N,C "Rollover" Cyclometalated Platinum(II) Hydrides: Mono- and Polynuclear Derivatives

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N,C cyclometalated platinum(II) hydrides were obtained by reaction of the "rollover" derivatives [Pt(N′−C(3))(Cl)(L)] (N−CH= 6-*tert*-butyl- and 6-phenyl-2,2′-bipyridine; L = DMSO, 3,5-Me_2-pyridine, PPh_3) with Na[BH_4]. Mono- or polynuclear hydrides, [Pt(N′−C(3))(H)(L)] or [Pt(N′−C(3))(μ-H)]$_n$, are formed depending on the nature of the neutral ligand, L. The unsaturated 14-electron fragments [Pt(N′−C(3))(μ-H)] assemble to form oligomers with bridging hydrides. Spectroscopic characterization provides evidence for tetramers both in solution (^{1}H NMR) and in vapor phase (ESI-MS). In the tetrameric systems the 2e−3c Pt−H−Pt bond is cleaved by π-acceptor ligands such as Ph_3P and CO to give stable mononuclear hydrides.

Introduction

Nitrogen ligands have never been popular in the chemistry of transition metal hydrido complexes, the ancillary ligands most frequently being π-acceptors, such as CO, Cp, and phosphorus donors.[1] As for the late transition metals, hydrides with nitrogen ligands, with a few exception, are rare.

In the particular case of platinum, a rich hydrido chemistry has been developed since the first report in the late 1950s;[2] nowadays an array of species are known in different oxidation states, mainly platinum(II) and platinum(IV), but also a few dinuclear, diamagnetic, platinum(I) compounds.[3]

Platinum(II) hydrides that contain metal−nitrogen bonds are rare, and most of them, in addition to nitrogen donors, also contain the more common classical phosphine ligands.[4] Compounds bearing only nitrogen ligands are few in number: they include a cationic species with a neutral diamino ligand, [Pt(=C(CH_3)OCH_2CH_2)(tmeda)H]$^+$ (tmeda = *N*,*N*′,*N*′,*N*′-tetramethylethylenediamine),[5] trispyrazolylborato mono- and dinuclear species,[6] and some recent olefin hydrido complexes.[7] In contrast, in recent years, much attention has been paid to the analogous platinum(IV) hydrides[8] due to the interest of diimine and diamine platinum(II) derivatives as models for the C−H bond activation step in selective oxidation of hydrocarbons[9] and as being effective homogeneous catalysts for methane oxidation by sulfuric acid.[10]

Platinum(II) hydrides containing cyclometalated rings arising from activation of nitrogen ligands, despite the great number of known systems, are even more rare: a perusal of the literature provides only few examples that comprise both terminal and bridging species. A dinuclear complex stabilized by a N−C−N pincer ligand, [(N−C−N)Pt(μ-H)Pt(N−C−N)]$^+$, H trans to C, was described several years ago:[11] the related terminal hydride, [Pt(N−C−N)(H)], was not isolated. Another dinuclear hydride, with terminal Pt−H bonds, [(H)Pt(PPh_3)$_2$($C_{10}N_8$)(PPh_3)$_2$Pt(H)] ($C_{10}N_8H_2$ = 4,4′,5,5′-tetracyano-2,2′-biimidazolo), was reported

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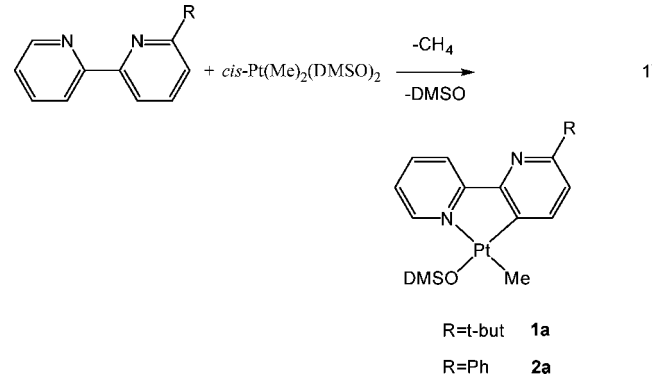
by Rasmussen et al.[12] Mono- and dinuclear derivatives with tridentate N−N−C ligands, [Pt(N−N−C)(H)] and [(N−N−C)Pt(μ-H)Pt(N−N−C)]$^+$, H trans to N (N−N−CH = 6-substituted-2,2′-bipyridines), have been preliminarily reported[13] and very recently described in detail by us.[14] The series includes species arising from activation of C−H bonds of alkyl, benzyl, and phenyl substituents, to give both [5,5] and [5,6] fused cyclometalated rings. Spectroscopic evidence for a similar mononuclear hydride has been given by Song and Morris.[15] Two other dinuclear complexes with terminal Pt−H bonds, where the metal atoms are bridged by a 2-fold deprotonated 2,2′:6′,2″-terpyridine, [Pt_2(terpy-2H)$(H)_2(L)_2$], have also been described.[16]

The N−N−C cyclometalated hydrides hitherto synthesized by us all entail activation of a C−H bond of a substituent of the 2,2′-bipyridine. Recently we have reported that reaction of 6-substituted-2,2′-bipyridines with electron-rich platinum intermediates, typically $(L)_2Pt(R)_2$ (R= Me, Ph), allowed us to achieve a different metalation, i.e., activation of a C−H bond of a pyridine ring, with elimination of methane or benzene. This interesting and still rare "rollover"[17] intramolecular metalation implies the formation of an N−C five-membered ring: the C−H activation occurs on the substituted pyridine ring to yield [Pt(N′,C(3))(R)(L)] complexes. Reaction of these methyl or phenyl derivatives with HCl gives the corresponding chlorides, e.g., [Pt(N′,C(3))(Cl)(DMSO)].

Here we report the synthesis and characterization of a series of terminal and bridging platinum(II) hydrides, [Pt(N′−C(3))(H)(L)] and [Pt(N′−C(3))(μH)]$_n$, all containing the N′−C(3) ring. The nature of the neutral ligand L is crucial in driving the synthesis toward a mononuclear terminal hydride or toward an oligomer resulting from assembly of the highly unsaturated, 14-electron, [Pt(N′−C(3))(H)] fragment.

