ORGANOMETALLICS

A New Cyclometalation Motif: Synthesis, Characterization, Structures, and Reactivity of Pallada- and Platinacycles with a Bidentate $\{C(sp^2,cyrhetrene),N\}^-$ Ligand

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Supporting Information

ABSTRACT: The synthesis, characterization, X-ray crystal structure, and study of the reactivity of the novel cyretrenyl ligand $[\{(\eta^{5}-C_{5}H_{4}-2-C_{5}H_{4}N)\}Re(CO)_{3} (1)$ with $Pd(OAc)_{2}$ or $[MCl_{2}(DMSO)_{2}]$ (M = Pd, Pt) are reported. These studies have allowed us to obtain the bis- μ -ligand cyclopalladated complexes $[Pd\{[\kappa^{2}-C_{n}N-(\eta^{5}-C_{5}H_{3})-2(C_{5}H_{4}N)]Re(CO)_{3}\}(\mu-X)]_{2}$ (X = OAc (2a), Cl (4a)) and monomeric pallada- and platinacycles of the general formula $[M\{[\kappa^{2}-C_{n}N-(\eta^{5}-C_{5}H_{3})-2(C_{5}H_{4}N)]Re(CO)_{3}\}(X)(L)]$ (M = Pd, L = PPh₃, X = OAc (3a), Cl (5a); M = Pd, L = DMSO, X = Cl (6a); M = Pt, X = Cl, L = PPh_{3} (5b), DMSO (6b)), where compound 1 acts as a $\{C(sp^{2},cyrhetrene),N\}^{-}$ bidentate ligand. All complexes were characterized by elemental analyses, infrared spectroscopy, and one- and two-dimensional NMR. The X-ray crystal structures of $5a \cdot 1/_{2}CH_{2}Cl_{2}$, 5b, $6a \cdot CH_{2}Cl_{2}$, and 6b confirm (a) the existence of the five-membered metallacycle, (b) the $\{C(sp^{2},cyrhetrene),N\}^{-}$ mode of binding of



the metallo ligand 1, and (c) the cis arrangement between the metalated carbon and the neutral L ligands (PPh₃ or DMSO) in these products. A comparative study of the structures, spectroscopic properties, and reactivities of the new cyclometalated compounds and those of their analogues with a bidentate $\{C(sp^2, ferrocene), N\}^-$ ligand is also reported.

INTRODUCTION

The synthesis of functionalized half-sandwich rhenium complexes derived from $[(\eta^5 \cdot C_5H_5)Re(CO)_3]$ (cyrhetrene) or $[(\eta^5 \cdot C_5H_5)Re(L^1)(L^2)(L^3)]$ (L¹, L², L³ = neutral monodentate ligands) is one of area of organometallic chemistry now experiencing increasing development.¹⁻⁵ This is mainly due to (a) their interesting and useful photochemical properties and reactivity,^{1,2} (b) their utility in the syntheses of heterodi-, heterotri-, and in general polymetallic organometallic compounds,¹⁻³ and (c) their potential applications in outstanding catalytic chemical processes,⁴ such as hydrogenation of enamines and allylic alkylations.⁴ More recently, cyrhetrenyl—hormone compounds have also been described.⁵

On the other hand, cyclopalladated and cycloplatinated complexes derived from N-donor ligands have attracted great interest for a long time.^{6–12} Most of the articles published so far have focused on complexes with a $\sigma\{M-C(sp^2,aryl)\}$ bond or to a lesser extent a $\sigma\{M-C(sp^3)\}$ bond.^{6–10} More recently, parallel

studies on cyclometalation of N-donor ferrocenyl ligands (i.e., amines, imines, azo derivatives, oximes, oxazines, and oxazolidines) have provided pallada- and platinacycles with $\{C(sp^2, ferrocene),N\}^-$ ligands.^{8b,c,11,12} Some of these products exhibit outstanding chemical and physical properties, catalytic and/or antitumoral activities,^{8b,c} and interesting applications in different fields, including their utility as precursors in organometallic synthesis^{12e,13} or even in the design of molecular machines (i.e., pH-based molecular switches).^{12c}

Despite these facts and the prochiral nature of the cyrhetrenyl unit in the cyclometalation process, 9f,14 examples of pallada- and platinacycles containing a bidentate {C(sp²,cyrhetrene),X}⁻ (X = N, P, S, O) ligand are extremely scarce.¹⁵ Only two types of palladacycles have been described¹⁵ (Figure 1), and in both cases the two donor atoms of the {C(sp²,cyrhetrene),P}⁻ unit belong to

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two different ligands of the rhenium complex. Furthermore, related platinum(II) complexes still remain unknown.

In view of these findings and due to our present interest in (a) cyrhetrene derivatives^{3,16} and (b) pallada- and platinacycles with bi- or terdentate ligands ({C(sp²,ferrocene,N)}⁻ and {C(sp², ferrocene),N,X}⁻, respectively),^{12,13c,17} we decided to prepare the novel cyrhetrene derivatives [$(\eta^{5}-C_{5}H_{4}R)Re(CO)_{3}$] with R groups having an additional heteroatom (such as N) with good donor ability and the proper orientation so as to allow the formation of metallacycles with {C(sp²,cyrhetrene),N}⁻ ligands.

Here, we report our first contribution in this field and in particular (a) the syntheses and characterization of the new cyrhetrene derivative [{(η^{5} -C₅H₄)-2-(C₅H₄N)}Re(CO)₃] (1), bearing a pyridyl group, (b) a new class of pallada- and platinacycles in which 1 behaves as a {C(sp²,cyrhetrene),N}⁻ ligand, and (c) a comparative study of the properties of these new metallacycles and those of their analogues with a {C(sp²,ferrocene),N}⁻ ligand.

RESULTS AND DISCUSSION

The Ligand $\{(\eta^5-C_5H_4)-2(C_5H_4N)\}$ Re(CO)₃ (1). The preparation of this product was carried out in one pot, following a strategy similar to that reported for di-, tri-, and tetraferrocene arenes.¹⁸ The method consisted of the sequence of reactions A-C depicted in Scheme 1. In the first step, cyrhetrene was easily converted into its lithium derivative by treatment with *n*-butyllithium (Scheme 1, step A). The subsequent reaction with ZnCl₂ produced the Zn(II) derivative (Scheme 1, step B), and finally a cross-coupling reaction of the product formed with 2-bromopyridine in the presence of catalytic amounts of [PdCl₂-(PPh₃)₂] gave, after workup, compound 1 in fairly good yield (88%) (Scheme 1, step C).

Elemental analysis of 1 agreed with the proposed formula, and its ESI⁺ mass spectrum showed a peak at m/z 414, which is consistent with the value expected for the cation $\{[M] + H\}^+$. The IR spectrum exhibited two intense bands at 2023 and 1929 cm⁻¹,



Figure 1. Mono- and dinuclear palladacycles derived from half-sandwich rhenium complexes described previously (X = Cl, Br, I and L = neutral ligand such as PR_3).¹⁵

Scheme 1^a

which are characteristic of the terminal CO ligands of related rhenium complexes. 16

The X-ray crystal structure of 1 confirmed the existence of molecules of $[\{(\eta^5\text{-}C_5\text{H}_4)\text{-}2(C_5\text{H}_4\text{N})\}\text{Re}(\text{CO})_3]$ (Figure 2) with the expected three-legged piano-stool structure and the presence of a pyridyl unit attached to the $C_5\text{H}_4$ ring. Average values of the Re–CO (1.908(6) Å) and C–O (1.147(2) Å) bond lengths and the Re–centroid distance (1.961(6) Å) are similar to those reported for $[\{(\eta^5\text{-}C_5\text{H}_4)\text{CH}_2\text{NH}(\text{C}_6\text{H}_4\text{-}4\text{-}\text{OCH}_3)\}\text{-}\text{Re}(\text{CO})_3]$ (1.904 Å).^{16a}

The C_5H_4N ring is planar and forms an angle of 9.6° with the (C_5H_4) cycle; its bond lengths and angles agree with those reported for complexes containing a 2-substituted pyridyl group.¹⁹

In the crystal, two proximal molecules of **1** are connected by two weak intermolecular N···H interactions (the distance N···H(2) is 2.739 Å), giving dimers. The assembly of these units through C–H···O contacts^{20–22} and C–H··· π intermolecular interactions^{20,23} results in a three-dimensional network.^{20,23}

Compound 1 was also characterized in solution by NMR experiments. The assignment of all signals detected in the ¹H and ¹³C{¹H} NMR spectra was achieved with the aid of twodimensional { $^{1}H-{}^{1}H$ } NOESY, { $^{1}H-{}^{13}C$ } HSQC and HMBC experiments. The ¹H NMR spectrum of 1 in CDCl₃ at 298 K exhibited (a) the typical pattern of monosubstituted cyrhetrene derivatives¹⁶ and (b) a group of four signals due to the pyridyl



Figure 2. ORTEP diagram of $[\{(\eta^5-C_5H_4)-2(C_5H_4N)\}Re(CO)_3](1)$. Hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and bond angles (in deg): Re(1)-G^{*}, 1.969; C(1)-C(9), 1.453(8); C(2)-C(1), 1.422(7); C(2)-C(1)-C(9), 125.7(5); C(5)-C(1)-C(9), 128.0(5); N(1)-C(9)-C(1), 116.3(5); C(3)-C(2)-C(1), 109.3(5); C(2)-C(1)-C(5), 105.9(5).



