Dinuclear C,N,C Cyclometalated Platinum Derivatives with Bridging Delocalized Ligands. Fourfold Deprotonation of 6,6′-Diphenyl-2,2′-bipyridine, H₄L, Promoted by "Pt(R)₂" Fragments (R = Me, Ph). Crystal Structures of [Pt₂(L)(3,5-Me₂py)₂] and {Pt₂(L)(dppe)}₂ (dppe = 1,2-Bis(diphenylphosphino)ethane). X-ray Powder Diffraction of [Pt₂(L)(CO)₂]

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cis-[Pt(R)₂(DMSO)₂] (R = Me, Ph) reacts with 6,6′-diphenyl-2,2′-bipyridine (H₄L) in a 2:1 molar ratio, giving the unusual, very slightly soluble dinuclear complex [Pt₂(L)(DMSO)₂] (**1**). The reaction implies activation of four C−H bonds: in **1** a fourfold deprotonated H₄L links two Pt−DMSO fragments acting as a delocalized C,N,C∧C,N,C 12-electron donor. From **1** more soluble dinuclear [Pt₂(L)(L′)₂] (L′ = bulky 2-electron donors such as PR₃ and substituted pyridines) species, **2**−**6**, and polynuclear {Pt₂(L)(L−L)}ₙ (L−L = Ph₂P(CH₂)ₓPPh₂ (x = 1, dppm; x = 2, dppe; x = 3, dppp)) species, **7**−**9**, have been obtained by substitution of the DMSO ligands. DMSO can also be displaced from **1** by CO, both in solution and in the solid state, to give the flat and completely insoluble complex [Pt₂(L)(CO)₂] (**10**). The structures of [Pt₂(L)(3,5-Me₂-Py)₂] (**5**) and {Pt₂(L)(dppe)}₂ (**8**) have been determined by single-crystal X-ray diffraction analysis, while a powder X-ray diffraction analysis has been performed on complex **10**, [Pt₂(L)(CO)₂]. With a 1:1 Pt:L molar ratio a mononuclear complex, [Pt(H₂L)(DMSO)] (**11**), is obtained, where the twofold deprotonated ligand is C,N,C coordinated. Also, the DMSO can be displaced from **11** by neutral ligands, L′, such as CO, PPh₃, and 3,5-Me₂-py to give [Pt(H₂L)(L′)] (**12**−**14**). Compounds **11**−**14** further react with *cis*-[Pt(R)₂(DMSO)₂] to give dinuclear complexes. This two-step approach allows us to obtain species with different ligands around each platinum atom, [Pt₂(L)(L′)(L″)] (**15**−**18**).

Introduction

Cyclometalated compounds of late transition metals with nitrogen ligands are well-known.[1] During the years they have been the subject of continuous research, due to their numerous potential applications in areas such as organic synthesis,[2] homogeneous catalysis,[3] medicinal and biological chemistry,[4] and the design of novel materials with attractive properties. Recently, cyclometalated derivatives of d⁸ metal ions have been studied as chemosensors,[5] switches,[6] metallomesogens,[7] and luminescent[8] devices. Square-planar platinum(II) and palladium-(II) species were also used as "building blocks" for complex systems such as supramolecular entities or dendrimers.[9]

In addition to the classical N,C compounds, great attention is now devoted to d⁸ complexes with terdentate ligands. Species having an N,N,C or an N,C,N sequence of donor atoms are common, whereas complexes with a C,N,C sequence are still rare.[10] The N,N,C cyclometalates having planar terdentate ligands, such as those arising from 6-phenyl-2,2′-bipyridine, imply a delocalized π system which can give rise to peculiar photophysical and photochemical properties involving, inter alia, weak noncovalent interactions such as d⁸−d⁸ or π−π interactions.[11]

Our previous work in this field was concentrated on the reactivity of d⁸ ions with 6-substituted 2,2′-bipyridines: platinum(II),[12] gold(III),[13] and palladium(II).[12a,b,e,14] N,N,C cyclometalated derivatives have been synthesized, with both metal−

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Scheme 1
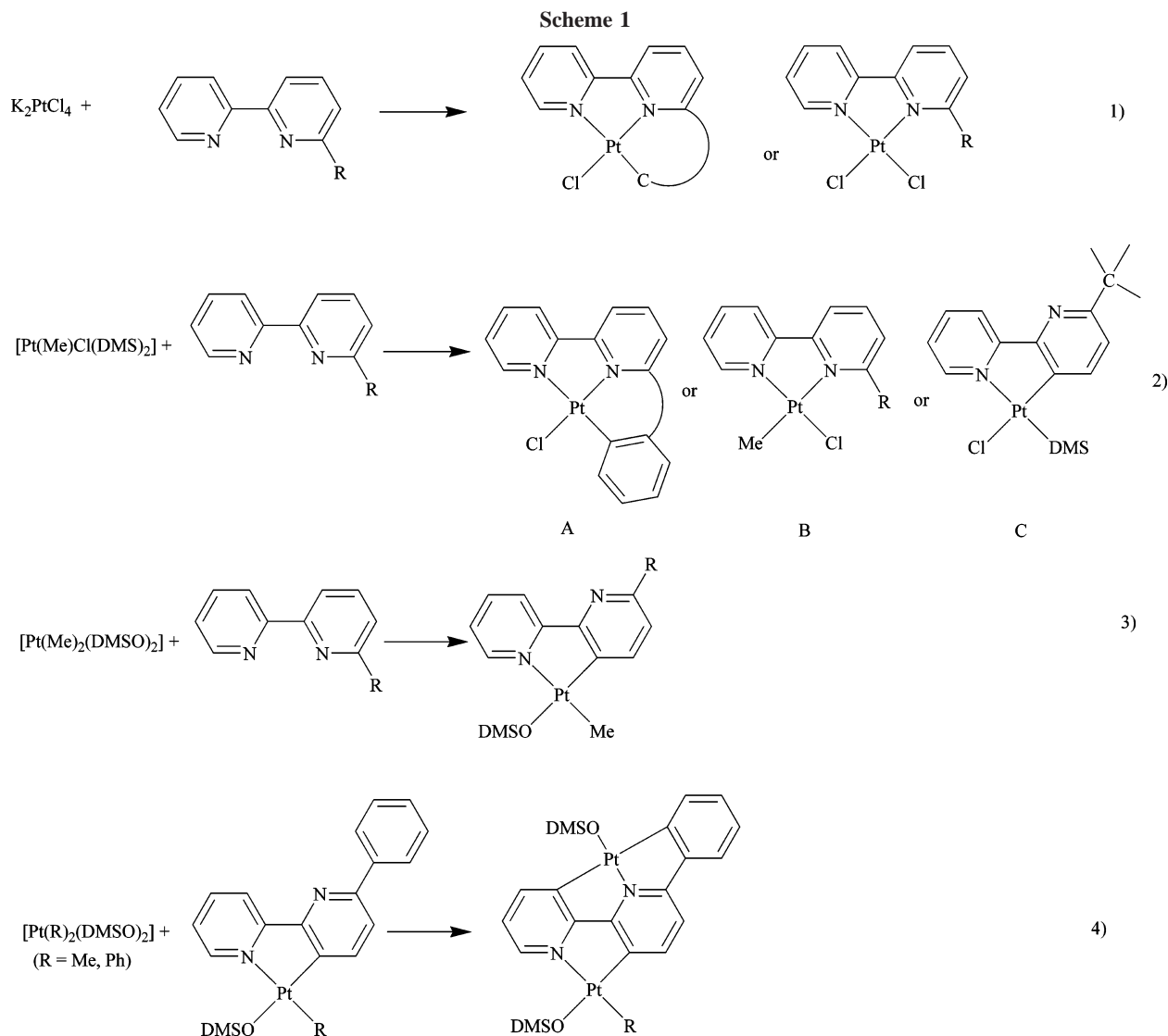
C(sp^2) and metal−C(sp^3) bonds. The behavior of these ligands is not easily predictable, especially in the case of palladium-(II), the reaction often being driven toward unexpected results.