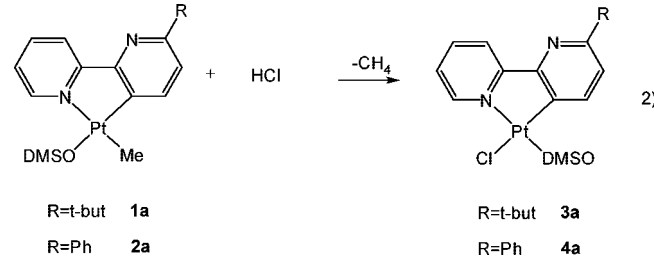
Results and Discussion

As starting platinum(II) derivatives two cyclometalates, [Pt(N′,C(3))(Me)(DMSO)], **1a** and **2a**, resulting from the ligands 6-*tert*-butyl-2,2′-bipy, **1**, and 6-phenyl-2,2′-bipy, **2**,[18] respectively, were chosen. Throughout this paper we can anticipate that the behavior of **1a** (alkyl-substituted ligand) and **2a** (aryl-substituted ligand), as for the reactivity here discussed, is the same. Compounds **1a** and **2a** were prepared, as previously reported,[17b] according to reaction 1:



The N′,C(3) five-membered ring is rather robust, and a variety of species, e.g., [Pt(N′,C(3))(Me)(CO)], **1b**, [Pt(N′,C(3))(Me)(3,5-Me_2-py)], **1c**, and [Pt(N′,C(3))(Me)(PPh_3)], **2d**, were obtained by substitution of DMSO with neutral ligands: CO, **b**, 3,5-Me_2-pyridine, **c**, and PPh_3, **d**. The easy displacement of DMSO is promoted by the metal−carbon bond in *trans* position.

From compounds **1a** and **2a** the corresponding chlorides, **3a** and **4a**, were obtained by reaction with HCl in acetone at room temperature (reaction 2):



One isomer is selectively formed: IR and ^{1}H NMR spectroscopic data, in particular the large ^3J(Pt−H) relevant to the protons of DMSO (24.7 Hz (**3a**) and 24.2 Hz (**4a**)), support a DMSO *trans* to the nitrogen atom. As in the case of **1a** and **2a**, likewise in **3a** and **4a** the coordinated DMSO can be displaced by CO, 3,5-Me_2-pyridine, and PPh_3, to give in good yields **3b**−**3d** and **4b**−**4d**, respectively.

Also in this series a comparative analysis of the ^{1}H NMR parameters, δ and J(Pt−H), accounts for the isomer formed, which entails, as expected, a *trans* Cl−Pt−C arrangement. The H(6′) resonances appear at very low field (δ ca. 9.4−9.8), as usually observed when a chlorine is in close proximity,[19] and the relevant ^3J(Pt−H) values fit in the order of *trans* influence of the ligand *trans* to nitrogen, e.g., **3c** 39.6 Hz, **3d** 27.0 Hz.

Taking advantage of the series of chlorides available through reaction 2, considering our interest in platinum(II) hydrides, we

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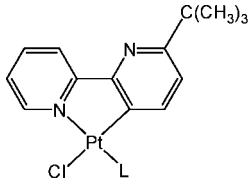
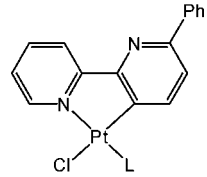


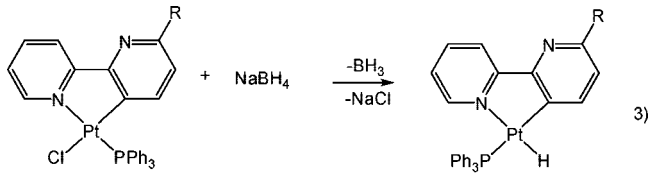
L = DMSO **3a**
L = CO **3b**
L = 3,5-Me_2-py **3c**
L = PPh_3 **3d**



L = DMSO **4a**
L = CO **4b**
L = 3,5-Me_2-py **4c**
L = PPh_3 **4d**

deemed it worthy to attempt to synthesize new hydrido derivatives with the N′−C(3) cyclometalated ligands. The attempt, carried out by reaction of all eight chlorides, **3a**−**3d** and **4a**−**4d**, with Na[BH_4], was successful and allowed us to achieve hydrido species. The outcome of the reaction however, under the same conditions, is not the same in all cases, being strongly dependent on the nature of the neutral co-ligands **a**−**d**.

Reaction of **3d** and **4d** with Na[BH_4], in THF at room temperature, provides, albeit in low yields (ca. 30%), mononuclear terminal hydrides, **5d** and **6d**, respectively (reaction 3):



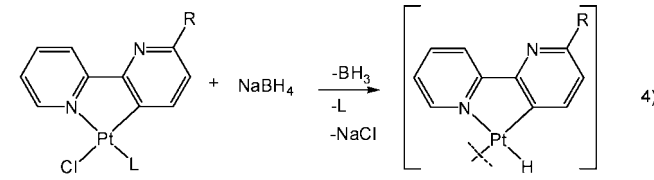
3)

R=t-but **3d** R=t-but **5d**
R=Ph **4d** R=Ph **6d**

Hydrides **5d** and **6d** can be isolated in the solid state, are stable in air, and are very soluble in most organic solvents. They were characterized by microanalyses and IR and NMR (^{1}H and ^{31}P) spectra. In the IR spectra a medium and sharp band around 2200 cm^{-1} is assignable to the stretch of the terminal Pt−H bond. In the ^{1}H NMR spectra the signal around δ −16 is diagnostic of a hydride: the resonance, coupled to ^{31}P, is accompanied by satellites due to ^{195}Pt (natural abundance ca. 33.8%, $I = 1/2$) in the correct ratio for a mononuclear species, 1:4:1. The ^1J(Pt−H) values, 1444 Hz, **5d**, and 1424 Hz, **6d**, are large but comparable with those previously reported[14] for cyclometalated [Pt(N−N−C)(H)] derivatives, H *trans* to nitrogen. In particular they are similar to the value, 1460 Hz, observed when N−N−CH is 6-phenyl-2,2′-bipyridine, which gives a five-membered C−N ring as in **5d** and **6d**. The ^{31}P{^{1}H} spectra show a singlet coupled to ^{195}Pt, with ^1J(Pt−P) 2147 Hz, **5d**, and 2174 Hz, **6d**. Taken together the NMR spectra unambiguously point, as expected, to the isomer having a *trans* H−Pt−N disposition. Compounds **5d** and **6d** are new examples of the capability of PPh_3 to stabilize terminal hydrides with nitrogen donors.[4]

We can anticipate here (see later) that terminal hydrides can also be obtained when CO is the co-ligand (**5b** and **6b**), but not directly through reaction 3. In the case of compounds with DMSO and 3,5-Me_2-py, **3a**, **3c** and **4a**, **4c**, under the same experimental conditions, the reaction with Na[BH_4] goes another way (reaction 4):

With both the *tert*-butyl- and the phenyl-substituted cyclometalates, **3a**, **3c** and **4a**, **4c**, the reaction occurs with extrusion of the neutral ligand to give coordinatively unsaturated 14-electron species, **7** and **8**, respectively. The new materials are obtained in good yields as red powders, stable in air in the solid