^a Legend: (i) in THF, n-butyllithium at -78 °C for 1.5 h; (ii) ZnCl₂ for 1.5 h; (iii) [PdCl₂(PPh₃)₂] and 2-bromopyridine for 1.5 h.

moiety in the same region as those reported by Butler et al.²⁴ for the ferrocene analogue.

The ¹³C{¹H} NMR spectrum of 1 showed (a) three signals in the range 80.0 < δ < 110.0 ppm, the least intense of which (at δ

Scheme 2^{*a*}



^{*a*} Legend: (i) $Pd(OAc)_2$ in HOAc, reflux for 24 h; (ii) PPh_3 in $CDCl_3$ for 3 min; (iii) NaCl in CH_2Cl_2/H_2O for 12 h; (iv) PPh_3 in benzene for 12 h; (v) $[MCl_2(DMSO)_2]$ (M = Pd(II), Pt(II)), in toluene, reflux for 12 h.

105.3) corresponds to the ipso carbon (C¹) of the C₅H₄ ring, (b) a singlet at $\delta \sim 194$ (due to the CO ligands), and (c) a group of resonances between 115 and 155 ppm assigned to the carbon-13 nuclei (C⁹-C¹³) of the 2-substituted pyridyl group.

Study of the Reactivity of 1 with Palladium(II) Salts or Complexes. In a first attempt to evaluate the binding ability of compound 1 toward palladium(II) and to elucidate if the activation of the σ {C(sp²,cyrhetrene)-H} bond could be induced by palladium(II) salts or complexes, we decided to use one of the most common procedures described for the cyclopalladation of N-donor ligands.^{6a,25} This method consists of the reaction between the ligand and Pd(OAc)₂ in acetic acid. Treatment of 1 with an equimolar amount of Pd(OAc)₂ in refluxing glacial acetic acid for 24 h gave, after workup, a brown solid (hereafter referred to as 2a) (Scheme 2, step A).

Elemental analyses of **2a** agreed with those expected for the cyclopalladated complex $[Pd\{[\kappa^2-C_rN-(\eta^5-C_5H_3)-2-(C_5H_4N)]]$ -Re(CO)₃ $\}(\mu$ -OAc)]₂. In the IR spectrum of **2a**, the separation between the bands due to the asymmetric and symmetric stretchings of the carboxylato moiety (at 1563 and 1415 cm⁻¹),²⁶ suggested, according to the bibliography,^{25,26} that the OAc⁻ groups behaved as a O,O' bridging ligands. All these findings, as well as the ESI⁺ mass spectrum of **2a**, agreed with data expected for $[Pd\{[\kappa^2-C_rN-(\eta^5-C_5H_3)-2(C_5H_4N)]Re(CO)_3\}(\mu$ -OAc)]₂, in which **1** adopted a {C(sp²,cyrhetrene),N}⁻ mode of binding. To the best of our knowledge, palladacycles with this type of bidentate ligand have not been described yet.

The ¹H NMR spectra of **2a** in acetone- d_6 at 298 K showed two sets of superimposed signals (Figure 3), thus suggesting the coexistence of two isomeric species (**2a**_I and **2a**_{II}) in solution. Variable-temperature NMR experiments revealed that the relative abundance of **2a**_I and **2a**_{II} did not change substantially on cooling (molar ratios **2a**_I:**2a**_{II} = 2.50 (at 298 K) and 2.56 (at 188 K)).



Figure 3. ¹H NMR spectrum (500 MHz) of $[Pd{[\kappa^2-C_rN-(\eta^5-C_5H_3)-2(C_5H_4N)]Re(CO)_3}(\mu-OAc)]_2$ (**2a**) in acetone- d_6 at 298 K, showing the two sets of superimposed signals ascribed to the two isomers **2a**₁ and **2a**₁, together with an expansion of the region 6.8 < δ < 8.3 ppm. Labeling of the peaks refers to the numbers assigned to the protons in Scheme 2, and the labels in italics correspond to the minor isomer present in solution (**2a**₁₁).

It is well-known that dimeric cyclopalladated complexes with bridging OAc⁻ groups may exhibit different isomeric forms depending on the relative arrangement of the halves of the molecule (cis or trans).^{25–27} Furthermore, the activation of one of the σ {C(sp²,cyrhetrene)-H} bonds on the ortho sites of 1 induces planar chirality.^{9f,14}

The $\{{}^{1}H-{}^{1}H\}$ NOESY spectrum of 2a revealed that $2a_{I}$ and $2a_{II}$ (a) adopted an open-book type structure (Chart 1) and (b) differed in the relative disposition of the two $\{C(sp^{2},cyr)$ multiplication (trans in $2a_{I}$ and cis in $2a_{II}$). However, no evidence of the interconversion $2a_{I} \rightleftharpoons 2a_{II}$ was detected.

Unfortunately attempts to separate $2a_I$ and $2a_{II}$ failed and only a poor-quality crystal was isolated. Despite this, X-ray diffraction studies²⁸ (Figure 4) confirmed the trans arrangement of the halves of the molecule and the open-book-like structure of the product. This is the most common arrangement of ligands found in palladacycles of the type $[Pd(C_rN)(\mu-OAc)]_2$.^{19,27}



When the crystal used for the X-ray studies was dissolved in acetone- d_6 , its ¹H NMR spectrum was identical with that of the crude product **2a**, indicating the presence of **2a**_I and **2a**_{II} in solution. It is well-known that the planar chirality of enantio- or diastereomerically pure complexes with {C(sp²,ferrocene),N}⁻ ligands and 1,2-disubstituted η^5 -C₅H₃ rings remains in solution. ¹⁷h_i,^{29,30} Thus, the formation of **2a**_{II} upon dissolution of the single crystal should be related to other factors. Previous studies on related palladacycles have demonstrated that the coexistence of isomers in solution is generally due to a trans \leftrightarrows cis isomerization of the dinuclear products.^{25,27}

Treatment of **2a** with PPh₃ (in the molar ratio PPh₃:**2a** = 2) produced [Pd{[κ^2 -*C*,*N*-(η^5 -C₅H₃)-2-(C₅H₄N)]Re(CO)₃}(OAc)-(PPh₃)] (**3a**) (Scheme 2, step **B**). Its ³¹P{¹H} NMR showed a singlet at δ 34.7. This chemical shift is indicative of a cis arrangement between the phosphine and the metalated carbon atom (C²), in good agreement with the so-called *transphobia effect.*³¹

When a CH₂Cl₂ solution of **2a** was treated with an excess of NaCl (in H₂O), a brown solid formed. It was identified as the di- μ -chloro derivative [Pd{[κ^2 -*C*,*N*-(η^5 -C₅H₃)-2-(C₅H₄N)]Re-(CO)₃}(μ -Cl)]₂ (**4a**) (Scheme 2, step C). Compound **4a** is airstable, but it is practically insoluble in the common solvents used for NMR studies. This is the typical behavior of most palladacycles of general formula [Pd{(κ^2 -(*C*,*N*-ligand)}(μ -Cl)]₂, and commonly their NMR spectra are registered in the presence of deuteriated pyridine (py-*d*₅).^{25f,32}

Addition of a slight excess of $py-d_5$ to a suspension of 4a in CDCl₃ at 298 K produced a pale yellow solution. Its ¹H and ³¹C{¹H} NMR spectra suggested the presence of [Pd{[κ^2 -C, $N-(\eta^5$ - C_5 H₃)-2-(C_5 H₄N)]Re(CO)₃}Cl(py-d_5)], which arises from the cleavage of the central "Pd(μ -Cl)₂Pd" ring and the



Figure 4. Molecular structure of the trans isomer $(2a_1)$ of $[Pd\{[\kappa^2-C_5N-(\eta^5-C_5H_3)-2-(C_5H_4N)]Re(CO)_3\}(\mu-OAc)]_2$ (2a).



Figure 5. ORTEP diagram of $[Pd\{[\kappa^2-C_rN-(\eta^5-C_5H_3)-2-(C_5H_4N)]$ -Re(CO)₃ $\}$ Cl(PPh₃)]· $^1/_2$ CH₂Cl₂ (5a· $^1/_2$ CH₂Cl₂). The solvate molecule and hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Pd(1)-C(2), 1.992(5); Pd(1)-N(1), 2.131(4); Pd(1)-P(1),2.254(13); Pd(1)-Cl(1), 2.371(13); C-(1)-C(9), 1.444(7); N(1)-Pd-Cl(1), 91,61(11); C(2)-Pd(1)-N(1), 81,59(17); C(2)-Pd(1)-P(1), 97.84(13); Cl(1)-Pd(1)-P(1), 88.97(5); C(2)-C(1)-C(9) 119.8(4); C(5)-C(1)-C(9), 131.0(5); N(1)-C(9)-C(1), 113.1(4).

incorporation of the py- d_s ligand in a cis arrangement with regard to the metalated carbon.