In the case of platinum(II) the results can be summarized as follows.

(1) Inorganic Pt(II) derivatives such as $[PtCl_4]^{2-}$ and $[(L')_2PtCl_2]$ (L' = neutral monodentate ligand) react with 6-substituted bipyridines (bipy^R) to afford 1:1 adducts, [PtCl$_2$-(bipy^R)], or cyclometalated compounds, [PtCl(bipy^R-H)]. The metalation implies elimination of HCl (Scheme 1, reaction 1).

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(2) With hybrid intermediates such as [PtCl(Me)(SMe$_2$)$_2$], either 1:1 adducts, [PtCl(Me)(bipy^R)], or metalated derivatives, [PtCl(bipy^R-H)] (R = Ph, CH$_2$Ph, C(Me)$_2$Ph), were obtained. In this case the metalation occurs with loss of CH$_4$. With 6-*tert*-butyl-2,2′-bipyridine an unexpected result was observed, probably due to the bulkiness of the substituent: the reaction proceeds at room temperature through C—H activation and methane elimination, but the activation does not involve a carbon on the substituent but one of the substituted pyridine rings. In compound C (Scheme 1, reaction 2) the bipyridine acts as a bidentate N′,C(3) ligand ("rollover" metalation[15]) to give a five-membered cycle.

(3) When electron-rich diorgano derivatives such as [Pt(R)$_2$-(DMSO)$_2$] (R = Me, Ph), are employed, the "rollover" metalation proceeds under mild conditions with many 6-substituted 2,2′-bipyridines (Scheme 1, reaction 3). The unusual room-temperature C—H activation is specific to 6-substituted bipyridines; N′,C(3) metalated derivatives were not obtained with the unsubstituted ligand or with a 6,6′-disubstituted bipy (R = Me).[15b]

(4) The rollover species obtained from the ligand 6-Ph-2,2′-bipy is able to react with a second molecule of [Pt(R)$_2$(DMSO)$_2$] (Scheme 1, reaction 4) to give dinuclear species. The bridging 3-fold deprotonated bipy acts as a terdentate C,N,C ligand toward one platinum and as a bidentate C∧N ligand toward the second one.[12g]

The last reaction is a rare example of multiple C—H bond activation, and the species obtained are unique in several respects: (i) the two platinum atoms are connected through a planar, delocalized, trianionic, 10-electron-donor ligand, derived from a threefold deprotonated 6-phenyl-2,2′-bipyridine; (ii) three five-membered C,N cycles are assembled in the same molecule; (iii) the terdentate dianionic system has a rare C∧N∧C sequence of donor atoms,[10] a sequence obtained through direct C—H activation only in a few cases; (iv) the neutral DMSO ligands are trans to atoms with different trans influences and trans effects. Moreover, the new organometallic species have a high thermal stability.

Following our previous studies, here we report an investigation on the related ligand 6,6′-diphenyl-2,2′-bipyridine, similar to 6-phenyl-2,2′-bipyridine but potentially able to undergo additional C—H activations providing more complex delocalized systems.

Results and Discussion

The ligand 6,6′-diphenyl-2,2′-bipyridine, H$_4$L, was synthesized according to literature methods.[16] To ascertain whether

the ligand was able to undergo a double "rollover" metalation, the reaction with [Pt(Me)$_2$(DMSO)$_2$] was carried out with a platinum/ligand molar ratio of 2/1, under conditions exactly like those used in the case of 6-Ph-2,2′-bipy (toluene, 80 °C). The reaction is slow and leads to the isolation of a yellow product that is insoluble in the reaction medium, is stable in air, and has high thermal stability.
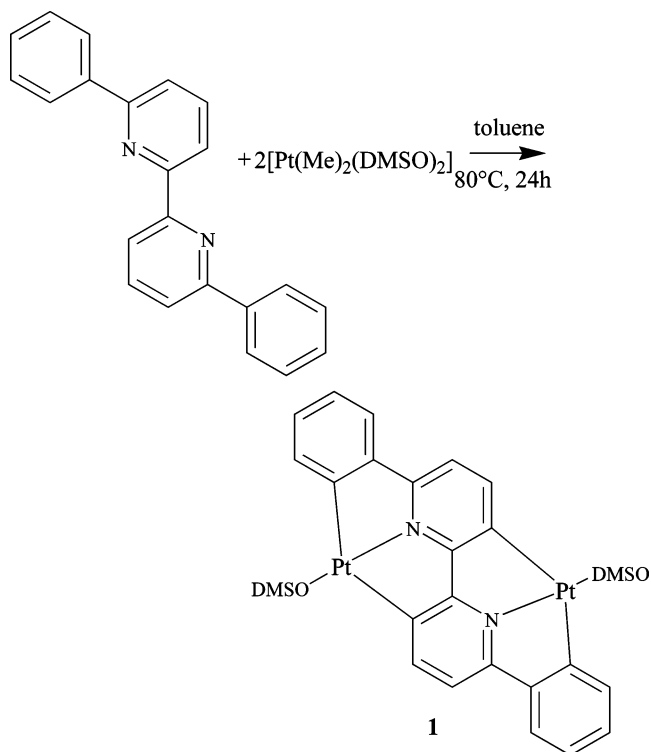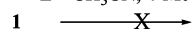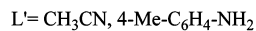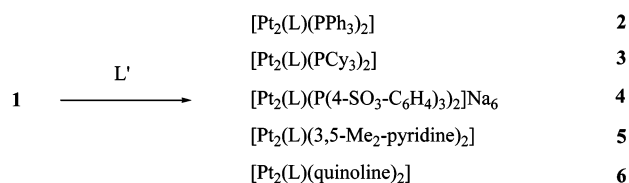