4)

R=t-but L = DMSO **3a**
L = 3,5-Me_2-py **3c**
R=Ph L = DMSO **4a**
L = 3,5-Me_2-py **4c**

R=t-but **7**
R=Ph **8**

state and very soluble in THF as well as in CH_2Cl_2, where however they are not indefinitely stable. Compounds **7** and **8** were easily identified as species with no neutral ligands by microanalyses (C,H,N) and IR and NMR spectra. ^{1}H NMR spectra show a single ligand environment, consistent with symmetric species; clear indication of the presence of a hydride is provided by a resonance at high field in the hydride region, δ ca. −14 (CD_2Cl_2). The pattern of the resonances is rather complex, the main signal being flanked by symmetric sets of satellites due to coupling with ^{195}Pt nuclei. On the whole the pattern is indicative of a bridging hydride: in agreement, in the IR spectra no absorption is observed in the region of terminal Pt−H bonds. At first sight the ^{1}H NMR spectra (see Experimental Section) allowed us to extract two ^1J(Pt−H) values, e.g., compound **7**, 1011 and 387 Hz, suggesting a hydride bridging two ^{195}Pt nuclei and being *trans* to a nitrogen and to a carbon atom. A simple centrosymmetric dimer for instance could account for the two coupling constants. The *transoid* disposition of the cyclometalated N,C ligands should be attained in order to prevent the hydride from being *trans* to two carbon atoms, C−Pt−H−Pt−C. The highly unsaturated coordination of **7** and **8** however makes a dimer most unlikely: the EAN rule, on the basis of a 16*e* closed shell, suggests each platinum connected to two other platinum atoms and implies a closed oligomer. Indeed a more careful analysis of the spectra allowed us also to detect a long-range coupling constant, ^3J(Pt−H), 39 Hz, **7**, confirming a nuclearity greater than 2.

To address the problem of nuclearity, ^{1}H NMR and ESI-MS spectra were obtained. The simulation of the spectrum of compound **7** was carried out by means of the gNMR 5.0.6.0 program.[20]

Both trimeric and tetrameric units were simulated. No significant differences are observed in the spectra, and both fit the experimental data. In detail we report here the simulation for the tetramer species [Pt(N′,C(3))(H)]$_4$; the spectrum of the trimer is reported as Supporting Information.

Taking account of the natural abundance of ^{195}Pt, 33.8%, the weight of the isotopomers A−E, expected for a symmetric tetramer (Chart 1), is as follows: A, Pt_4, 19.21%; B, $^{195}PtPt_3$, 39.22%; C, $^{195}Pt_2Pt_2$, 30.04%; D, $^{195}Pt_3Pt$, 10.22%; E, $^{195}Pt_4$, 1.31%.

The simulation was performed for each isotopomer separately and, finally, for the entire system. The simulated spectra of all the isotopomers are reported as Supporting Information: the overall simulated and experimental spectra are shown in Figure 1.

Isotopomer A (Pt_4H_4, 19.21%) is an A_4 spin system with four magnetically equivalent hydrides and gives an intense singlet at δ −14.46. Species B, the major isotopomer ($^{195}PtPt_3H_4$,

(20) Budzelaar, P. H. M. *gNMR*, version 5.0.6.0; NMR Simulation Program; IvorySoft, 2006.

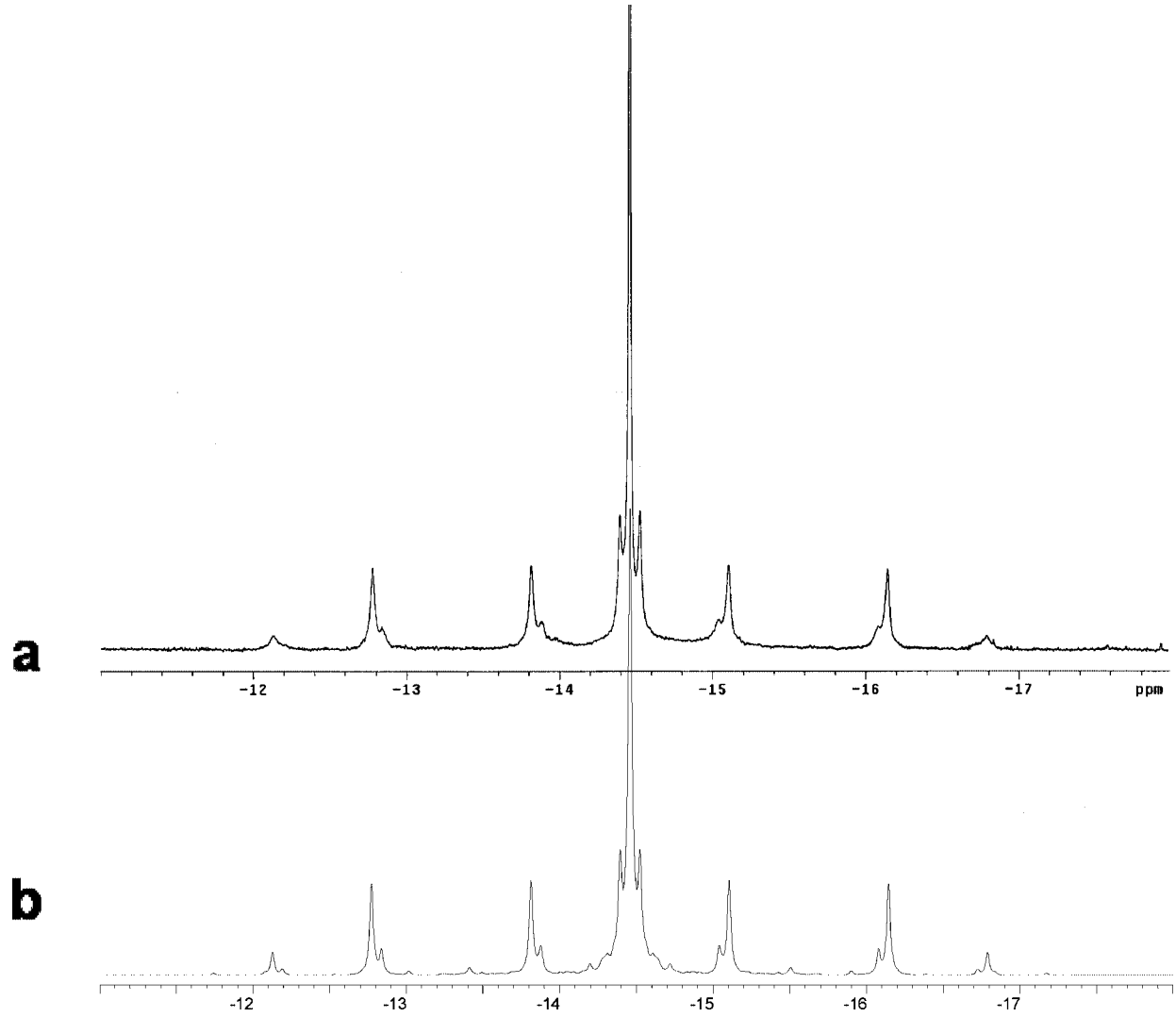
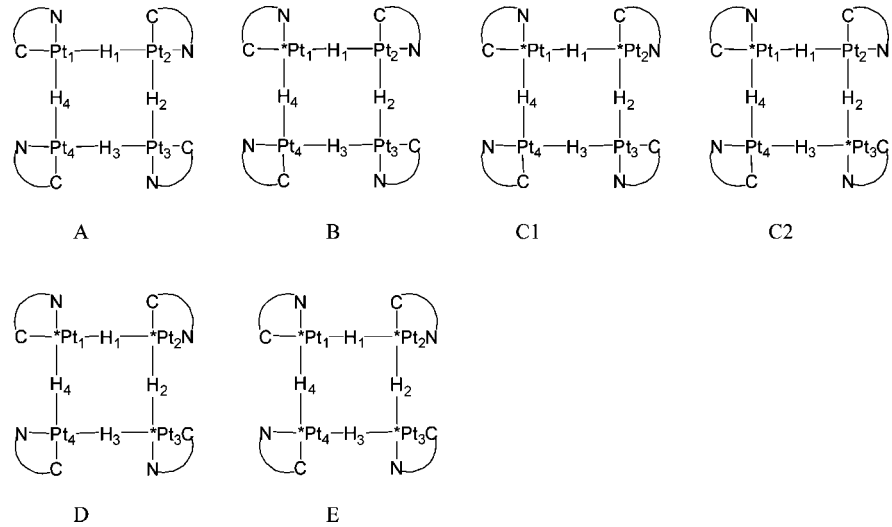