Treatment of a suspension of **4a** in benzene with PPh₃ (in the molar ratio phosphine: **4a** = 2; Scheme 2, step **D**) produced, after recrystallization, [Pd{[κ^2 -C,N-(η^5 -C₅H₃)-2-(C₅H₄N)]Re(CO)₃}-Cl(PPh₃)]·¹/₂CH₂Cl₂ (**5a**·¹/₂CH₂Cl₂). Characterization data (see the Experimental Section) agreed with the proposed formula, and its X-ray crystal structure confirmed the existence of [Pd{[κ^2 -C,N-(η^5 -C₅H₃)-2-(C₅H₄N)]Re(CO)₃}Cl(PPh₃)] (**5a**) and CH₂Cl₂ molecules in a 2:1 molar ratio. In **5a** (Figure 5), the palladium(II) is in a slightly distorted square-planar environment, ³³ bound to the N and the C(2) atoms of the cyrhetrenyl moiety. This confirms (a) the {C(sp²,cyrhetrene),N}⁻ mode of binding of **1** in the complex and (b) the existence of a five-membered metallacycle. This cycle is practically planar and forms angles of 5.2 and of 3.4° with the C₅H₃ unit and the pyridyl ring, respectively.

The two remaining coordination sites are occupied by a chloride (Cl(1)), and the phosphorus of the PPh₃ ligand. Bond lengths and angles around the palladium fall in the range expected for most palladacycles with "Pd{(C,N),Cl,P}" cores.^{17fg,19,30} The value of the C(2)–Pd–P bond angle (97.84(13)°)} confirms the cis arrangement between the C(2) atom and the neutral ligand, in good agreement with the conclusions reached by NMR and the transphobia effect.³¹

In the crystal, there are two weak C–H···Cl intermolecular interactions between the hydrogen atoms of the CH₂Cl₂ and the Cl⁻ ligands of two different units of **5a** (distance Cl(1)····H(32A) = 2.634 Å)³⁴ and C–H····O contacts between the pair of oxygen atoms O(2) and O(3) of a molecule at (*x*, *y*, *z*) and two hydrogen atoms (H(11) and H(21)) of vicinal units at (-x, 2 - y, -z) and $(^{1}/_{2} - x, ^{1}/_{2} - y, ^{1}/_{2} - z)$, respectively. The activation of the σ {C(sp²,cyrhetrene)–H} bond was also

The activation of the σ {C(sp²,cyrhetrene)-H} bond was also achieved by reaction of equimolar amounts of 1, [PdCl₂(DMSO)₂],



Figure 6. ORTEP diagram of $[Pd\{[\kappa^2-C_N.(\eta^5-C_5H_3)-2-(C_5H_4N)]]$ -Re(CO)₃Cl(DMSO)] (6a). Hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Pd-C(2), 1.979(3); Pd-N, 2.091(3); Pd-S, 2.2283(12); Pd-Cl, 2.3964(13); C(1)-C(9), 1.455(5); C(2)-Pd-N, 80.93(14); N-Pd-Cl, 95.21(10); C(2)-Pd-S, 94.63(11); Cl-Pd-S, 90.12(5); C(1)-C(2)-C(3), 107.0(7); C(2)-C(1)-C(9), 118.3(3); C(1)-C(9)-N, 112.0(5).

O(2)

and NaOAc·3H₂O in refluxing toluene for 12 h (Scheme 2, step E). Characterization data of the yellowish crystalline solid isolated agreed with those expected for $[Pd\{[\kappa^2-C_N-(\eta^5-C_5H_3)-2-(C_5H_4N)]Re(CO)_3\}Cl(DMSO) \cdot CH_2Cl_2]$ (6a·CH₂Cl₂). In the heterodimetallic units (6a) (Figure 6) the palladium(II) is bound to the C(2) and N atoms of 1. The difference between the Pd-C(2) bond lengths in 6a (1.979(11) Å) and 5a (1.992(5) Å) does not clearly exceed 3 σ , while the variation of the Pd-N bond length (2.091(3) Å in 6a and 2.131(4) Å in 5a) can be attributed to the different trans influences of the neutral ligands (L = PPh₃ (in 5a), DMSO (in 6a)). The sulfur atom of the DMSO occupies the coordination site adjacent to the Pd-C(2) bond, and a Cl⁻ ligand fullfils the coordination sphere. The Pd-Cl bond length (2.3964(13) Å) is similar to that found in $[Pd\{[\kappa^2-C_N-(2,4-Me_2-C_6H_2)CH=NNHC(O)C_6H_5)\}Cl(DMSO)].^{35}$

The relative arrangement of the three rings forming the [5.5.6] tricyclic system is similar to that of **5a** (the mean plane of the C_5H_3 ring forms angles of 5.2 and 7.9° with those of the metallacycle and the pyridyl unit, respectively).

In the crystal state molecules of **6a** are connected by weak $C-H\cdots O$ interactions²⁰ between the O(4) and the H(15A) atoms of close units. In addition to that, there are short $C-H\cdots$. Cl contacts between the peripheral atoms of the CH_2Cl_2 and units of **6a**.²⁰

It should be noted that since crystals of $5a \cdot {}^{1}/{}_{2}CH_{2}Cl_{2}$ and $6a \cdot CH_{2}Cl_{2}$ are centrosymmetric, they contain a mixture of the two enantiomers S_{p} and R_{p} . This is consistent with the absence of any factor inducing chirality in the reaction medium.

¹H and ¹³C{¹H} NMR data of **5a** are presented in the Experimental Section. The position of the singlet detected in its ³¹P{¹H} NMR spectrum (at δ 33.9) is similar to that of **3a**



Figure 7. ORTEP diagram of $[Pt\{[\kappa^2-C,N-(\eta^5-C_5H_3)-2-(C_5H_4N)]Re-$ (CO)₃}Cl(DMSO)] (6b). Hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Pt-C(2), 1.995(6); Pt-N, 2.102(5); Pt-S, 2.203(2); Pt-Cl(1), 2.386(2); C(1)-C(9), 1.476(10); C(2)-Pt-N, 80.6(2); N-Pt-Cl(1), 93.91(16); C(2)-Pt-S, 95.01(19); Cl(1)-Pt-S, 90.40(8); 105.5(5); C(2)-C(1)-C(9), 116.6(5); C(11)-C(9)-N, 113.2(5).

(δ 34.7). These signals are shifted upfield in comparison with those of $[Pd\{C(sp^2, ferrocene), N\}(X)(PPh_3)]$ complexes $(X = OAc^-, Cl^- (37.0 < \delta < 39.0))^{17f, 30, 36}$ but fall in the range reported for palladacycles with terdentate ligands $\{C(sp_{i}^{2}, ferrocene), N, E\}^{q}$ (q = -1 (for E = N, S, O), -2 (for E = O)).^{17b,37}

When the reaction was performed in the absence of NaOAc· 3H₂O under identical experimental conditions, the formation of 6a was also detected but the yield decreased from 78 to 56%.

 $[Pd{[\kappa^2-C,N-(\eta^5-C_5H_3)-2-(C_5H_4N)]Re(CO)_3}Cl-$

(DMSO)] (6a) could be easily transformed into 5a by treatment with PPh₃ in benzene at 298 K (Scheme 2, step F). Compound 5a was also obtained from ligand 1 through three consecutive reactions (A, C, and D in Scheme 2, path I). However, the procedure summarized in steps E and F of Scheme 2 (path II) allows the isolation of 5a (a) in shorter reaction periods, (b) with greater yields (global yields 70% (path II) versus 32% (path I)), and (c) in a cheaper way. Thus, the use of cis-[PdCl₂(DMSO)₂] as metalating agent followed by treatment with PPh₃ appears to be the most convenient method for the preparation of 5a.

Study the Reactivity of 1 with Platinum(II) Salts or Complexes. In view of the increasing interest in platinacycles $^{8a-c,10d,12a,12c,17h,17i,37a}$ and the lack of compounds with "Pt{C(sp²,cyrhetrene),N}" cores, we also studied the reactivity of 1 toward platinum(II). For comparison purposes, we decided to follow the same methodology as for the synthesis of 6a (Scheme 2, step E), but using cis-[PtCl₂(DMSO)₂] as starting material. The final product isolated under identical experimental conditions was identified (see below) as $[Pt{[\kappa^2-C_5H_3]} 2-(C_5H_4N)$ [Re(CO)₃ Cl(DMSO)] (6b). Further treatment of 6b with an equimolar amount of PPh₃ in benzene produced $\left[Pt\{ [\kappa^2 - C_5 N - (\eta^5 - C_5 H_3) - 2 - (C_5 H_4 N)] Re(CO)_3 \} Cl(PPh_3) \right] (5b)$ (Scheme 2, step F).



Figure 8. ORTEP diagram of $[Pt\{[\kappa^2 - C_{J}N - (\eta^5 - C_5H_3) - 2 - (C_5H_4N)]Re-$

(CO)₃{Cl(PPh₃)] (5b). Hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Pt-C(2), 1.969(5); Pt-N, 2.127(4); Pt-P, 2.2295(15); Pt-Cl, 2.3814(16); C(1)-C(9), 1.437(7); C(2)-Pt-N, 80.48(18); N-Pt-Cl, 92.42(13); Cl-Pt-P, 86.85(6); C(2)-Pt-P, 100.20(4); C(2)-C(1)-C(9), 116.9(5); C(5)-C(1)-C(9), 134.2(5); C(1)-C(9)-N, 114.7(5).