The solid obtained, yield ca. 80%, is almost insoluble in most of the common organic solvents, so that characterization in solution is hampered. The IR spectrum (Nujol mull) gives evidence for a coordinated DMSO; the analytical data (C, H, N) are in agreement with a ligand/platinum/DMSO molar ratio of 1/2/2. The complex was tentatively formulated as [Pt$_2$(L)-(DMSO)$_2$] (**1**), in which a fourfold deprotonated ligand bridges the two platinum atoms. These should both be in an uncommon C—N—C environment with a coordinated DMSO molecule to fulfill square-planar coordination. On the whole, owing to the highly delocalized bridging system, the molecule can be predicted to be almost planar. Species of this type are usually insoluble materials, due to association between the planes of monomeric units by metal—metal or π—π interactions.

Starting from complex **1**, we planned to synthesize new compounds, by substitution of the DMSO ligands, with two

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Scheme 2

$[Pt_2(L)(PPh_3)_2]$ **2**

$[Pt_2(L)(PCy_3)_2]$ **3**

1 $\xrightarrow{\quad L' \quad}$ $[Pt_2(L)(P(4\text{-}SO_3\text{-}C_6H_4)_3)_2]Na_6$ **4**

$[Pt_2(L)(3,5\text{-}Me_2\text{-}pyridine)_2]$ **5**

$[Pt_2(L)(quinoline)_2]$ **6**

L'= CH$_3$CN, 4-Me-C$_6$H$_4$-NH$_2$

1 $\xrightarrow{\quad X \quad}$

divergent purposes: (i) to obtain more soluble species easily characterizable in solution, and (ii) to obtain completely flat molecules. To discourage association among monomeric units, and thus obtain more soluble derivatives, rather bulky ligands were chosen. Replacement of coordinated DMSO with tertiary phosphines and heterocyclic sp^2 nitrogen ligands was successful, with compounds **2**−**6**, [Pt$_2$(L)(L')$_2$] (Scheme 2: L'= Ph$_3$P (**2**), Cy$_3$P (**3**), Na$_3$(4-SO$_3$-C$_6$H$_4$)$_3$P (**4**), 3,5-dimethylpyridine (**5**), quinoline (**6**)), being isolated in moderate to good yields. With an amine such as 4-Me-C$_6$H$_4$-NH$_2$ (N sp^3) or a nitrile (CH$_3$CN; N sp), substitution of DMSO was not observed.

Compounds **2**−**6** are soluble enough to be characterized by NMR spectroscopy. The ^{1}H spectra show only 6 resonances for the 12 bipyridine protons, indicating that the species are symmetric. Furthermore, only one set of signals is observed for the ancillary ligands; for example, there is only one signal in the ^{31}P{^{1}H} NMR spectra of compounds **2** and **3**. The ^{195}Pt−^{31}P coupling constants are in agreement with those of a phosphorus nucleus trans to a nitrogen atom.[12i,17]

Complex **5** has been characterized in depth in solution by means of ^{13}C, ^{1}H NOE difference and COSY spectra and in the solid state by X-ray diffraction. In the FAB mass spectrum (positive ions), besides the molecular ion [M]$^+$ at *m/z* 909, other peaks at *m/z* 802 and 694 correspond to the loss of one and two molecules of 3,5-Me$_2$-py, respectively.

Red crystals of **5**·2CHCl$_3$ suitable for single-crystal X-ray diffraction analysis were isolated by diffusion of *n*-pentane into a dilute chloroform solution. An ORTEP view of **5** is given in Figure 1. Principal bond parameters are reported in the caption of Figure 1.

The structure consists of the packing of **5** and CHCl$_3$ molecules in the molar ratio 1:2. The CHCl$_3$ molecules are partially disordered (see Experimental Section). The molecule of **5** lies on a crystallographic inversion center. The structure confirms that the ligand L behaves as a terdentate dianion toward

each platinum atom, with a "rollover" double cyclometalation. The two Pt atoms are connected by a planar bridging moiety, which acts as a 12-electron donor. The resulting widely delocalized system is quite original. The Pt atoms display an essentially square-planar coordination, with a very slight tetrahedral distortion, maximum deviations from the least-squares plane being −0.027(5) Å for N(1) and +0.021(6) Å for C(3). The Pt−N distances are normal,[18] whereas the Pt−C distances are elongated by the mutual trans influence. The deviation from linearity of the C(3)−Pt−C(10) angle, 162.2°, is obviously due to the bite of the terdentate ligand and has been observed previously.[18] The dihedral angle between the metal coordination plane and the lutidine plane is 48.3(2)°. The expected noncoplanarity of the lutidine ligand prevents the formation of significant intermolecular interactions and determines the solubility of the species.

It is noteworthy that the parent compound **1** can be obtained in one step through multiple activation of C−H bonds of both phenyl and pyridyl rings, with the loss of four molecules of methane. Complexes **2**−**6** are achieved by replacement of DMSO in compound **1** with neutral ligands. The eight condensed rings form a highly delocalized bridging motif where the two platinum atoms are connected by a substituted bipyridine unit which acts as a hexadentate, 12-electron ligand.