Figure 1. Experimental (a) and simulated (b) ^{1}H NMR spectrum (hydride region, 300.0 MHz) of complex **7**.

Chart 1



39.22%), is an AA′A″A‴X spin system. The spectrum consists of four different sets of signals centered at δ −14.46: three doublets (H *trans* to N, ^{1}J(Pt−H) = 1011 Hz; H *trans* to C, ^{1}J(Pt−H) = 387 Hz; H remote from ^{195}Pt, ^{3}J(Pt−H) = 39 Hz) and a singlet, H remote from ^{195}Pt with no detectable Pt−H coupling (likely H_2 in species B, Chart 1). The isotopomers C1 and C2 ($^{195}Pt_2Pt_2H_4$, 30.04% of the total) are both AA′A″A‴XX′ spin systems and were simulated separately. They are present in a 2:1 relative ratio: C1, for symmetric reasons, has double intensity with respect to C2. The simulated spectra consist of several lines, corresponding to experimental signals, and indicate that the major coupling constants (^{1}J = 1011 and 387 Hz) are

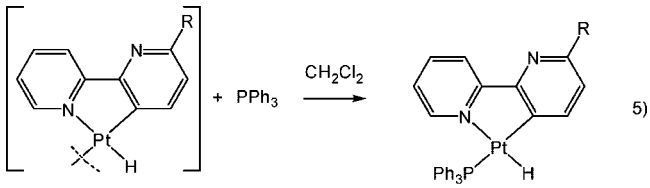
of opposite sign with respect to the minor one ($^3J = -39$ Hz). Furthermore, a ^1J(Pt−Pt) and a ^2J(Pt−Pt) coupling constant should be envisaged: the best fitting values appear to be greater than ca. 3000 and ca. 200 Hz, respectively. These data are in agreement with literature data for direct and long-range Pt−Pt coupling constants.[21] Isotopomer D ($^{195}Pt_3PtH_4$, 10.22%, AA′A″A‴XX′X″ spin system) provides a minor contribution to the overall spectrum, the signal being split into several lines. Finally, isotopomer E ($^{195}Pt_4H_4$, AA′A″A‴XX′X″X‴ spin system), 1.31% of the total, gives a complex spectrum that, however, can be ignored taking account of its small abundance.

Overall, the simulation indicates that, of the three ^{195}Pt−H coupling constants, the major ones (1011 and 387 Hz) are of opposite sign with respect to the minor one (−39 Hz). Furthermore, a ^1J(Pt−Pt) > ca. 3000 Hz and a ^2J(Pt−Pt) > ca. 200 Hz fit the experimental data.

Definitive evidence for the nuclearity of compounds **7** and **8** was achieved from mass spectrometric investigations. The electrospray ionization mass (ESI) spectra of compounds **7** and **8**, registered in CH_2Cl_2, show the molecular ion peaks at *m/z* 1629 and 1709, corresponding to the protonated tetrameric units [**7** + H]$^+$ and [**8** + H$^+$], respectively: no significant peaks consistent with a trimeric species are detected. Thus it seems that, at least in vapor phase, **7** and **8** are present as tetramers. Unfortunately, in spite of numerous attempts, up to now only amorphous samples were obtained, unsuitable for single-crystal or even powder X-ray structural analysis.

To get insight into the relationship between the mono- and the polynuclear hydrides, the stability of the oligomeric hydrides **7** and **8** toward neutral ligands was investigated by reaction with DMSO, CO, 3,5-Me_2-py, and PPh_3.

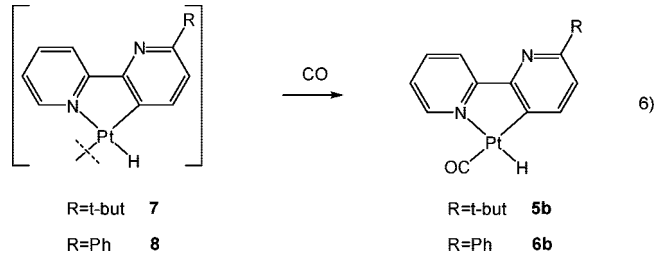
With PPh_3 both **7** and **8** react with opening of the oligomer to give the mononuclear terminal hydrides **5d** and **6d**, respectively (reaction 5) confirming the contribution given by the



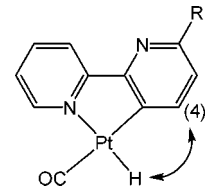
phosphine ligands to the stability of the platinum(II) 16-electron hydrides. The reaction occurs in very mild conditions, i.e., at room temperature with a 1:1 molar ratio: compounds **5d** and **6d** are isolated in fairly good yields.