The crystal structures of **5b** and **6b** confirmed the existence of the heterodimetallic molecules of $[Pt\{[\kappa^2-C_{,N}-(\eta^5-C_5H_3) 2-(C_5H_4N)$ Re(CO)₃ Cl(L) with L= DMSO (in **6b**) or PPh₃ (in **5b**) (Figures 7 and 8, respectively). In compounds **6b** and **5b**, the Pt(II) atom is in a slightly distorted square-planar environment³⁸ and the distribution of ligands is identical with those of their palladium(II) analogues (6a and 5a, respectively).

The Pt–C bonds of **5b** (1.969(5) Å) and **6b** (1.985(6) Å) are a bit shorter than those of $[Pt\{[\kappa^2-C_sN-(\eta^5-C_5H_3)-C(Me)=N(C_6H_4-4-Br)]Fe(\eta^5-C_5H_5)\}Cl(PPh_3)]^{39}$ and platinacycles $[Pt{C(sp^{2}, ferrocene), N(sp^{2}, imine)]Cl(DMSO)]}$ (in the range 1.98–2.05 Å), ^{17h,i,40} but the Pt–Cl distance does not vary significantly from the values reported.

The pyridyl ring is planar and nearly coplanar with the 1,2disubstituted η^5 -C₅H₃. cycle as reflected in the values of the torsion angles N-C(9)-C(1)-C(2) (5.08° (in **5b**) and 2.36° (in **6b**)).

In the crystals of 5b two molecules are assembled by weak $C-H \cdot \cdot \cdot Cl$ interactions forming dimers, which are connected by intermolecular C(23)-H(23)····O(2) and C(22)-H(22)··· π interactions, while in **6b** there is a $R_2^2(8)$ hydrogen bond structural motif⁴¹ between the O(4) and H(14C) atoms of two DMSO ligands.

On the other hand, it is well-known that an upfield shift in ¹⁹⁵Pt NMR is related to a strong donor interaction.^{12a,c,17i,42,43} Thus, the differences detected in the ¹⁹⁵Pt chemical shifts of **5b** (δ –4062 (d, $^{1}J_{P-Pt}$ = 4098 Hz)) and 6b (δ - 3664) and those of their analogues $[Pt{C(sp^2, ferrocene), N}Cl(L)]$ (with L = PPh₃ (-4150 > δ > -4300). DMSO $(-3800 > \delta > -3900)$)^{12a,c,17i} can be used as a measure of the different donor abilities of these two types of bidentate ligands $\{C(sp^2, cyrhetrene), N\}^-$ and $\{C(sp^2, ferrocene), N\}^-$ N⁺ in the metallacycles.



Figure 9. UV–visible spectra of the free ligand (1) and the mononuclear cyclometalated complexes 5a and 6a in CH₂Cl₂ at 298 K.

Further treatment of $[M{[\kappa^2-C_sN-(\eta^5-C_5H_3)-2-(C_5H_4N)]}-Re(CO)_3]Cl(PPh_3)]$ (M = Pd (5a), Pt (5b)) with PPh₃ in CH₂Cl₂ or CDCl₃ at 298 K did not produce the opening of the metallacycle and the incorporation of a second PPh₃ molecule in the coordination sphere of the M(II) atom. This behavior, also observed for their analogues containing ferrocenylimines as chelating ligands, suggested that the M–N bond exhibits low lability.

It should be noted that when $[Pd\{[\kappa^2-C_rN-(\eta^5-C_5H_3)-2-(C_5H_4N)]Re(CO)_3\}(\mu-Cl)]_2$ (4a) was treated with MeO₂CC \equiv CCO₂Me (in molar ratios alkyne:4a = 2, 4) in CH₂Cl₂ or CHCl₃ under reflux for 72 h, evidence of the insertion of this alkyne in the σ {Pd-C(sp²,cyrhetrene)} bond was not detected by ¹H NMR spectra of the crude material. This indicated that 4a is less reactive than its analogues with {C(sp²,ferrocene),N}⁻ ligands. Furthermore, attempts to achieve platinum(IV) complexes by treatment of 6b with an excess of CH₃I in refluxing acetone failed, thus showing that in 6b the Pt(II) center is not prone to undergo the oxidative addition process.

Electronic Spectroscopy. It is well-known that some squareplanar platinum(II) complexes are photoluminescent, with emissive states usually arising from intraligand $\pi \rightarrow \pi$ (IL), metal-toligand charge transfer (MLCT), or even ligand-to-ligand charge transfer (LL'CT).⁴⁴ In view of these facts, we also studied the effect produced by the cyclometalation on the spectroscopic properties of the new ligand.

Absorption spectra of CH₂Cl₂ solutions of the free ligand (1) and complexes $[M{[\kappa^2-C_rN-(\eta^5-C_5H_3)-2-(C_5H_4N)]Re(CO)_3}-Cl(L)]$ (M = Pd, Pt and L = PPh₃ (**5a** and **6a**, respectively) or DMSO (**5b** and **6b**)) were also measured at 298 K (Figure 9 and Table 1). The UV-vis spectra of **5a**,**b** and **6a**,**b** (Table 1 and Figure 9) showed a band in the range 300 nm < λ_3 < 400 nm with extinction coefficients between 2.5 × 10³ and 3.0 × 10³ M⁻¹ cm⁻¹ (Table 1). This absorption was not present in the spectrum of the free ligand, and its position was dependent on the nature of the M(II) ion, the neutral L ligand (PPh₃ or DMSO), and the polarity of the solvent (Table 1). This absorption was Table 1. Absorption and Emission Properties of the Free Ligand [{(η^{5} -C₅H₄-2-C₅H₄N)}Re(CO)₃] (1) and the Monomeric Pallada- and Platinacycles [M{[κ^{2} -C₇N-(η^{5} -C₅H₃)-2-(C₅H₄N)]Re(CO)₃}Cl(L)] (M = Pd, Pt and L = PPh₃, DMSO) in CH₂Cl₂ Solution (at 298 K)^{*a*}

			absorpt	absorption spectroscopic data b				
			λ_1	λ_2	λ_3	emission data		
compd	М	L	$(\log \varepsilon_1)$	$(\log \varepsilon_2)$	$(\log \varepsilon_3)$	$\lambda_{ m max}$		
1			229 (3.3)	274 (3.1)		none		
			230 (3.6)	269^{b}				
5a	Pd	PPh ₃	228 (3.7)	245 ^c	316 (2.9)	367		
			227 (3.5)	d	308 (2.7)	е		
5b	Pt	PPh ₃	230 (3.5)	262 (2.9)	342 (2.5)	394		
			231 (3.4)	255 (2.8)	330 (2.2)	е		
6a	Pd	DMSO	229 (3.5)	258 ^c	326 (2.9)	354		
			229 (3.3)	d	312(2.7)	е		
6b	Pt	DMSO	230 (3.1)	263 (2.9)	365 (2.3)	386		
			228 (3.0)	257 (2.6)	353 (2.7)	е		

^{*a*} Wavelengths λ_i (i = 1-3) and λ_{max} are given in nm and extinction coefficient ε_i in M⁻¹ cm⁻¹. ^{*b*} For comparison purposes, absorption spectroscopic data in acetone at 298 K are presented in italics. ^{*c*} Shoulder. ^{*d*} This band was partially overlapped by that at higher energies (λ_1), and its resolution did not allow us to determine accurately the position of the maximum. ^{*e*} Not studied in acetone.

assigned as a metal-to-ligand charge transfer (MLCT) transition from the 4d or 5d orbitals (for M = Pd(II), Pt(II), respectively) to a π orbital of the ligand.

For platinacycles **Sb** and **6b**, two additional bands in the same region as 1 were also observed in the spectra, but for **5a** and **5b**, the band at $\lambda_2 \sim 255$ nm was poorely defined. These absorptions are due to metal-perturbed intraligand charge transfer transitions (MPILCT) ($\pi \rightarrow \pi^*$).

Due to the increasing interest on the photooptical properties of metallacycles, we also studied the potential emissive properties of the free ligand and compounds **5a,b** and **6a,b**. The results obtained (Table 1) revealed that 1 is not luminescent in CH₂Cl₂ solution at 298 K. In contrast with these results, for **5a,b** and **6a,b** the excitation at the corresponding λ_3 produced a weak emission at λ_{max} (in the range $350 \le \lambda_{max} \le 400$ nm, Table 1 and Figure 10). Comparison of data (Table 1) shows that when Pd(II) in **5a** (or **6a**) is replaced by Pt(II) in **5b** (or **6b**), the emission shifts to the lower energy region. This variation is greater than that produced by the neutral ligand (DMSO in **5b** (or **6b**) or PPh₃ in **5a** (or **6a**)). It should be noted that for the four complexes the excitation spectra at this low-energy band (λ_{max}) resemble their corresponding absorption spectra, thus suggesting that the emissive states come from the same absorbing species.