In an alternative strategy designed to give soluble species, compound **1** was reacted with bidentate ligands, which are able to position themselves between two platinum atoms and so keep the molecular planes apart.

Reaction of compound **1** with the diphosphines Ph$_2$P(CH$_2$)$_n$-PPh$_2$ (*n* = 1 (dppm), 2 (dppe), 3 (dppp)) in a 1:1 molar ratio gives complete substitution of DMSO and isolation of three new soluble complexes, **7** (*n* = 1), **8** (*n* = 2), **9** (*n* = 3).

The ^{31}P{^{1}H} NMR spectra of compounds **7**−**9** show only one resonance, with a chemical shift in the range expected for a bridging ligand[12d] and coupling constants comparable to those observed for compounds **2**−**4**. The NMR spectra, indicative of symmetric species, taken together with the analytical data, enable us to assume that **7**−**9** are poly- or at least tetranuclear species, the dinuclear units being connected by two diphosphines (Chart 1).

For complex **8** (dppe) the tetranuclearity of the species was confirmed by determination of the structure of **8**·1.5CHCl$_3$·H$_2$O by single-crystal X-ray diffraction. The structure consists of the packing of molecules of **8**, CHCl$_3$, and H$_2$O in the molar ratio 1:1.5:1. The solvent molecules are disordered (see Experimental Section). An ORTEP view of **8** is shown in Figure 2. Principal bond parameters are reported in Table 2. As expected, the molecule comprises two dinuclear units connected by two diphosphines, which act as hexabidentate ligands. Each of the four platinum atoms displays a square-planar coordination with a slight tetrahedral distortion. Average bond lengths involving the four Pt atoms are Pt−P = 2.217 Å, Pt−N = 2.025 Å, Pt−C(phenyl) = 2.075 Å, and Pt−C(pyridine) = 2.115 Å. All these values compare well with those found in [Pt$_2$(L)Cl(PPh$_3$)$_2$] (compound **19**, H$_3$L = 6-phenyl-2,2′-bipyridine),[12i] where one of the Pt atoms is in the same environment as the Pt atoms in **8**; in **19** Pt−P = 2.231(1) Å, Pt−N = 2.024(3) Å, Pt−C(phenyl) = 2.071(4) Å, and Pt−C(pyridine) = 2.104(6) Å). The dihedral angle between the least-squares planes of Pt(1) and Pt(2) is 8.9(6)°, and that between the least-squares planes of Pt(3) and Pt(4) is 16.5(3)°. Therefore, in this case the two dinuclear units

(13) (a) Cinellu, M. A.; Zucca, A.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1996**, 4217−4225. (b) Cinellu, M. A.; Minghetti, G.; Pinna, M. V.; Stoccoro, S.; Zucca, A.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1998**, 1735−1741. (c) Cinellu, M. A.; Minghetti, G.; Pinna, M. V.; Stoccoro, S.; Zucca, A.; Manassero, M. *Eur. J. Inorg. Chem.* **2003**, *12*, 2304−2310. (d) Cinellu, M. A.; Minghetti, G.; Pinna, M. V.; Stoccoro, S.; Zucca, A.; Manassero, M. *J. Chem. Commun.* **1998**, 2397−2398.

(14) (a) Zucca, A.; Cinellu, M. A.; Pinna, M. V.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Sansoni, M. *Organometallics* **2000**, *19*, 4295−4304. (b) Stoccoro, S.; Soro, B.; Minghetti, G.; Zucca, A.; Cinellu, M. A. *J. Organomet. Chem.* **2003**, *679*, 1−9.

(15) (a) Skapski, A. C.; Sutcliffe, V. F.; Young, G. B. *Chem. Commun.* **1985**, 609−611. (b) Minghetti, G.; Stoccoro, S.; Cinellu, M. A.; Soro, B.; Zucca, A. *Organometallics* **2003**, 4770−4777.

(16) (a) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P. *Tetrahedron Lett.* **1982**, *23*, 5291−5294. (b) Leadbeater, N. E.; Resouly, S. M. *Tetrahedron Lett.* **1999**, *40*, 4253−4246.

(17) E.g.: Lu, W.; Chan, M. C. W.; Zhu, N.; Che, C. M.; Hui, L. Z. *J. Am. Chem. Soc.* **2004,** *126*, 7639−7651.

(18) Lu, W.; Chan, M. C. W.; Cheung, K. K.; Che, C. M. *Organometallics* **2001**, *20*, 2477−2486.
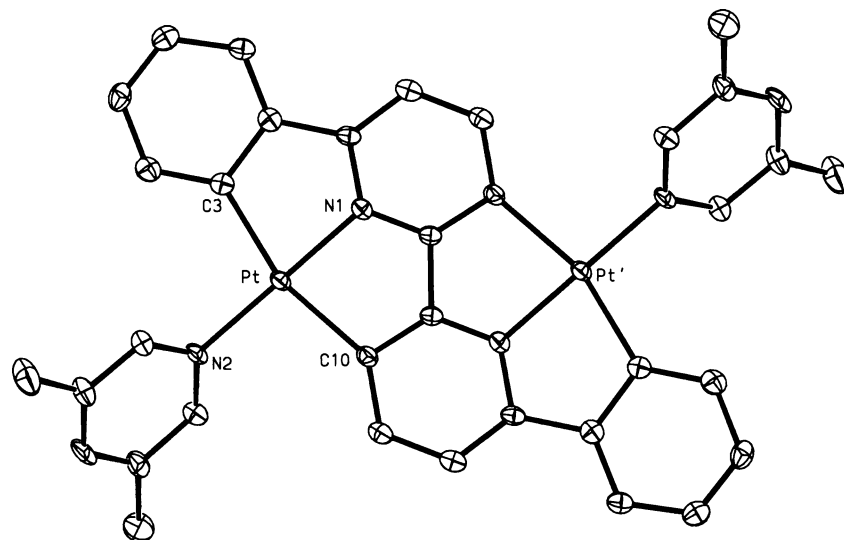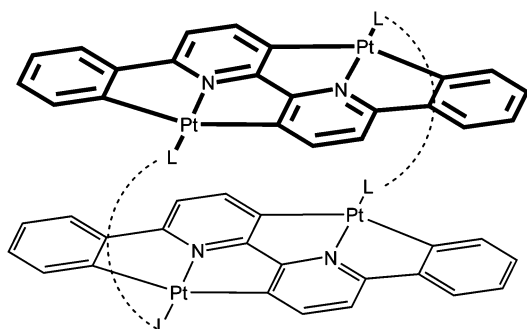
Figure 1. ORTEP view of compound **5**. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg) in **5**, with estimated standard deviations (esd's) on the last figure in parentheses: Pt−N(1) = 1.983(5), Pt−N(2) = 2.037(5), Pt−C(3) = 2.054(6), Pt−C(10) = 2.104(6); N(1)−Pt−N(2) = 178.4(2), N(1)−Pt−C(3) = 80.1(2), N(1)−Pt−C(10) = 82.1(2), N(2)−Pt−C(3) = 99.9(2), N(2)−Pt−C(10) = 98.0(2), C(3)−Pt−C(10) = 162.2(2).