The analogous derivatives with CO in place of PPh_3, not obtained through reaction of the corresponding chlorides with $Na[BH_4]$, were attained from **7** and **8** (reaction 6): The reaction can be carried out by bubbling CO into a CH_2Cl_2 solution of the hydrides at room temperature: in these conditions some decomposition to metal occurs in the workup of the solution, so that it is difficult to get pure samples. Remarkably, the reaction occurs also in the solid state: analytically pure **5b** and **6b** can be isolated keeping the hydrides **7** and **8** under a CO atmosphere at room temperature for several hours.

The new hydrides, **5b** and **6b**, were characterized as usual: in the IR spectra two bands in the region 2200−2000 cm^{-1} (see Experimental Section) can be assigned to a terminal Pt−H



stretch and to the coordinated CO, e.g., compound **5b**, 2179 and 2048 cm^{-1} (Nujol), respectively. Compared with the corresponding chloride, **3b**, ν_{CO} 2104 cm^{-1}, the CO stretching vibration is significantly displaced to lower wavenumbers in the more electron-rich hydride. In the ^{1}H NMR spectra the hydride resonance at δ ca. −13 is coupled to ^{195}Pt with ^1J(Pt−H) 1459 Hz, a value consistent with a hydride residing opposite the nitrogen atom. The *trans* H−Pt−N disposition around the platinum atom was confirmed by a NOE difference spectrum on complex **5b**. In the spectrum, a contact between the hydride and the double doublet at δ 8.08 due to the H_4 proton shows the hydride coordinated *cis* to the C(3) atom and, as a consequence, *trans* to the nitrogen. Furthermore, the multiplicity of the H_4, (dd) is due to a small ^4J(H−H) (1.3 Hz) coupling with the hydride: a selective irradiation of the hydride signal transformed the double doublet at δ 8.08 into a simple doublet.



Thus it seems that conversion of the polynuclear hydrides into the mononuclear 16-electron species is easily performed, under mild conditions, by π-acceptor ligands such as CO and PPh_3. It is not surprising therefore that most of the known platinum(II) hydrides with nitrogen ligands, as noted in the Introduction, are stabilized by phosphine ligands. At variance, the ligands DMSO and 3,5-Me_2-py do not react with the polynuclear hydrides **7** and **8** under comparable conditions; for example, **7** does not react in neat DMSO at room temperature or with an equivalent amount of 3,5-Me_2-py. Under more harsh conditions (e.g., heating compound **7** in DMSO) and a large excess of ligand, the equilibrium can be shifted toward the terminal hydrides as shown by the IR and ^{1}H NMR spectra. The NMR spectra, in particular, registered in d_6-DMSO or in d_5-pyridine (deuterated 3,5-Me_2-py not being available) give clear evidence for terminal hydrides: a resonance around δ −14 is flanked by two satellites in 1:4:1 ratio. The large value of J(Pt−H), ca. 1550 Hz, is in line with a terminal hydride *trans* to a nitrogen donor. Attempts to isolate these new hydrides either by concentration of their solution (DMSO or pyridine) or by addition of hydrocarbons (*n*-pentane or *n*-hexane) failed: the terminal hydrides have short lives in the absence of a large excess of the neutral ligand, and the oligomeric species are reformed.

It is worth noting that the corresponding methyl complexes [Pt(N′,C(3))(Me)(L)] (L = **a**−**d**) are stable and can be isolated in the solid state.

Experimental Section

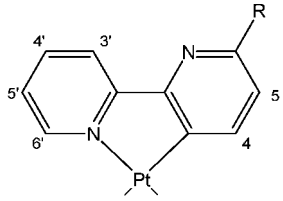
The ligands were prepared as previously described.[18] The compounds [Pt(bipy^R-H)(Me)(DMSO)] and [Pt(bipy^R-H)(Cl)(DM-

(21) Still, B. M.; Kumar, P. G. A.; Aldrich-Wright, J. R.; Price, W. S. *Chem. Soc. Rev.* **2007**, *36*, 665–686.

SO) (bipy^R = 6-*tert*-butyl-2,2′-bipyridine and 6-phenyl-2,2′-bipyridine) were synthesized according to ref 17b.

All the solvents were purified and dried according to standard procedures.[22] Elemental analyses were performed with a Perkin-Elmer 240B analyzer by Mr. Antonello Canu (Dipartimento di Chimica, Università degli Studi di Sassari, Italy). Infrared spectra were recorded with a FT-IR Jasco 480P. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 300.0 and 121.4 MHz, respectively. NOE difference experiments were performed by means of standard pulse sequences. Chemical shifts are given in ppm relative to internal TMS (^{1}H) and external 85% H_3PO_4 (^{31}P). NMR simulations were performed by means of the gNMR software.[20]

The ESI mass spectrometric measurements were performed on a quadrupole time-of-flight nanoESI-Q-TOF instrument (Q-Tof Ultima, Waters, Manchester, UK) equipped with a nanoelectrospray ion source, calibrated in positive mode.



NMR numbering scheme

Synthesis of [Pt(bipy^R-H)(Cl)CO], 3b and 4b. Into a solution of [Pt(bipy^R-H)(Cl)DMSO] (0.187 mmol) in CH_2Cl_2 (15 mL), CO was bubbled at room temperature for 3 h, then the solution was concentrated to small volume under vacuum and treated with *n*-pentane. The precipitate formed was filtered, washed with *n*-pentane, and vacuum-pumped to give the analytical sample as a yellow solid.

R = t-Bu, **3b**: yield 77%, mp 117 °C. Anal. Calcd for $C_{15}H_{15}ClN_2OPt$: C, 38.35; H, 3.22; N, 5.96. Found: C, 38.38; H, 2.92; N, 5.78. ^{1}H NMR ($CDCl_3$): 9.44 (dd, 1H, J_{H-H} = 5.4 Hz, J_{Pt-H} = 34.5 Hz, $H_{6'}$), 8.29 (dd, 1H, J_{H-H} = 7.2 Hz, $H_{3'}$), 8.04 (td, 1H, J_{H-H} = 7.2 Hz, J_{H-H} = 1.5 Hz $H_{4'}$), 7.66 (d, 1H, J_{H-H} = 8.1 Hz, J_{Pt-H}= 60.9 Hz H_4), 7.47 (ddd, 1H, J_{H-H} = 7.2 Hz, J_{H-H} = 5.4 Hz, J_{H-H} = 1.5 Hz, $H_{5'}$), 7.09 (d, 1H, J_{Pt-H} = 10.2 Hz, J_{H-H} = 8.1 Hz, H_5), 1.38 (9H, CH_3). FT-IR (CH_2Cl_2): 2104 cm^{-1}, s.