CONCLUSIONS

The new cyrhetrenyl-pyridine ligand [$\{(\eta^5-C_5H_4)-2-(C_5H_4N)\}$ -Re(CO)₃] (1) and the first examples of pallada- (2a-6a) and platinacycles (5b and 6b), with a { $C(sp^2, cyrhetrene),N$ }⁻ ligand have been prepared and characterized. The crystal structures of $5a \cdot {}^1/_2CH_2Cl_2$, $6a \cdot CH_2Cl_2$, 5b, and 6b confirmed (a) the mode of binding of 1 in the complexes, (b) a cis arrangement between the metalated carbon and the neutral ligand (PPh₃ (in 5a and 5b) or DMSO (in 6a and 6b)), and (c) the existence of weak



Figure 10. Emission spectra of compounds 5a,b and 6a,b in CH_2Cl_2 at 298 K.

 $C-H\cdots O$ (in **6b**) and $C-H\cdots Cl$ (in the remaining cases) intermolecular interactions.

We have also proved that (a) compounds $[M{[\kappa^2-C,N-(\eta^5-C_5H_3)-2-(C_5H_4N)]Re(CO)_3}Cl(L)]$ (L = PPh₃ (**5a**,**b**), DMSO (**6a**,**b**)) are not prone to undergo the cleavage of the M–N bond, (b) the $\sigma{Pd-C(sp^2,cyrhetrene)}$ bond of $[Pd{[\kappa^2-C,N-(\eta^5-C_5H_3)-2-(C_5H_4N)]Re(CO)_3}(\mu-Cl)]_2$ (**4a**) is less reactive than the $\sigma{Pd-C(sp^2,ferrocene)}$ bond of complexes arising from the metalation of the ferrocene, and (c) complex **6b** is reluctant to oxidize in the presence of MeI.

Furthermore, the UV-vis spectra of 5a,b and 6a,b in CH₂Cl₂ at 298 K showed a metal-to-ligand charge transfer (MLCT) band in the range $300 \le \lambda_3 \le 400$ nm and excitation at this wavelength (λ_3) produced a weak emission. Despite the fact that these emissive properties are not spectacular, the complexes presented here are attractive in view of their potential utility in a variety of fields. For instance, they are valuable precursors to achieve related metallacycles with improved photooptical properties or reactivity (i.e., by (a) incorporation of ligands such as -CCR or acetylacetonate (that prevent the deactivation of the lowest emitting exciting state⁴⁴) or (b) substitution of one (or more) of the CO ligands of the " $Re(CO)_3$ " moiety, respectively). In addition, they also appear to be excellent candidates for studying not only their catalytic or antitumoral activities but also their interaction with DNA.⁴ Thus, the results presented here constitute the first step of further work centered on these fields. Studies on these areas are currently underway.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under nitrogen using standard Schlenk techniques. All solvents except benzene were purified and dried by conventional methods and distilled under nitrogen prior to use.⁴⁵ The complexes [$(\eta^5-C_5H_5)Re(CO)_3$], [PdCl₂(PPh₃)₂], and [MCl₂(DMSO)₂] (M = Pd, Pt) were prepared by the published procedures,⁴⁶ while the remaining reagents were obtained from Aldrich and used as received. *Caution!* Some of the preparations described here required the use of benzene which should be handled with care.

IR spectra were recorded on a Perkin-Elmer FT-1605 spectrophotometer using KBr pellets (for solid samples) or NaCl disks (for solution studies). Elemental analyses (C, H, N, and S) were carried out at the Serveis Cientifico-Técnics (Universitat de Barcelona). Mass spectra (ESI⁺) were registered at the Servei de Espectrometría de Masses (Universitat de Barcelona) with a LC/MSD-TOF Agilent Technologies instrument. Routine ¹H NMR spectra and ¹³C{¹H} NMR spectra were obtained with a Mercury-400 instrument. High-resolution ¹H NMR spectra and the two-dimensional $({^{1}H}-{^{1}H})$ -NOESY and -COSY, ${^{1}H}-{^{13}C}$ heteronuclear single quantum coherence (HSQC), and heteronuclear multiple bond coherence (HMBC)) NMR experiments were recorded with either a Varian VRX-500 or a Bruker Advance-DMX 500 instrument at 20 °C. The latter instrument was also used for the variabletemperature NMR studies in the range 188-298 K. ³¹P{¹H} NMR spectra of 5a,b were obtained with a Varian 300 MHz instrument at 298 K, and the ¹⁹⁵Pt{¹H} NMR spectra of **5b** and **6b** were measured under identical conditions with a Bruker 250-DXR instrument. The references used were P(OMe)₃ (δ (³¹P) 140.17) and H₂PtCl₆ (δ (¹⁹⁵Pt) 0.0), respectively. In all cases the NMR studies were performed in $CDCl_3$ (99.8%) using SiMe₄ as internal reference, except for 2a, for which the solvent was acetone- d_6 . The chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz.⁴⁷ UV-vis spectra of CH_2Cl_2 solutions of the free ligand 1 and complexes 5a,b and 6a,b were recorded at 298 K with a Cary 100 scan 388 Varian UV spectrometer, and their emission and excitation spectra were obtained on a Horiba Jobin-Yvon SPEX Nanolog-TM spectrofluorimeter at 298 K.

Preparation of the Compounds. $[\{(\eta^5-C_5H_4)-2-(C_5H_4N)\}Re (CO)_3$] (1). A 200 mg amount of $[(\eta^5 - C_5H_5)Re(CO)_3]$ (6.0 × 10⁻⁴ mol) was dissolved in THF (15 mL). The solution was cooled to 175 K, and then 0.63 mL (9.6×10^{-4} mol) of a 1.6 M solution of butyllithium in hexane was added. The mixture was stirred at 175 K for 1.5 h. After this period ZnCl₂ (82 mg, 6.9×10^{-4} mol) was added, and the reaction mixture was warmed to room temperature and then kept stirring for 1.5 h. Afterward $[PdCl_2(PPh_3)_2]$ (21 mg, 3.0×10^{-5} mol) suspended in THF (2 mL) and a solution of 2-bromopyridine (57 μ L, 6.0 \times 10⁻⁵ mol) in THF (2 mL) were added. The mixture was stirred for 1.5 h at room temperature and then poured into water (15 mL), and the residue was extracted with CH2Cl2. The extracts were dried over Na2SO4, filtered through Celite, and evaporated under reduced pressure. The oily residue that formed was chromatographed over silica gel. Elution with a hexane/ CH_2Cl_2 (4/1) mixture produced a band that was collected and concentrated to ca. 3 mL, giving 1 as a white solid. This product was later recrystallized by slow diffusion of hexane into a CH₂Cl₂ solution of 1 at -10 °C (yield 217 mg, 3.8×10^{-4} mol, 88%). Anal. Calcd for C₁₃H₈-NO3Re: C, 37.86; H, 1.96; N, 3.40. Found: C, 37.9; H, 2.1; N, 3.2. MS (ESI⁺) m/z: 414 [M + H]⁺. IR: 2023 (s) and 1929 (vs) cm⁻¹, ν (CO). ¹H NMR: 5.41 (t, 2H, ${}^{3}J_{H-H} = 2.3$, H³ and H⁴); 6.06 (t, 2H, ${}^{3}J_{H-H} = 2.3$, H² and H⁵); 7.15 (m, 1H, H¹²); 7.32 (d, 1H, ${}^{3}J_{H-H} = 8.3$, H¹⁰); 7.62 (dt, 1H, ${}^{3}_{J_{H-H}}$ = 8.0, ${}^{4}_{J_{H-H}}$ = 1.5, H¹¹); 8.51 (d, 1H, ${}^{3}_{J_{H-H}}$ = 4.8, H¹³). 1³C{¹H} NMR: 83.4 (C² and C⁵); 84.7 (C³ and C⁴); 105.3 (C¹); 119.4 (C¹²); 122.9 (C¹⁰); 136.7 (C¹¹); 149.6 (C⁹); 151.2 (C¹³); 193.7 $(C^{6}, C^{7}, and C^{8}).$

 $[Pd\{[\kappa^2-C,N-(\eta^5-C_5H_3)-2-(C_5H_4N)]Re(CO)_3\}(\mu-OAc)]_2$ (2). To a solution of 1 (100 mg, 2.4×10^{-4} mol) in glacial acetic acid (15 mL) was added Pd(OAc)₂ (54 mg, 2.4×10^{-4} mol), and the mixture was refluxed for 24 h. After this period, the brown-black solution was concentrated under vacuum, the residue was extracted with CH2Cl2, and the solution was filtered through Celite. Then the filtrate was concentrated under reduced pressure to ca. 3 mL. Addition of diethyl ether (15 mL) gave a brown solid, which was collected by filtration, washed with two (10 mL) portions of diethyl ether, and dried. Afterward this solid was recrystallized by slow diffusion of hexane into a CH_2Cl_2 solution of 2 at -10 °C (yield 86 mg, 1.5×10^{-4} mol, 62%). Anal. Calcd for $C_{30}H_{20}N_2O_{10}Pd_2$ -Re₂: C, 31.23; H, 1.75; N, 2.43. Found: C, 30.9; H, 1; N, 2.6. MS (ESI⁺) $m/z: 1143.8 \{ [M - CO] + H_2O \}^+; 1084.8 \{ [M - CO - OAc] + H_2O \}^+.$ IR: 2011(s) and 1921 (vs), v(CO); 1563 (m) and 1413 (m) cm⁻ $\nu(-\text{COO})$. Two isomers (2a_I and 2a_{II}) coexisted in acetone-d₆ in the molar ratios $2a_{II}:2a_{II} = 1.00:0.40$ (at 298 K) and 1.00:0.39 (at 188 K).