Chart 1

are not completely planar, probably because of the π stacking forces, and are staggered, not eclipsed, with respect to one another. The distances between the two dinuclear units are in the range 3.26(1)−3.58(1) Å.
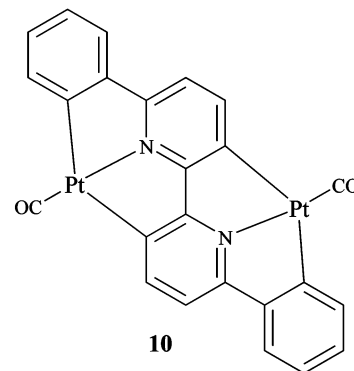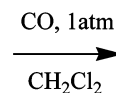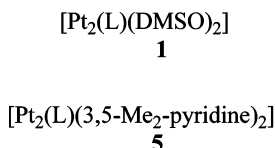
We were eager to study how the length of the CH_2 chain in the diphosphine affects the nuclearity of derivatives **7** and **9**, as well as the overall dimension of the inside cage. Unfortunately, however, crystals suitable for a X-ray analysis could not be obtained.

For comparison, the reaction of the ligand 6,6′-diphenyl-2,2′-bipyridine (H$_4$L) has been carried out with *cis*-[Pt(Ph)$_2$(DMSO)$_2$] (molar ratio 1:2) and found to give compound **1**, isolated as an almost insoluble solid that, by treatment with Ph$_3$P, affords compound **2** (NMR criterion). The double "rollover" cyclometalation implies elimination of benzene instead of methane in this case, proving that loss of methane is not an essential condition for the multiple C−H activation. This reaction, however, is less favored. Some decomposition to metal is observed, and yields are lower:

$$2 \; cis\text{-}[Pt(Ph)_2 (DMSO)_2] \xrightarrow[\text{(ii) PPh}_3]{\text{(i) H}_4\text{L}}$$
$$[Pt_2(L)(PPh_3)_2] + 4C_6H_6 + 4DMSO$$
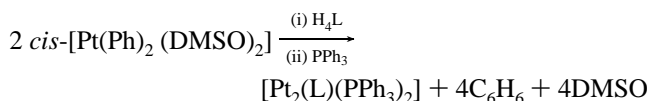
To synthesize a completely flat molecule, complex **1** was reacted with carbon monoxide in a CH_2Cl_2 suspension. Sub-

stitution of CO for DMSO occurs at room temperature, giving complex **10**, [Pt$_2$(L)(CO)$_2$].

$$[Pt_2(L)(DMSO)_2]$$
1

$$[Pt_2(L)(3,5\text{-Me}_2\text{-pyridine})_2]$$
5

$$\xrightarrow[\text{CH}_2\text{Cl}_2]{\text{CO, 1atm}}$$

10

The reaction also proceeds in solution starting from **5** and, notably, even by passing a stream of CO over complex **1** in the solid state. Yields are good, 75−85%. Complex **10** is a brick red material which is completely insoluble in common solvents, suggesting strong association of the planar dinuclear units. The thermal stability is unusual for an organometallic species, the complex not melting or decomposing in air up to 270 °C. The IR spectrum shows a sharp absorption at 2063 cm^{-1}, in the region of terminal carbonyls, a reasonable value for a CO trans to a nitrogen atom in a neutral platinum(II) complex.[12i] The coordinated CO is easily displaced by Ph$_3$P to give compound **2** but, surprisingly, not by 3,5-Me$_2$-py. Samples of complex **10** suitable for a single-crystal X-ray diffraction analysis could not be obtained. The structure was therefore studied by X-ray powder diffraction.

The structure of complex **10** was determined from powder X-ray diffraction data by a direct space method, as implemented in the software package Dash.[19] The structural solution obtained
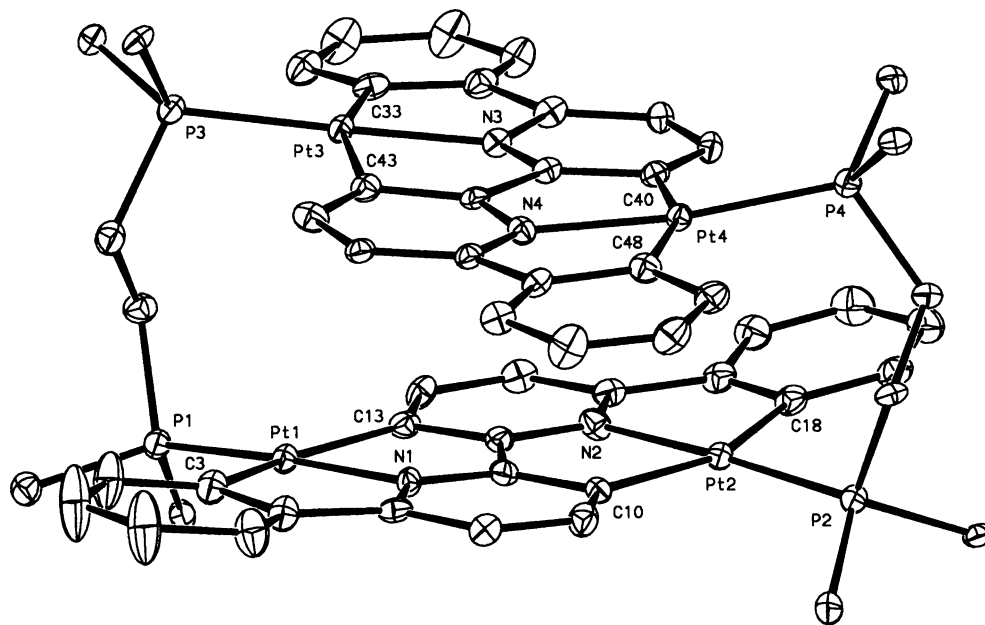
Figure 2. ORTEP view of compound **8**. Ellipsoids are as in Figure 1. Only the first atoms of the phosphinic phenyl rings have been shown, for clarity.

