH−*(C*H$_3$)$_2$), 0.96 (d, 24H, $^3J_{HH}$ = 6.19, N−CH$_2$−CH$_2$−CH−(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.48 MHz, CDCl$_3$, room temp): δ 189.67 (*C*S), 103.32, 100.64 (cymene $C^{1,4}$), 84.29, 83.37 (cymene $C^{2,3,5,6}$), 60.96 (N−*C*H$_2$−), 34.92 (N−CH$_2$−*C*H$_2$−), 31.20 (cymene *C*H−(CH$_3$)$_2$), 27.00 (N−CH$_2$−CH$_2$−*C*H−), 22.68 (cymene CH−(*C*H$_3$)$_2$), 22.60 (N−CH$_2$−CH$_2$−CH−(*C*H$_3$)$_2$), 18.95 (cymene *C*H$_3$). ^{195}Pt{^{1}H} NMR (64.23 MHz, CDCl$_3$, room temp): δ 510. Anal. Calcd for $C_{44}H_{72}Cl_2N_4PtRu_2S_4$ (MW 1253.47): C, 42.16; H, 5.79; N, 4.47. Found: C, 42.35; H, 5.62; N, 4.50. Yield: 35%.

3b$_1$. ^{1}H NMR (300.13 MHz, CDCl$_3$, room temp): δ 7.54−7.27 (m, 20H, phenyl protons), 5.67, 5.01 (2d, 4H, AB spin system), 4.80, 4.65 (2d, unresolved AA′XX′ spin system, 8H, cymene ring protons), 2.05 (seven lines, 2H, $^3J_{HH}$ = 6.96 Hz, cymene C*H*−(CH$_3$)$_2$), 1.89 (s, 6H, cymene CH_3), 0.88 (d, 12H, cymene CH−(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.48 MHz, CDCl$_3$, room temp): δ 189.11 (*C*S), 136.91 (phenyl *q*-Ph), 128.62−127.75 (*o*,*m*,*p*-Ph), 96.05, 90.80 (cymene $C^{1,4}$), 81.87, 81.80 (cymene $C^{2,3,5,6}$), 65.40 (N−*C*H$_2$−), 30.76 (cymene *C*H−(CH$_3$)$_2$), 22.54 (cymene CH−(*C*H$_3$)$_2$), 18.98 (cymene *C*H$_3$). ^{195}Pt{^{1}H} NMR (64.23 MHz, CDCl$_3$, room temp): δ 520. Anal. Calcd for $C_{52}H_{56}Cl_2N_4PtRu_2S_4$ (MW 1333.43): C, 46.84; H, 4.23; N, 4.20. Found: C, 46.80; H, 4.42; N, 4.30. Yield: 30%.

3c$_1$. ^{1}H NMR (300.13 MHz, CDCl$_3$, room temp): δ 5.42, 5.08 (2d, unresolved AA′XX′ spin system, 8H, cymene ring protons), 3.73 (s, 12H, N−CH_3), 2.67 (seven lines, 2H, $^3J_{HH}$ = 6.61 Hz, cymene C*H*−(CH$_3$)$_2$), 2.20 (s, 6H, cymene CH_3), 1.15 (d, 12H, $^3J_{HH}$ = 6.61 Hz, cymene CH−(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.48 MHz, CDCl$_3$, room temp): δ 189.46 (*C*S), 103.04, 102.36 (cymene $C^{1,4}$), 84.89, 83.38 (cymene $C^{2,3,5,6}$), 48.92 (N−*C*H$_3$), 31.40 (cymene *C*H−(CH$_3$)$_2$), 22.52 (cymene CH−(*C*H$_3$)$_2$), 19.04 (cymene *C*H$_3$). ^{195}Pt{^{1}H} NMR (64.23 MHz, CDCl$_3$, room temp): δ 550. Anal. Calcd for $C_{28}H_{40}Cl_2N_4PtRu_2S_4$ (MW 1029.03): C, 32.68; H, 3.92; N, 5.44. Found: C, 32.65; H, 4.02; N, 5.59. Yield: 28%.

3a$_2$. ^{1}H NMR, ^{13}C NMR, and analysis already reported.[3] ^{195}Pt{^{1}H} NMR (64.23 MHz, CDCl$_3$, room temp): δ 381.