¹H NMR for $2a_{I}$: 2.83 (s, 6H, 2OAc); 4.92 (dd, 2H, ${}^{3}J_{H-H} = 2.5$, ${}^{4}J_{H-H} =$ 1.0, 2H³); 5.18 (t, 2H, ${}^{3}J_{H-H}$ = 2.5, 2H⁴); 5.83 (dd, 2H, ${}^{3}J_{H-H}$ = 3.0, ${}^{4}J_{H-H} = 1.0, 2H^{5}$; 7.20 (td, 2H, ${}^{3}J_{H-H} = 7.0, {}^{4}J_{H-H} = 1.5, 2H^{12}$); 7.42 (dd, 2H, ${}^{3}J_{H-H} = 8.0$, ${}^{4}J_{H-H} = 0.5$, 2H¹⁰); 7.88 (dt, 2H, ${}^{3}J_{H-H} = 8.0$, ${}^{4}J_{H-H} = 10.5$, 2H¹⁰); 7.88 (dt, 2H, ${}^{3}J_{H-H} = 10.5$, 2H¹⁰); 7.88 (dt, 2H, {}^{3}J_{H-H} = 10.5, 2H¹⁰); 7.88 (dt, 2H, {}^{3}J_{H-H} = 10.5, 2H¹⁰); 7.88 (dt, 2H, {}^{3}J_{H-H} = 10.5, 2 1.5, $2H^{11}$); 8.22 (ddd, 2H, ${}^{3}J_{H-H} = 5.5$, ${}^{4}J_{H-H} = 1.5$, ${}^{5}J_{H-H} = 1.0$, $2H^{13}$). ¹H NMR for **2a_{II}**: 2.05 (s, 3H, OAc); 2.12 (s, 3H, OAc); 5.10 (dd, 2H, ${}^{3}J_{H-H} = 2.5, {}^{4}J_{H-H} = 1.0, 2H^{3}$; 5.39 (t, 2H, ${}^{3}J_{H-H} = 2.5, 2H^{4}$); 6.06 (dd, 2H, ${}^{3}J_{H-H} = 2.7$, ${}^{4}J_{H-H} = 1.2$, $2H^{5}$); 6.98 (td, 2H, ${}^{3}J_{H-H} = 6.6$, ${}^{4}J_{H-H} = 1.3$, $2H^{12}$; 7.36 (ddd, 2H, ${}^{3}J_{H-H} = 8.0$, ${}^{4}J_{H-H} = 1.0$, ${}^{5}J_{H-H} = 0.5$, $2H^{10}$); 7.72 (td, 2H, ${}^{3}J_{H-H} = 7.7$, ${}^{4}J_{H-H} = 1.5$, 2H¹¹); 8.01 (ddd, 2H, ${}^{3}J_{H-H} = 5.5$, ${}^{4}J_{H-H} = 1.5$, ${}^{5}J_{H-H} = 0.5$, 2H¹³). ${}^{13}C{}^{1}H$ NMR data for 2a₁: 24.3 (MeCOO); 83.1 (C⁵); 84.2 (C³); 85.1 (C⁴); 118.0 (C¹²); 122.4 (C¹⁰); 139.2 (C^{11}) 152.3 (C^{9}) ; 151.9 (C^{13}) ; 184.2 (COO^{-}) ; 196.4 $(C^{6}, C^{7}, and$ C^{8}). The signals due to the quaternary carbon atoms C^{1} and C^{2} could not be detected in the ${}^{13}C{}^{1}H$ NMR spectrum. ${}^{13}C{}^{1}H$ NMR data for $2a_{II}$: 23.2 (MeCOO); 82.8 (C⁵); 83.8 (C³); 85.3 (C⁴); 118.8 (C¹²); 122.4 (C^{10}) ; 140.8 (C^{11}) 152.0 $(C^{13}$, partially masked by the signal due to the C^{13} atom of $2a_{II}$); 183.3 (-COO⁻); 196.2 (C^{6} , C^{7} , and C^{8}).

[*Pd*{[κ^2 -*C*,*N*-(η^5 -*C*₅*H*₃)-2-(*C*₅*H*₄*N*)]*Re*(*CO*)₃}(*OAc*)(*PPh*₃)] (**3a**). This compound was prepared in solution on an NMR scale and characterized by ¹H and ³¹P{¹H} NMR spectroscopy. Compound **2a** (13 mg, 1.1 × 10⁻⁵ mol) was introduced into an NMR tube, and then 0.4 mL of CDCl₃ was added. The resulting suspension was treated with a solution containing triphenylphosphine (6.0 mg, 2.3 × 10⁻⁵ mol) and 0.3 mL of CDCl₃. The solution was shaken vigorously at 298 K for 3 min. This produced the complete dissolution of **2a**, giving a pale brown solution. ¹H NMR: 1.46 (br, 3H, OAc); 4.04 (d, 1H, ³J_{H-H} = 2.5, H³); 4.87 (t, 1H, ³J_{H-H} = 7.2, ⁴J_{H-H} = 1.5, H¹²); 7.30 (d, 1H, ³J_{H-H} = 7.8, H¹⁰); 7.46 (m, 6H, aromatic protons of PPh₃); 7.74 (dd, 1H, ³J_{H-H} = 7.8, ⁴J_{H-H} = 1.5, H¹¹); 7.80 (m, 9H, aromatic protons of PPh₃); 8.43 (br, 1H, H¹³). ³¹P{¹H} NMR: 34.7.

 $[Pd\{[\kappa^2-C,N-(\eta^5-C_5H_3)-2-(C_5H_4N)]Re(CO)_3\}(\mu-Cl)\}]_2 \cdot CH_2Cl_2$ (**4a**). A solution of 2 (100 mg, 9.0×10^{-5} mol) in CH₂Cl₂ (10 mL) was added to a saturated solution of NaCl in water (10 mL), and the mixture was stirred overnight at room temperature. The brown solid formed was collected by filtration, washed with two (10 mL) portions of H₂O and then with CH_2Cl_2 (2 × 10 mL), and dried under vacuum (yield 67 mg, 5.6 \times 10⁻⁵ mol, 65%). Anal. Calcd for C₂₆H₁₄Cl₂N₂O₆Pd₂Re₂. CH₂Cl₂: C, 27.22; H, 1.35; N, 2.35. Found: C, 27.25; H, 1.4; N, 2.5. MS (ESI⁺) m/z: 1049.74 {[M] - 2CO}⁺; 1152.83 {[M - Cl] + $2CH_3CN^{+}$. IR: 2019 (s) and 1917 (vs) cm⁻¹, ν (CO). ¹H NMR (in presence of py- d_5 , selected data): 4.43 (dd, 1H, ${}^{3}J_{H-H} = 2.4$, ${}^{4}J_{H-H} = 1.2$, H³); 5.25 (t, 1H, ${}^{3}J_{H-H} = 2.8$, H⁴); 5.78 (dd, 1H, ${}^{3}J_{H-H} = 2.8$, ${}^{4}J_{H-H} = 1.2$, H⁵); 7.14 (td, 1H, ${}^{3}J_{H-H} = 6.0$, ${}^{4}J_{H-H} = 1.6$, H¹²); 7.27 (m, 1H, 14), H^{10}); 7.77 (td, 1H, ${}^{3}J_{H-H} = 7.6$, ${}^{4}J_{H-H} = 1.6$, H^{11}); 9.33 (br, 1H, H^{13}). $^{13}C{^{1}H}$ NMR (in the presence of py- d_5 , selected data): 81.9 (C⁴); 83.7 (C^3) ; 86.2 (C^5) ; 108.8 (C^1) ; 109.6 (C^2) ; 118.9 (C^{10}) ; 123.2 (C^{12}) ; 124.4 (C¹¹); 151.0 (C⁹); 153.9 (C¹³); 195.7 (C⁶, C⁷ and C⁸).

 $[Pd\{[\kappa^{2}-C,N-(\eta^{5}-C_{5}H_{3})-2-(C_{5}H_{4}N)]Re(CO)_{3}\}(PPh_{3}/CI]\cdot^{1}/_{2}CH_{2}Cl_{2} ($ **5a** $\cdot 1)/_{2}CH_{2}Cl_{2}). This compound was obtained using two alternative procedures that differ in the nature of the starting material: the di-<math>\mu$ -chloro complex [Pd{[κ^{2} -C,N-(η^{5} -C₅H₃)-2-(C₅H₄N)]Re(CO)_{3}(μ -Cl)]₂·CH₂Cl₂ (**4a** · CH₂Cl₂) (method a) and [Pd{[κ^{2} -C,N-(η^{5} -C₅H₃)-2-(C₅H₄N)]Re(CO)_{3}(μ -Cl)]₂·CH₂Cl₂ (**4a** · CH₂Cl₂) (method a) and [Pd{[κ^{2} -C,N-(η^{5} -C₅H₃)-2-(C₅H₄N)]Re(CO)_{3}(DMSO)Cl]·CH₂Cl₂ (**6a** · CH₂Cl₂) (method b).