Table 1. Crystallographic Data

	5·2CHCl₃	8·1.5CHCl₃·H₂O
formula	C₃₈H₃₂Cl₆N₄Pt₂	C₉₇.₅H₇₅.₅Cl₄.₅N₄OP₄Pt₄
M_r	1147.60	2383.01
color	red	red
cryst syst	orthorhombic	orthorhombic
space group	*Pbca*	$P2_12_12_1$
a/Å	11.710(1)	16.140(1)
b/Å	15.240(1)	19.532(1)
c/Å	21.610(2)	27.911(2)
V/Å³	3856.5(6)	8798.8(1.0)
Z	4	4
F(000)	2184	4580
D_c/g cm⁻³	1.976	1.799
T/K	150	150
cryst dimens/mm	0.22 × 0.23 × 0.33	0.20 × 0.22 × 0.44
μ(Mo Kα)/cm⁻¹	77.8	66.7
min and max transmissn factors	0.479−1.000	0.631−1.000
scan mode	ω	ω
frame width/deg	0.30	0.30
time per frame/s	25	15
no. of frames	2450	2450
detector−sample dist/cm	4.00	4.00
θ range/deg	3−27	3−27
reciprocal space explored	full sphere	full sphere
no. of rflns (total, indep)	52 032, 4222	122 297, 19 667
R_{int}	0.0779	0.0637
final R_2 and R_{2w} indices[a] (F^2, all rflns)	0.068, 0.090	0.051, 0.066
conventional R1 index ($I > 2\sigma(I)$)	0.037	0.027
no. of rflns with $I > 2\sigma(I)$	3035	15 476
no. of variables	244	1063
goodness of fit[b]	1.05	0.98

[a] $R_2 = [\sum(|F_o^2 - kF_c^2|/\sum F_o^2]$, $R_{2w} = [\sum w/(F_o^2 - kF_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [b] $[\sum w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (pF_o^2)^2]^{1/2}$, N_o is the number of observations, N_v the number of variables, and *p*, the ignorance factor, is 0.03 for **5**·2CHCl₃ and 0.02 for **8**·1.5CHCl₃·H₂O.

was subjected to rigid-body Rietveld refinement.[20] The molecule, which lies on a 2-fold rotation axis in the structure, is shown in Figure 3. As predicted, the molecule deviates only

(19) David, W. I. F.; Shankland, K. Dash, Program for Structure Solution from Powder Diffraction Data; Cambridge Crystallographic Data Centre, Cambridge, U.K., 2004.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in 8, with Estimated Standard Deviations (Esd's) on the Last Figure in Parentheses

Pt(1)−P(1)	2.217(2)	Pt(1)−N(1)	2.027(5)
Pt(1)−C(3)	2.054(6)	Pt(1)−C(13)	2.101(6)
Pt(2)−P(2)	2.227(2)	Pt(2)−N(2)	2.038(5)
Pt(2)−C(10)	2.122(6)	Pt(2)−C(18)	2.081(6)
Pt(3)−P(3)	2.209(2)	Pt(3)−N(3)	2.006(5)
Pt(3)−C(33)	2.084(6)	Pt(3)−C(43)	2.110(6)
Pt(4)−P(4)	2.213(2)	Pt(4)−N(4)	2.028(5)
Pt(4)−C(40)	2.128(6)	Pt(4)−C(48)	2.081(6)
P(1)−Pt(1)−N(1)	174.3(1)	P(1)−Pt(1)−C(3)	105.2(2)
P(1)−Pt(1)−C(13)	95.1(2)	N(1)−Pt(1)−C(3)	78.8(2)
N(1)−Pt(1)−C(13)	81.3(2)	C(3)−Pt(1)−C(13)	159.4(2)
P(2)−Pt(2)−N(2)	177.3(1)	P(2)−Pt(2)−C(10)	98.0(2)
P(2)−Pt(2)−C(18)	103.5(2)	N(2)−Pt(2)−C(10)	80.9(2)
N(2)−Pt(2)−C(18)	77.8(2)	C(10)−Pt(2)−C(18)	158.4(2)
P(3)−Pt(3)−N(3)	174.4(1)	P(3)−Pt(3)−C(33)	106.3(2)
P(3)−Pt(3)−C(43)	93.7(2)	N(3)−Pt(3)−C(33)	78.5(2)
N(3)−Pt(3)−C(43)	81.6(2)	C(33)−Pt(3)−C(43)	159.8(2)
P(4)−Pt(4)−N(4)	173.2(1)	P(4)−Pt(4)−C(40)	98.2(2)
P(4)−Pt(4)−C(48)	102.5(2)	N(4)−Pt(4)−C(40)	81.6(2)
N(4)−Pt(4)−C(48)	77.8(2)	C(40)−Pt(4)−C(48)	159.4(2)

slightly from planarity, with maximum deviations from the least-squares plane through the non-hydrogen atoms of the molecule of +0.1 and −0.1 Å for atoms O(1) and C(5), respectively. The dihedral angle between the least-squares planes of the platinum atoms is 6°.