3a$_3$. ^{1}H NMR (300.13 MHz, CDCl$_3$, room temp): δ 8.16 (d, 4H, J_o = 6.00 Hz, pyridine H^6), 7.81 (m, 8H, pyridine H^{3,4}), 7.53 (d, 4H, J_o = 7.50 Hz, phenyl H$^{3'}$), 7.14 (m, 4H, pyridine H^5), 6.85 (m, 4H, phenyl H$^{4'}$), 6.74 (m, 4H, phenyl H$^{5'}$), 6.11 (d, 4H, J_o = 7.30 Hz, phenyl H$^{6'}$), 3.44 (m, 8H, N−CH_2−), 1.23 (m, 8H, N−CH$_2$−CH_2−), 1.01 (m, 4H, N−CH$_2$−CH$_2$−CH−), 0.37, 0.34, 0.33 (4d, two overlapped, 24 H, $^3J_{HH}$ = 6.47 Hz, N−CH$_2$−CH$_2$−CH−(CH_3)$_2$, meso and rac isomers). ^{13}C{^{1}H} NMR (75.48 MHz, CDCl$_3$, room temp): δ 186.12 (*C*S), 170.70 (phenyl $C^{1'}$), 165.23 (pyridine C^2), 150.24 (pyridine C^6), 143.23 (phenyl $C^{2'}$), 136.80 (pyridine C^4), 132.20 (phenyl $C^{6'}$), 129.30 (phenyl $C^{5'}$), 123.30 (phenyl $C^{3'}$), 122.20 (pyridine C^5), 122.00 (phenyl $C^{4'}$), 118.50 (pyridine C^3), 53.27 (N−*C*H$_2$−), 34.50 (N−CH$_2$−*C*H$_2$−), 26.30 (N−CH$_2$−CH$_2$−*C*H−), 22.80, 22.00 (N−CH$_2$−CH$_2$−CH−(*C*H$_3$)$_2$). ^{195}Pt{^{1}H} NMR (64.23 MHz, CDCl$_3$, room temp): δ 413, 414 (meso and rac isomers). Anal. Calcd for $C_{68}H_{76}N_8PtRh_2S_4$ (MW 1534.56): C, 53.22; H, 4.99; N, 7.30. Found: C, 53.29; H, 5.02; N, 7.41. Yield: 70%.

3a$_4$. ^{1}H NMR (300.13 MHZ CDCl$_3$): δ 3.90 (broad singlet, 8H, COD C*H*), 3.08 (m, 8H, N−CH_2), 2.41 (m, 8H, COD CH_2), 1.84 (m, 8H, COD CH_2), 1.54 (m, 12H, N−CH$_2$−CH_2−CH−), 0.86 (d, 24H, $^3J_{HH}$ = 6.10 Hz, N−CH$_2$−CH$_2$−CH−(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.48 MHz, CDCl$_3$, room temp): δ 194.43 (*C*S), 82.88 (d, J_{Rh-C} = 12.08 Hz, COD *C*H), 50.44 (N−*C*H$_2$−), 35.62 (N−CH$_2$−*C*H$_2$−), 30.67 (COD *C*H$_2$), 27.01 (N−CH$_2$−CH$_2$−*C*H−), 22.54 (N−

$CH_2-CH_2-CH-(CH_3)_2$). $^{195}Pt\{^1H\}$ NMR (64.23 MHz, $CDCl_3$, room temp): δ 364. Anal. Calcd for $C_{40}H_{68}N_4PtRh_2S_4$ (MW 1534.56): C, 42.36; H, 6.04; N, 4.94. Found: C, 42.38; H, 5.98; N, 5.01. Yield: 79%.

3a$_5$. ^1H NMR (300.13 MHz, $CDCl_3$, room temp): δ 4.36, 3,69 (2m, 8H, ABX_2 spin system, $N-CH_2-$), 1.83−1.63 (m, 12H, $N-CH_2-CH_2-CH-$), 1.59 (s, 30H, cyclopentadienyl CH_3), 0.93 (d, 24H, $^3J_{H-H} = 6.30$ Hz, $N-CH_2-CH_2-CH-(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, room temp): δ 189.81 (*C*S), 94.60 (d, $J_{RhC} = 7.40$ Hz, cyclopentadienyl ring carbons), 56.97 ($N-CH_2-$), 34.73 ($N-CH_2-CH_2-$), 27.14 ($N-CH_2-CH_2-CH-$), 22.71, 22.50 ($N-CH_2-CH_2-CH-(CH_3)_2$), 8.99 (cyclopentadienyl methyl carbons). $^{195}Pt\{^1H\}$ NMR (64.23 MHz, $CDCl_3$, room temp): δ 481. Anal. Calcd for $C_{44}H_{74}Cl_2N_4PtRh_2S_4$ (MW 1259.15): C, 41.97; H, 5.92; N, 4.45. Found: C, 41.80; H, 6.01; N, 4.47. Yield: 77%.

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