Method a. To a suspension of $4a \cdot \text{CH}_2\text{Cl}_2$ (50 mg, 4.2×10^{-5} mol) in benzene (10 mL) was added triphenylphosphine (24 mg, 9.1 × 10^{-5} mol). The reaction mixture was stirred at room temperature overnight and then concentrated to dryness, and the residue that formed was treated with the minimum amount of CH₂Cl₂. Addition of hexane produced the precipitation of $5a \cdot \frac{1}{_2}\text{CH}_2\text{Cl}_2$ as a pale yellow solid that was collected and dried. This product was recrystallized in a hexane/ CH₂Cl₂ (1/3) mixture at -10 °C (yield 27.8 mg, 3.2×10^{-5} mol, 38.6%). *Method b.* Triphenylphosphine (21 mg, 8×10^{-5} mol) was added to a solution of **6a** · CH₂Cl₂ (50 mg, 7.0 × 10⁻⁵ mol) in benzene (10 mL). The reaction mixture was stirred at room temperature overnight and then concentrated under vacuum. The residue was dissolved in the minimum amount of CH₂Cl₂. Addition of hexane produced the precipitation of a pale yellow solid, which was collected, dried, and recrystallized as described in method a (yield 53.2 mg, 7.4 × 10⁻⁴ mol, 89%).

Characterization data for $5a \cdot \frac{1}{2}CH_2Cl_2$ are as follows. Anal. Calcd for $C_{31}H_{22}ClNO_3PPdRe \cdot \frac{1}{2}CH_2Cl_2$: C, 44.09; H, 2.70; N, 1.63. Found: C, 44.1; H, 2.7; N, 1.6. MS (ESI⁺) m/z: 779.99 [M – Cl]⁺; 821 {[M – Cl] + CH₃CN}⁺. IR: 2014 (s) and 1920 (vs) cm⁻¹, v(CO). ¹H NMR: 3.42 (dd, 1H, $^{3}J_{H-H} = 2.5$, $^{4}J_{H-H} = 1.0$, H³); 4.95 (td, 1H, $^{3}J_{H-H} = 3.0$, $^{4}J_{H-H} = 1.0$, 1H, H⁴); 5.85 (dd, 1H, $^{3}J_{H-H} = 3.0$, $^{4}J_{H-H} = 1.5$, H⁵); 7.19 (m, 1H, H¹²); 7.27 (dd, 1H, $^{3}J_{H-H} = 7.5$, $^{4}J_{H-H} = 0.5$, H¹⁰); 7.43 (m, 9H, aromatic protons of PPh₃); 7.74 (td, 1H, $^{3}J_{H-H} = 7.5$, $^{4}J_{H-H} = 1.0$, H¹¹); 7.81 (m, 6H, aromatic protons of PPh₃); 9.40 (br, 1H, H¹³). ^{13}C {¹H} NMR: 83.7 (C⁴); 85.6 (C⁵); 89.6 (C³); 108.5 (C¹); 109.5 (C²), 118.0 (C¹⁰); 122.9 (C¹²); 132.2 (C¹¹); 151.4 (C¹³); 159.4 (C⁹); 195.8 (C⁶, C⁷, and C⁸); four additional doublets centered at 129.5, 131.1, 132.2, 136.3 (due to the four types of carbon-13 nuclei of the PPh₃ ligand). ³¹P{¹H} NMR: 33.9.

 $[M{[\kappa^2-C,N-(\eta^5-C_5H_3)-2-(C_5H_4N)]Re(CO)_3}(DMSO)C] \cdot nCH_2CI_2 (M =$ Pd and n = 1, **6a**; M = Pt and n = 0, **6b**). A 2.4×10^{-4} mol amount of the corresponding $[MCl_2(DMSO)_2]$ complex (with M = Pd (80.2 mg), Pt (101 mg)), ligand 1 (100 mg), and a 2-fold excess of NaOAc · 3H₂O (68.0 mg, 5.0×10^{-4} mol) were suspended in 20 mL of toluene. The resulting mixture was refluxed for 12 h; afterward, it was concentrated under reduced pressure to ca. 3 mL and the addition of diethyl ether (20 mL) followed by vigorous stirring at room temperature produced the precipitation of complexes $6a \cdot CH_2Cl_2$ and 6b (as yellowish microcrystalline products), which were later collected and dried under vacuum (yields 119 mg (1.65×10^{-4} mol), 68% for **6a** · CH₂Cl₂ and 141 mg $(1.97 \times 10^{-4} \text{ mol})$, 81% for **6b**). Characterization data for **6a** · CH₂Cl₂ are as follows. Anal. Calcd for C15H13CINO4PdReS·CH2Cl2: C, 28.44; H, 2.39; N, 2.22; S, 5.08. Found: C, 28.39; H, 2.35; N, 2.2; S, 5.0. MS $(\text{ESI}^+) m/z$: 637.97 { $[M - \text{Cl}] + \text{CH}_3\text{CN}$ }⁺; 545.88 $[M - 3\text{CO}]^+$. IR: 2014 (s) and 1920 (vs) cm⁻¹, ν (CO), ¹H NMR: 3.52 (s, 3H, Me-(DMSO)); 3.54 (s, 3H, Me(DMSO)); 5.40 (t, 1H, ${}^{3}J_{H-H} = 2.8, H^{4});$ 5.75 (dd, 1H, ${}^{3}J_{H-H} = 2.8$, ${}^{4}J_{H-H} = 1.2$, H³); 5.79 (dd, 1H, ${}^{3}J_{H-H} = 2.8$; ${}^{4}J_{H-H} = 1.2, H^{5}$); 7.22 (td, 1H, ${}^{3}J_{H-H} = 7.2; {}^{4}J_{H-H} = 1.2; H^{12}$); 7.35 (d, 1H, ${}^{3}J_{H-H} = 7.6; {}^{4}J_{H-H} = 7.6; {}^{4}J_{H-H} = 1.2; H^{12}$); 7.35 (d, 1H, ${}^{3}J_{H-H} = 7.6; {}^{4}J_{H-H} = 7.6; {}^{4}J_{H-H} = 1.2; H^{11}$); 9.17 (d, 1H, ${}^{3}J_{H-H} = 5.6, H^{13}$). ${}^{13}C{}^{1}H{}^{3}$ NMR: 47.2 (Me(DMSO)); 47.4 (Me(DMSO)); 83.8 (C^4); 86.3 (C^5); 86.9 (C^3); 117.7 (C^{10}); 121.8 (C¹²); 140.75 (C¹¹); 150.2 (C¹³); 153.1 (C⁹); 196.1 (C⁶; C⁷, and C^8). Characterization data for **6b** are as follows. Anal. Calcd for C15H13ClNO4PtReS: C, 25.02; H, 1.82; N, 1.95; S, 4.45. Found: C, 25.1; H, 1.7, N, 1.9; S, 4.4. MS (ESI⁺) m/z: 725.00 {[M - Cl] + CH_3CN ⁺; 683.97 $[M - Cl]^+$. IR: 2015 (s) and 1922 (vs) cm⁻ ν (CO). ¹H NMR: 3.59 (s, 3H, ³ J_{Pt-H} = 21.0, DMSO); 3.61 (s, 3H, ³ J_{Pt-H} = 21.5, DMSO); 5.45 (t, 1H, ³ J_{H-H} = 3.0, H³); 5.68 (dd, 1H, ³ J_{H-H} = 2.5, ⁴ J_{H-H} = 1.5, H⁴); 5.71 (dd, 1H, ³ J_{H-H} = 2.5, ⁴ J_{H-H} = 1.5, ${}^{J}_{H-H} = 2.5, \, {}^{J}_{H-H} = 1.5, H^{+}); 5.71 (dd, 1H, \, {}^{J}_{H-H} = 2.5, \, {}^{J}_{H-H} = 1.5, H^{+}); 7.26 (td, 1H, \, {}^{3}_{J}_{H-H} = 6.5; \, {}^{4}_{J}_{H-H} = 1.5, H^{12}); 7.36 (dm, 1H, \, {}^{3}_{J}_{H-H} = 8.0, H^{10}); 7.84 (td, 1H, \, {}^{3}_{J}_{H-H} = 7.5, \, {}^{4}_{J}_{H-H} = 1.5, H^{11}); 9.40 (ddd, 1H, \, {}^{3}_{J}_{H-H} = 5.75, \, {}^{4}_{J}_{H-H} = 1.5, \, {}^{5}_{J}_{H-H} = 1, H^{13}). \, {}^{13}C{}^{1}_{H} NMR: 47.7 ({}^{2}_{J}_{Pt-C} = 52.9, Me(DMSO)); 47.9 ({}^{2}_{J}_{C-Pt} = 54.2, Me(DMSO)); 81.6 ({}^{3}_{J}_{C-Pt} = 44.2, C^{4}); 86.5 (\, {}^{3}_{J}_{C-Pt} = 79.13, C^{5}); 88.1 ({}^{2}_{J}_{C-Pt} = 43.8, C^{3}); 100.2 (C^{1}); 109.9 (C^{2}); 118.8 (C^{10}); 122.9 (C^{12}); 141.9 (C^{11}); 151.4 (C^{13}); 161.1 (C^{9}); 196.2 (C^{6}, C^{7}, and C^{8}). \, {}^{195}Pt{}^{1}_{H} NMR: -3664.$