As can be seen in Figure 3, the molecule that is formed from the symmetrically equivalent halves in the refined solution is chemically reasonable, with the bond distance C(3)−C(3_4) being 1.45 Å. The bond distance Pt(1)−C(4_4) is 2.15 Å, which is similar to equivalent Pt−C(pyridine) bond distances found in the solid-state structures of **5** and **8** (see above). The geometry around the platinum atom, which displays a square-planar coordination with a slight tetrahedral distortion, is very similar to that found in the structures of **5** and **8**, with the C(7)−Pt(1)−C(4_4) angle being 159°. All other geometrical parameters are unremarkable and are within the corresponding ranges of values as determined from related molecules found in the Cambridge Structural Database (CSD).[21]

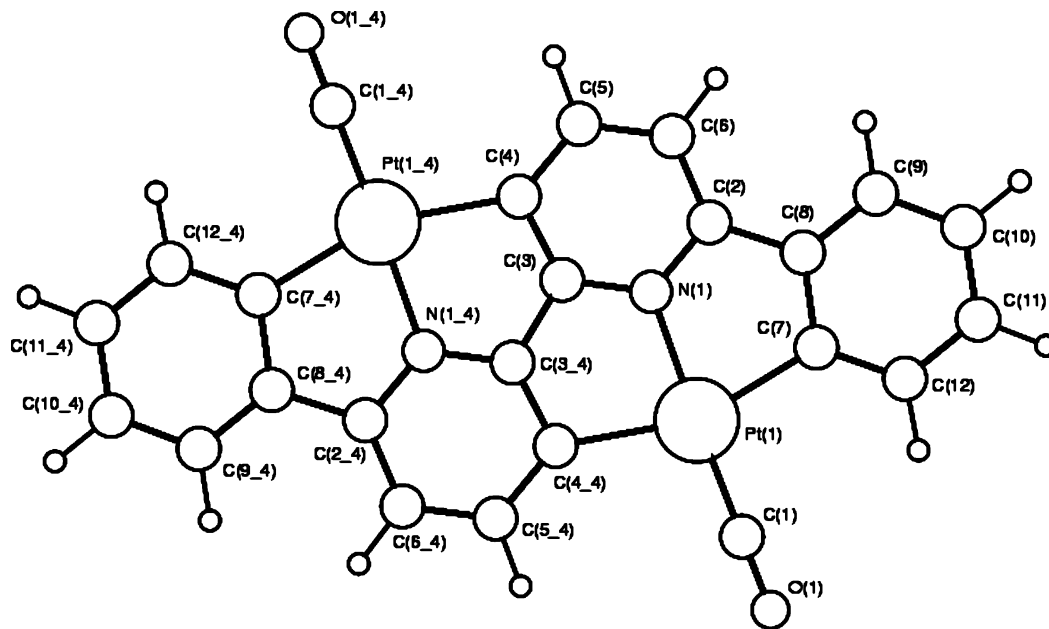(20) Rietveld, H. M. *J. Appl. Crystallogr.*, **1969**, *2*, 65−71.

Figure 3. View of compound **10** showing the atomic numbering scheme.
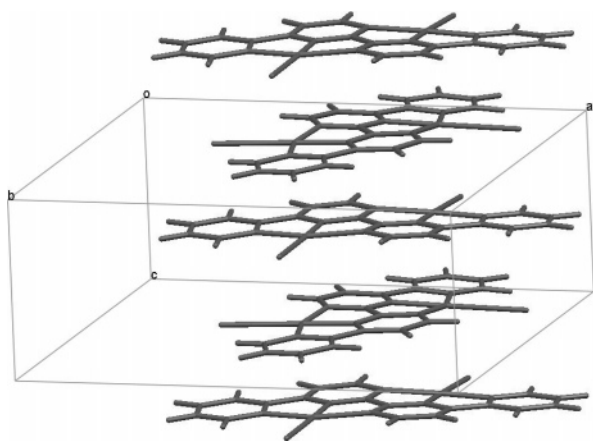

Figure 4. Column of molecules formed along the (001) direction through $\pi-\pi$ interactions in the solid-state structure of compound **10**.

As predicted, the planar nature of the molecules in this structure results in the formation of $\pi-\pi$ interactions, as shown in Figure 4. Columns of molecules are formed in the (001) direction, with the planes of the molecules being parallel and the aromatic ring systems being offset, resulting in a favorable intermolecular interaction[22] (see Figure 5). The interplanar distance is 3.4 Å, corresponding to the closest Pt···Pt distance of 3.4 Å.

Attempts to obtain another flat molecule by substitution of CH_3CN for DMSO or CO in **1** or **10** respectively, failed.

All the chemistry described up to this point has started from the reaction of the ligand L with the platinum intermediates $[Pt(R)_2(DMSO)_2]$ in a 1:2 molar ratio. Building of the delocalized bridging unit, involving C−H activation of both the phenyl substituents, was achieved in a single step. To further investigate the reactivity of the ligand H_4L, the reaction was also carried out with a 1:1 Pt:L molar ratio. Yields can be improved by operating with an excess of H_4L (see Experimental Section). Multiple C−H bond activation occurs even in this case, giving a mononuclear species, $[Pt(H_2L)(DMSO)]$ (**11**). The double

(21) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380−388.
(22) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534.

deprotonation arises from a "rollover" metalation and a Ph−H bond activation, with loss of methane:
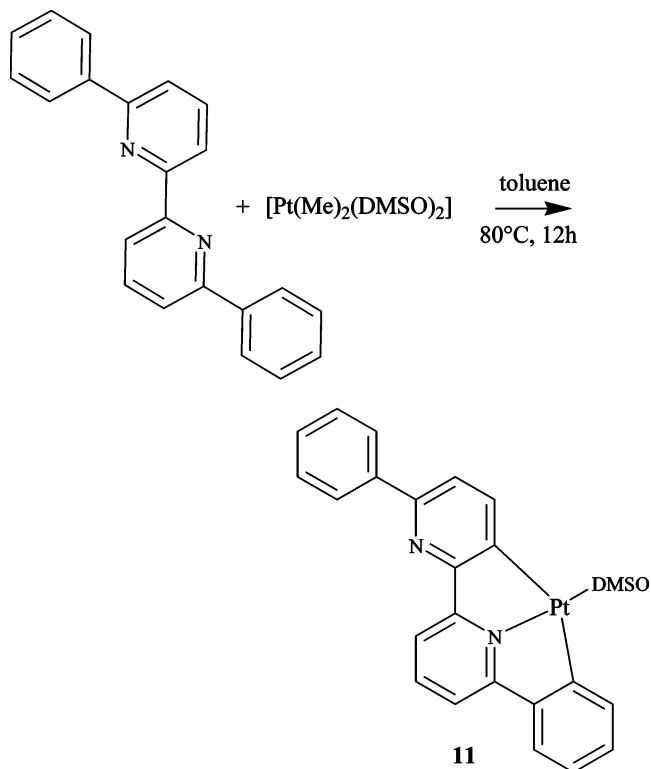
Complex **11**, in contrast with **1**, is soluble. This is likely to be due to the presence of the nonmetalated phenyl ring which, not being constrained in the coordination plane, discourages the formation of interactions between planes. The ^1H NMR spectrum of **11** is more complex than those of the dinuclear species **2**−**6**, due to the lack of symmetry of the bipyiridine unit. The DMSO signal (δ 3.68 ppm, $^3J_{Pt-H}$ = 26.8 Hz) is indicative of an S-bonded ligand coordinated trans to a nitrogen atom.[12g] A ^1H COSY spectrum, in addition to ^1H NOE difference spectra, assisted us in the assignment of the proton signals. The NOE difference spectra showed, inter alia, the presence of a strong
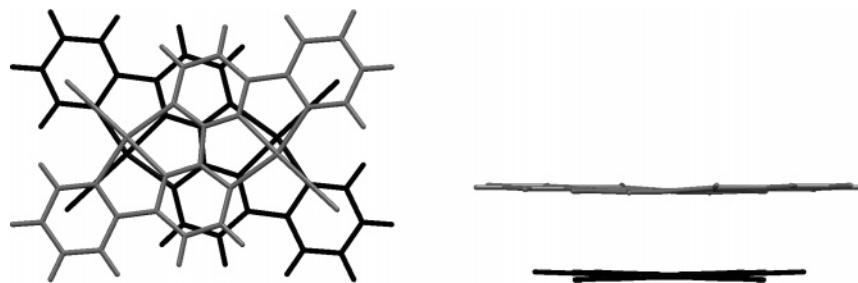
Figure 5. Two views of a pair of molecules connected by $\pi-\pi$ interactions in the solid-state structure of compound **10**. The view on the left is taken perpendicular to the least-squares plane through the non-hydrogen atoms of one of the molecules, and the view on the right is taken along this plane.