R = Ph, **4b**: yield 67%, mp 234 °C (dec). Anal. Calcd for $C_{17}H_{11}ClN_2OPt$: C, 41.69; H, 2.26; N, 5.72. Found: C, 39.82: H, 1.43; N,5.36. ^{1}H NMR ($CDCl_3$): 9.49 (d, 1H, J_{H-H} = 5.2 Hz, J_{Pt-H} = 34 Hz, $H_{6'}$), 8.40 (d, 1H, J_{H-H} = 7.2 Hz, $H_{3'}$), 8.08−8.06 (m, 3H, $H_{o(Ph)}$+$H_{4'}$), 7.80 (d, 1H, J_{H-H} = 8.0 Hz, J_{Pt-H} = 61.1 Hz H_4), 7.52−7.45 (m, 5H, $H_{m+p(Ph)}$+H_5+$H_{5'}$). FT-IR (Nujol): 2112 cm^{-1}, s.

Synthesis of [Pt(bipy^R-H)(Cl)(3,5-Me$_2$Py)], 3c and 4c. To a solution of [Pt(bipy^R-H)(Cl)DMSO] (0.420 mmol) in 25 mL of $CHCl_3$ was added 4.2 mmol of 3,5-Me$_2$Py (10-fold excess). The solution was stirred and heated to reflux for 8 h, then it was concentrated to small volume under vacuum and treated with *n*-pentane. The precipitate formed was filtered, washed with *n*-pentane, and vacuum-pumped to give the analytical sample as a yellow solid.

R = t-Bu, **3c**: yield 95%, mp 210 °C (dec). Anal. Calcd for $C_{21}H_{24}ClN_3Pt$: C, 45.95; H, 4.41; N, 7.65. Found: C, 45.75; H, 3.92; N, 7.65. ^{1}H NMR ($CDCl_3$): 9.62 (dd, 1H, J_{H-H} = 5.4 Hz, J_{Pt-H} = 39.6 Hz, $H_{6'}$), 8.62 (s, 2H, J_{Pt-H} = 46.2 Hz, $H_{o\text{-}lutidine}$), 8.14 (dd, 1H, J_{H-H} = 7.8 Hz, $H_{3'}$), 7.88 (td, 1H, J_{H-H} = 7.8 Hz, J_{H-H} = 1.5 Hz $H_{4'\ nv}$), 7.48 (s, 1H, $H_{p\text{-}lutidine}$), 7.23 (m, 1H,overlapping $CDCl_3$ $H_{5'}$), 6.94 (d, 1H, J_{H-H} = 8.1 Hz, H_5), 6.57 (d, 1H, J_{H-H} = 8.1 Hz, J_{Pt-H} = 45 Hz, H_4), 2.36 (s, 6H, CH_3 3,5-lutidine), 1.35 (s, 9H, CH_3 t-Bu).

R = Ph, **4c**: yield 94%, mp 235 °C (dec). Anal. Calcd for $C_{23}H_{20}ClN_3Pt$; C, 48.55; H, 3.54; N,7.39. Found: C, 47.97; H, 3.21; N, 7.22. ^{1}H NMR ($CDCl_3$): 9.68 (dd, 1H, J_{H-H} = 5.7 Hz, J_{Pt-H} = 39.3 Hz, $H_{6'}$), 8.65 (s, 2H, J_{Pt-H} = 44.4 Hz, $H_{o\text{-}lutidine}$), 8.27 (dd, 1H, J_{H-H} = 7.8 Hz, $H_{3'}$), 8.05 (dd, 2H, J_{H-H} = 7.2 Hz, H_{oPh}), 7.94 (td, 1H, J_{H-H} = 7.8 Hz, $H_{4'}$), 7.51−7.28 (m, 6H, H_5+$H_{5'}$+H_{mPh}+H_{pPh}+$H_{p\text{-}lutidine}$), 6.75 (d, 1H, J_{H-H} = 8.1 Hz, J_{Pt-H} = 40 Hz, H_4), 2.40 (s, 6H, CH_3 3,5-lutidine).

Synthesis of [Pt(bipy^R-H)(Cl)(PPh$_3$)], 3d and 4d. To a solution of [Pt(bipy^R-H)(Cl)DMSO] (0.140 mmol) in 15 mL of CH_2Cl_2 was added 0.140 mmol of PPh_3. The solution was stirred for 2 h, concentrated to small volume under vacuum, and treated with *n*-pentane. The precipitate formed was filtered, washed with *n*-pentane, and vacuum-pumped to give the analytical sample as a yellow solid.

R = t-Bu, **3d**: yield 88%, mp > 260 °C. Anal. Calcd for $C_{32}H_{30}ClN_2PPt \cdot H_2O$: C, 53.22; H, 4.47; N, 3.88. Found: C, 53.01; H, 3.96; N, 3.97. ^{1}H NMR ($CDCl_3$): 9.81 (m, 1H, J_{Pt-H} = 27.0 Hz, J_{P-H} = ca. 4.5 Hz, $H_{6'}$); 8.23 (d, 1H, J_{H-H} = 7.5 Hz, $H_{3'}$); 7.95 (t, 1H, J_{H-H} = 7.5 Hz, $H_{4'}$); 7.79 (m, 6H, H_o PPh_3), 7.41 (m, 10H, H_p + H_m + $H_{5'}$), 6.74 (dd, 1H, J_{Pt-H} = 48.6 Hz, J_{P-H} = 2.7 Hz, J_{H-H} = 8.1 Hz, H_4), 6.46 (d, 1H, J_{H-H} = 8.1 Hz, H_5), 1.28 (s, 1H, CH_3 t-Bu). ^{31}P{^{1}H} NMR ($CDCl_3$): 23.65 (s, J_{Pt-P} = 4308 Hz). FT-IR (Nujol): 1098 cm^{-1} (P−C) s.

R = Ph, **4d**: yield 97%, mp >260 °C. Anal. Calcd for $C_{34}H_{26}ClN_2PPt$; C, 56.40; H, 3.62; N, 3.87. Found: C, 56.06; H, 3.88; N, 3.92. ^{1}H NMR ($CDCl_3$): 9.86 (m, 1H, J_{Pt-H} = ca. 30 Hz, $H_{6'}$); 8.46 (d, 1H, J_{H-H} = 7.8 Hz, $H_{3'}$); 8.0 (m, 3H, $H_{4'}$); 7.85−7.78 (m, 6H, H_o PPh_3), 7.48−7.26 (m, 13H), 6.90 (m, 2H, H_4+H_5 overlapping). ^{31}P{^{1}H} NMR ($CDCl_3$): 23.63 (s, J_{Pt-P} = 4286 Hz).

Synthesis of [Pt(bipy^R-H)(H)(PPh$_3$)], 5d and 6d. Method A. To a solution of [Pt(bipy^R-H)(Cl)(PPh_3)] (0.10 mmol) in 30 mL of THF was added a suspension of $NaBH_4$ (0.20 mmol, 2-fold excess) in the same solvent (10 mL). The mixture was stirred for 1 h, cooled, kept at 0 °C for 5 min, filtered over Celite, and concentrated to dryness at room temperature. The residue was recrystallized from acetone/*n*-pentane to give the analytical sample as a dark yellow solid.