[$Pt{[\kappa^2-C,N-{(\eta^5-C_5H_3)-2(C_5H_4N)Re(CO)_3}(PPh_3)C]]}$ (*5b*). This complex was isolated as a pale yellow solid following the procedure described in method b for **5a** · $^{1}/_{2}CH_{2}Cl_{2}$, but with **6b** (60 mg, 8.3 × 10⁻⁵ mol) and PPh₃ (26 mg, 1.0 × 10⁻⁴ mol) as starting materials (yield 64 mg, 3.4 × 10⁻⁵ mol, 85%). Anal. Calcd for C₃₁H₂₂ClNO₃PPtRe: C, 41.18; H, 2.45; N, 1.55. Found: C, 41.4; H, 2.5; N, 1.4. MS (ESI⁺) *m/z*: 868.05

	1	$5a \cdot 1/_2 CH_2 Cl_2$	5b	$6a \cdot CH_2Cl_2$	6b
empirical formula	C ₁₃ H ₈ NO ₃ Re	$C_{31}H_{22}NO_3PPdClRe \cdot 1/_2CH_2Cl_2$	C ₃₁ H ₂₂ NO ₃ PPtRe	$C_{15}H_{13}NO_3PdReS \cdot CH_2Cl_2$	C ₁₅₁ H ₁₃ NO ₃ PtReS
formula wt	412.40	857.98	904.21	716.30	720.06
T/K	293(2)	293(2)	293(2)	195(2)	293(2)
cryst size/mm	$0.40\times0.40\times0.30$	0.50 imes 0.50 imes 0.30	$0.20\times0.10\times0.10$	$0.20\times0.10\times0.08$	$0.20\times0.10\times0.10$
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	Cc	$P\overline{1}$	$P\overline{1}$	$P2_1/n$
a/Å	11.0260(6)	37.933(3)	9.282(4)	9.806(4)	9.776(3)
b/Å	8,3465(4)	9.1354(7)	10.126(4)	10.001(2)	17.657(6)
c/Å	13.8932(7)	19.5917(16)	16.423(4)	11.644(4)	10.232(8)
$lpha/{ m deg}$	90.0	90.0	107.84(2)	100.81(2)	90.0
β /deg	107.5920(10)	116.8010(10)	92.51(2)	103.05(2)	99.46(16)
γ/deg	90.0	90.0	104.11(3)	101.79(2)	90.0
Volume/Å ³	1218.78(11)	6059.9(8)	1417.6(8)	1055.8(6)	1742.2(16)
Ζ	4	8	2	2	4
$D_{\rm calcd}/{ m Mg}~{ m m}^{-3}$	2.248	1.881	2.118	2.253	2.745
μ/mm^{-1}	9.968	4.848	9.378	7.079	15.255
F(000)	768	3304	848	676	1312
no. of collected rflns	9403	22 909	12 832	9992	5068
no. of unique rflns, R(int)	2715, 0.0341	6629, 0.0304	7040, 0.0748	5225, 0.0391	5068, 0.0000
no. of params	164	367	328	224	217
R indices (all data)	R1 = 0.0399,	R1 = 0.0561,	R1 = 0.0518,	R1 = 0.0327,	R = 0.0645,
	wR2 = 0.0690	wR2 = 0.0748	wR2 = 0.1390	wR2 = 0.0870	wR2 = 0.0767
R indices $(I > 2\sigma(I))$	R1 = 0.0319,	R1 = 0.0366,	R1= 0.0502,	R1 = 0.0327,	R1 = 0.0333,
	wR2 = 0.0663	wR2 = 0.0701	wR2 = 0.1371	wR2 = 0.0864	wR2 = 0.0701

Table 2. Crystal Data and Details of the Refinement of the Crystal Structures of the Free Ligand [{(η^5 -C₅H₄)-2(C₅H₄N)}Re-(CO)₃}] (1) and the Cyclometalated Compounds 5a·¹/₂CH₂Cl₂, 5b, 6a·CH₂Cl₂, and 6b

$$\begin{split} & [M - Cl]^+; \ 909.08 \ \{[M - Cl] + CH_3CN\}^+. \ IR: \ 2014 \ (s) \ and \ 1920 \\ & (vs) \ cm^{-1}, \ \nu(CO). \ ^1H \ NMR: \ 3.41 \ (dd, \ ^3J_{H-H} = 4.8, \ ^4J_{H-H} = 0.8, \ 1H, \\ & H^3); \ 4.95 \ (t, \ ^3J_{H-H} = 2.4, \ 1H, \ H^4); \ 5.83 \ (dd, \ ^3J_{H-H} = 2.5, \ ^4J_{H-H} = 1, \ 1H, \\ & H^5); \ 7.22 \ (m, \ 1H, \ H^{12}); \ 7.35 \ (dd, \ ^3J_{H-H} = 6.4, \ ^4J_{H-H} = 0.4, \ 1H, \ H^{10}); \\ 7.43 \ (m, \ 1H, \ H^{11}); \ 7.45 - 7.84 \ (m, \ 15H, \ aromatic \ protons \ of \ PPh_3); \ 9.68 \\ & (t, \ ^3J_{H-H} = 4.5, \ 1H, \ H^{13}). \ ^{13}C\{\ ^{1}H\} \ NMR: \ 84.4 \ (^{3}J_{C-Pt} = 44.7, \ C^4); \ 85.1 \\ & (^{3}J_{C-Pt} = 36.1, \ C^5); \ 88.5 \ (^{2}J_{C-Pt} = 108.2, \ C^3); \ 100.4 \ (C^1); \ 108.0 \ (C^2); \\ & 118.0 \ (C^{10}); \ 122.7 \ (C^{12}); \ 140.8 \ (C^{11}); \ 150.2 \ (C^{13}); \ 160.3 \ (C^9); \ 196.1 \\ & (C^6, \ C^7 \ and \ C^8); \ four \ additional \ doublets \ at \ 129.3, \ 131.1, \ 132.2, \ 136.3 \ due \ to \ the \ PPh_3 \ ligand. \ ^{19}Pt\{^1H\} \ NMR: \ -4062 \ (d, \ ^{1}J_{P-Pt} = 4098). \ ^{31}P\{\ ^{1}H\} \ NMR: \ 12.2 \ (\ ^{1}J_{P-Pt} = 4103). \end{split}$$

Crystallography. A prismatic crystal (sizes in Table 2) of 1, $\mathbf{5a} \cdot \mathbf{1}_2 \operatorname{CH}_2 \operatorname{Cl}_2$, $\mathbf{5b}$, $\mathbf{6a} \cdot \operatorname{CH}_2 \operatorname{Cl}_2$, or $\mathbf{6b}$ was selected and mounted on a Bruker-Siemens Smart CCD diffractometer (equipped with a normalfocus, 2.4 kW sealed-tube X-ray source Mo K α radiation and operating at 50 kV and 20 mA) for 1 and $\mathbf{5a} \cdot \mathbf{1}_2 \operatorname{CH}_2 \operatorname{Cl}_2$, on a MAR345 diffractometer for $\mathbf{5b}$ and $\mathbf{6a} \cdot \operatorname{CH}_2 \operatorname{Cl}_2$, or on a Enraf- Nonius CAD4 four-circle diffractometer with an image plate detector for $\mathbf{6b}$. In the last two cases, intensities were collected with graphite-monochromated Mo K α radiation. For $\mathbf{6b}$, three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarization and absorption corrections were made.

These structures were solved by direct methods using the SHELXS computer program⁴⁸ and refined by full-matrix least-squares methods with the SHELX97 computer program⁴⁹ using 2455 (for 1), 5321 (for **5a** $\cdot^{1}/_{2}$ CH₂Cl₂), 12 832 (for **5b**), 9992 (for **6a** \cdot CH₂Cl₂), or 5068 (for **6b**) reflections (very negative intensities were not assumed). The function minimized was $\Sigma w ||F_{o}|^{2} - |F_{c}|^{2}|^{2}$, where $w = [\sigma^{2}(I) + (0.0289P)^{2} + 1.3732P]^{-1}$ (for **1**), $w = [\sigma^{2}(I) + (0.0289P)^{2} + 24.3025P]^{-1}$ (for **5a** $\cdot^{1}/_{2}$ CH₂Cl₂), $w = [\sigma^{2}(I) + (0.0951P)^{2} + 0.6924P]^{-1}$ (for **5b** \cdot CH₂Cl₂),

 $w = [\sigma^2(I) + (0.0563P)^2 + 0.1984P]^{-1}$ (for **6a** · CH₂Cl₂), and $w = [\sigma^2(I) + (0.0400P)^2]^{-1}$ (for **6b**). $P = (|F_o|^2 + 2|F_c|^2)/3$; *f*, *f'*, and *f''* were taken from the bibliography.⁵⁰ In all cases, H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which to which it is linked. The final *R* indices and other relevant parameters concerning the resolution of the crystal structures of these compounds are presented in Table 2.

ASSOCIATED CONTENT

Supporting Information. CIF files giving full details of the crystallographic analyses of compounds 1, $5a \cdot {}^{1}/{}_{2}CH_{2}Cl_{2}$, **5b**, $6a \cdot CH_{2}Cl_{2}$, and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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