R = t-Bu, **5d**: yield 30%, mp 150 °C (dec). Anal. Calcd for $C_{32}H_{31}N_2PPt \cdot 0.5H_2O$: C, 56.63; H,4.75; N,4.13. Found: C, 56.70; H, 4.43; N, 4.13. ^{1}H NMR ($(CD_3)_2CO$): 8.34 (d, 1H, J_{H-H} = 7.5 Hz, $H_{3'}$), 8.18 (ddd, 1H, J_{H-H} = 7.8 Hz, J_{P-H} = 6.1 Hz, J_{H-H} = 1.2 Hz, J_{Pt-H} = ca. 63 Hz, H_4), 7.97 (td, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.5 Hz, $H_{4'}$), 7.73 (m, 6H, H_o PPh_3), 7.63 (d, partially overlapping, 1H, J_{H-H}= 5.5 Hz, $H_{6'}$), 7.50 (m, 9H, H_m+ H_p PPh_3), 7.15 (dd, 1H, J_{H-H} = 7.8 Hz, J_{P-H} = 1 Hz, H_5), 6.96 (ddd, 1H, J_{H-H} = 1.5 Hz, J_{H-H} = 7.5 Hz, J_{H-H} = 5.5 Hz, $H_{5'}$), 1.39 (s, 9H, CH_3 t-Bu), −15.95 (d, 1H, J_{P-H} = 24 Hz, J_{Pt-H} = 1444 Hz, H$^-$). ^{31}P{^{1}H} NMR $CDCl_3$: 33.6 (s, J_{Pt-P} = 2147 Hz). FT-IR (Nujol): 2204 cm^{-1} (Pt−H) s, 1097 cm^{-1} (P−C) s.

R = Ph, **6d**: yield 30%, mp 173 °C (dec). Anal. Calcd for $C_{34}H_{27}N_2PPt \cdot 2H_2O$: C, 56.27; H, 4.31; N, 3.86. Found: C, 56.12; H, 3.72; N,3.71. ^{1}H NMR (CD_2Cl_2), 8.46 (d, 1H, J_{H-H} = 7.5 Hz, $H_{3'}$); 8.35 (ddd, 1H, J_{H-H} = 1 Hz, J_{H-H} = 7.8 Hz, J_{P-H} = 7.3 Hz H_4); 8.14 (d, 2H, J_{H-H} = 7.2 Hz, H_{oPh}); 7.86 (td, 1H, J_{H-H} = 1.5 Hz, J_{H-H} = 7.5 Hz $H_{4'}$), 7.68 (m, 6H, H_{oPPh3}), 7.62 (d, 1H, J_{H-H} = 5.4 Hz, $H_{6'}$), 7.56 (dd, 1H, J_{P-H} = 1 Hz, J_{H-H} = 7.8 Hz, H_5); 7.43 (m, 12H, $H_{(m+p)PPh3}$+$H_{(m+p)Ph}$); 6.84 (ddd, 1H, J_{H-H} = 1.5 Hz, J_{H-H} = 5.4 Hz, J_{H-H} = 7.5 Hz, $H_{5'}$); −15.91 (d, 1H, J_{Pt-H} = 1424 Hz, J_{P-H} = 24 Hz, Pt−H). ^{31}P{^{1}H} NMR (CD_2Cl_2): 32.8 (s, J_{Pt-P} = 2174 Hz). FT-IR (Nujol): 2196 cm^{-1} (Pt−H) s, 1097 cm^{-1} (P−C) s.

Method B. To a solution of [Pt(bipy^R-H)(H)]$_4$ (0.061 mmol) in 15 mL of CH_2Cl_2 was added 0.061 mmol of PPh_3. The solution

(22) *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman Scientific and Technical: Harlow, 1989.

was stirred at room temperature for 10 min, concentrated to small volume under vacuum, and treated with *n*-pentane. The precipitate formed was filtered, washed with *n*-pentane, and vacuum-pumped to give the analytical sample as a yellow solid. R = t-Bu, **5d**: yield 59%, R = Ph, **6d**: yield = 75.1%.

Synthesis of [Pt(bipy^{R}-H)(H)]$_4$, 7 and 8. Method A. To a solution of [Pt(bipy^{R}-H)(Cl)(3,5-Me$_2$-py)] (0.53 mmol) in 120 mL of THF was added 1.06 mmol of $NaBH_4$ (2-fold excess). The mixture was stirred for 1 h, cooled, kept at 0 °C for 5 min, filtered over Celite, and evaporated to dryness at room temperature. The residue was washed with cold acetone and filtered to give the analytical sample as a red solid.

R = t-Bu, **7**: yield 70%, mp 210 °C (dec). Anal. Calcd for $(C_{14}H_{16}N_2Pt)_4$: C, 41.28; H,3.96; N 6.88. Found: C, 41.36; H, 4.14; N, 7.02. ^{1}H NMR (CD_2Cl_2): 8.88 (d, 1H, J_{H-H} = 5.4 Hz, J_{Pt-H} = ca.38 Hz, $H_{6'}$), 7.97 (d, 1H, J_{H-H} = 7.8 Hz, J_{Pt-H} = 49 Hz, H_4), 7.74 (dd, 1H, J_{H-H} = 7.5 Hz, $H_{3'}$), 7.56 (td, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.5 Hz, $H_{4'}$), 6.88 (d, 1H, J_{H-H} = 7.8 Hz, H_5), 6.52 (td, 1H, J_{H-H} = 7.2 Hz, J_{H-H} = 5.6 Hz, J_{H-H} = 1.4 Hz, $H_{5'}$), 1.32 (s, 9H, CH_3 t-Bu), −14.46 (s, 1H, J_{Pt-H} = 1011 Hz, J_{Pt-H} = 387 Hz, J_{Pt-H} = 39 Hz, H$^-$). ESI-MS (CH_2Cl_2): *m*/*z* 1629 [MH$^+$].

R = Ph, **8**: yield ca. quantitative, mp >260 °C. Anal. Calcd for $(C_{16}H_{12}N_2Pt)_4$: C, 44.97; H, 2.83; N, 6.56. Found: C, 44.75; H, 3.02; N, 6.38. ^{1}H NMR (CD_2Cl_2): 9.01 (dd, 1H, J_{H-H} = 5.6 Hz, J_{Pt-H} = ca. 36 Hz, $H_{6'}$), 8.20 (d, 1H, J_{H-H} = 7.8 Hz, J_{Pt-H} broad, H_4), 8.03 (dd, 2H, J_{H-H} = 6.9 Hz, H_o), 7.92 (dd, 1H, J_{H-H} = 7.8 Hz, $H_{3'}$), 7.62 (td, 1H, J_{H-H} = 7.8 Hz $H_{4'}$), 7.50−7.38 (m, 3H, H_m+H_p), 7.31 (d, 1H, J_{H-H} = 7.8 Hz H_5), 6.59 (ddd, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 5.6 J_{H-H} = 1.5 Hz, $H_{5'}$), −14.29 (s, 1H, J_{Pt-H} = 1008.9 Hz, J_{Pt-H} = 389.1 J_{Pt-H} = 39 Hz, H$^-$). ESI MS (CH_2Cl_2): *m*/*z* 1709 [MH$^+$], 1475 [M − bipy − H]$^+$, 855 [M/2]$^+$.

Method B. To a solution of [Pt(bipy^{R}-H)(Cl)(DMSO)] (0.223 mmol) in 30 mL of THF was added 0.445 mmol of $NaBH_4$ (2 -fold excess). The mixture was stirred for 1 h, then cooled at 0 °C for 5 min, filtered over Celite, and evaporated to dryness at room temperature. The residue was washed with cold acetone and filtered to give the analytical sample as a red solid. R = t-Bu, **7**: yield 41%, R = Ph, **8**: yield = 33%.

Synthesis of [Pt(bipy^{R}-H)(H)CO], 5b and 6b. Solid [Pt(bipy^{R}-H)(H)]$_4$ (0.014 mmol) was kept at room temperature under 1 atm of CO for 72 h, to give the analytical sample in quantitative yield.

R = t-Bu, **5b**: mp 70 °C (dec). Anal. Calcd for $C_{15}H_{16}N_2OPt$: C, 41.38; H, 3.70, N, 6.43. Found: C, 41.75; H, 3.44; N, 6.52. ^{1}H NMR (CD_2Cl_2): 8.61 (d, 1H, J_{H-H} = 5.4 Hz, J_{Pt-H} = ca. 18 Hz, $H_{6'}$), 8.32 (dd, 1H, J_{H-H} = 7.7 Hz, $H_{3'}$), 8.08 (dd, 1H, J_{H-H} = 7.8 Hz, J_{Pt-H} = 60 Hz, J_{H-H} = 1.3 Hz, H_4), 8.03 (td, 1H, J_{H-H} = 1.5 Hz, J_{H-H} = 7.7 Hz, $H_{4'}$), 7.36 (ddd, 1H, J_{H-H} = 1.4 Hz, J_{H-H} = 5.4 Hz, J_{H-H} = 7.7 Hz, $H_{5'}$), 7.16 (d, 1H, J_{H-H} = 7.8 Hz, J_{Pt-H} = 11.2 Hz, H_5), 1.36 (s, 9H, CH_3 t-Bu), −12.93 (s, 1H, J_{Pt-H} = 1459 Hz, Pt−H). FT-IR (Nujol): 2179 cm^{-1} (Pt−H) s, 2048 cm^{-1} (CO) s.

R = Ph, **6b**: mp 107 °C (dec). Anal. Calcd for $C_{17}H_{12}N_2OPt$: C, 44.84; H, 2.66; N, 6.15. Found: C, 44.54; H, 2.81; N, 5.87. ^{1}H NMR (CD_2Cl_2): 8.68 (dd, 1H, J_{H-H} = 0.7 Hz, J_{H-H} = 5.4 Hz, J_{Pt-H} = ca. 18 Hz, $H_{6'}$), 8.45 (dd, 1H, J_{H-H} = 0.7 Hz, J_{H-H} = 7.7 Hz, $H_{3'}$), 8.24 (dd, 1H, J_{H-H} = 7.7 Hz, J_{Pt-H} = 60.7 Hz, J_{H-H} = 1.2 Hz, H_4), 8.12−8.04 (m, 3H), 7.58 (d, 1H, J_{H-H} = 7.7 Hz, J_{Pt-H} = 11.5 Hz, H_5), 7.51−7.37 (m, 4H), −12.92 (s, 1H, J_{Pt-H} = 1458 Hz, Pt−H). FT-IR (CH_2Cl_2): 2196 cm^{-1}, m, Pt−H; 2061 cm^{-1} (CO) s.

Synthesis of [Pt(bipy^{R}-H)(D)]$_4$, 9, and [Pt(bipy^{R}-H)(D)(CO)], 10 (R = Ph). To a solution of [Pt(bipy^{R}-H)(Cl)(3,5-Me$_2$-pyridine)] (R = Ph, 100 mg, 0.176 mmol) in 60 mL of THF was added 6.87 mg of $NaBD_4$ (0.2 mmol 15% excess); the mixture was stirred for 2.5 h, then cooled at 0 °C, filtered over Celite, and evaporated to dryness at room temperature. The residue was recrystallized from acetone/*n*-pentane to give the analytical sample as a red solid.

9: yield 62%, mp > 260 °C. Anal. Calcd for $C_{16}H_{12}N_2PtD$: C, 44.86; H, 3.06: N, 6.54. Found: C, 44.55; H,3.14; N, 6.25. ^{1}H NMR ($CDCl_3$): 9.01 (d, 1H, J_{H-H} = 5.7 Hz, J_{Pt-H} broad, $H_{6'}$), 8.26 (d, 1H, J_{H-H} = 7.8 Hz, J_{Pt-H} broad, H_4), 8.03 (dd, 2H, J_{H-H} = 6.9 Hz, H_o), 7.93 (d, 1H, J_{H-H} = 7.8 Hz, $H_{3'}$), 7.58 (td, 1H, J_{H-H} = 7.8 Hz $H_{4'}$), 7.51−7.40 (m, 3H, H_m+H_p), 7.21 (d, 1H, overlapping $CDCl_3$, H_5), 6.55 (ddd, 1H, J_{H-H} = 5.7 Hz, J_{H-H} = 7.8 Hz, $H_{5'}$).

Complex **10** was obtained by bubbling CO at room temperature into a CH_2Cl_2 solution of complex **9**. ^{1}H NMR (CD_2Cl_2): 8.68 (dd, 1H, J_{H-H} = 5.4 Hz, J_{Pt-H} = ca.18 Hz, $H_{6'}$), 8.48 (dd, 1H, J_{H-H} = 7.7 Hz, $H_{3'}$), 8.24 (d, 1H, J_{H-H} = 7.7 Hz, J_{Pt-H} = 60 Hz, H_4), 8.12−8.02 (m, 3H), 7.58 (d, 1H, J_{H-H} = 7.7 Hz, J_{Pt-H} = 11.5 Hz, H_5), 7.51−7.38 (m, 4H). FT-IR (CH_2Cl_2): 2061 cm^{-1} (CO) s.

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