NOE contact between the DMSO methyl protons and the adjacent protons H3″ (7.62 ppm), and H4′ (8.27 ppm) (see Chart 2 for the numbering scheme). The H4′ proton shows a $^3J_{Pt-H}$ value of 18 Hz, in line with values previously observed.

Substitution of DMSO in **11** by CO, PPh$_3$, and 3,5-Me$_2$-py gives [Pt(H$_2$L)(CO)] (**12**), [Pt(H$_2$L)(PPh$_3$)] (**13**), and [Pt(H$_2$L)-(3,5-Me$_2$-py)] (**14**), respectively. The IR spectrum of **12** in Nujol shows an absorption at 2063 cm^{-1} (in CH$_2$Cl$_2$, 2065 cm^{-1}), the same value as that observed in the dinuclear complex **10**. In the ^{1}H NMR spectra of **13** and **14** the signals of the H3″ and H4′ protons are shifted strongly upfield with respect to those of compound **11**, due, respectively, to the presence of the adjacent PPh$_3$ and 3,5-Me$_2$-py ligands.

The mononuclear complex **11** reacts further with [Pt(Me)$_2$-(DMSO)$_2$] to give complex **1**, which implies that dinuclear species can be obtained in two steps. Such a two-step approach
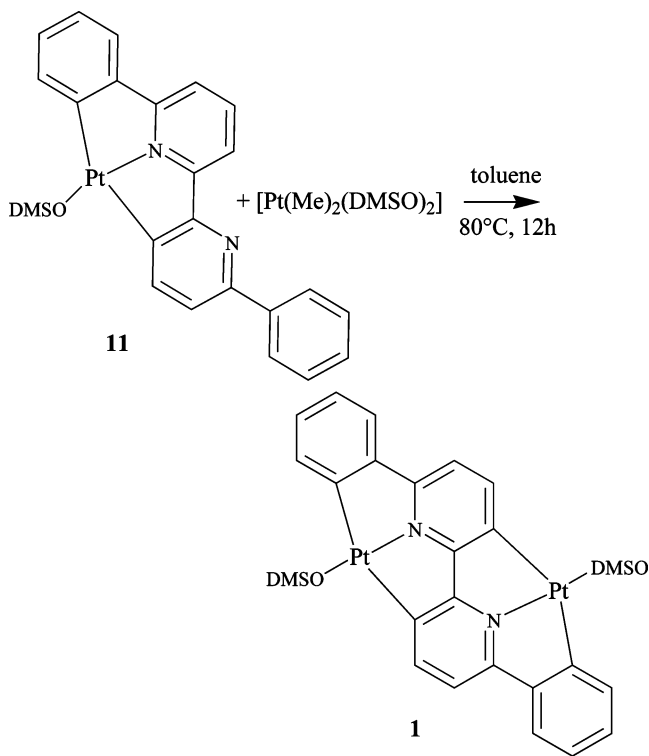
allows molecules with different environments around the two platinum atoms to be synthesized (Scheme 3).

Comparison of the stretching vibration of the coordinated CO in the dinuclear compounds **10**, **17**, and **18**, ν_{CO} ∼2063, 2052, 2052 cm^{-1}, respectively, indicates that the interaction between the two platinum atoms through the delocalized bridging system is not negligible.

Chart 2.   Numbering Scheme for the Dinuclear and the Mononuclear Derivatives
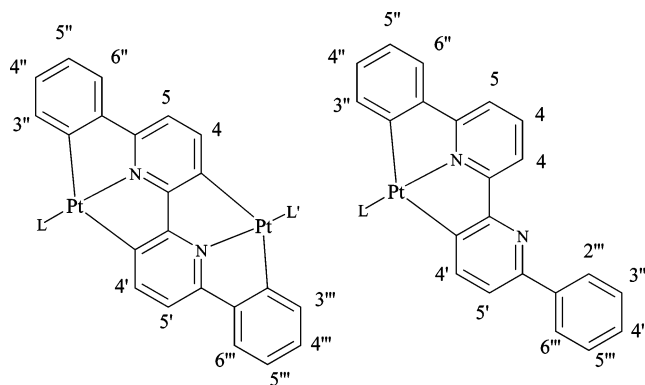

Conclusions

We have shown the remarkable ability of the electron-rich derivatives [Pt(R)$_2$(L′)$_2$] to promote multiple C−H activations. In the case of the reaction with 6,6′-diphenyl-2,2′-bipyridine, a molecule poorly investigated in coordination chemistry thus far, simultaneous activation of aryl and pyridyl C−H bonds occurs. The outcome of this activation process, a "rollover" and an arylic metalation, is the building up of deprotonated ligands able to trap platinum ions in a C−N−C environment, an arrangement not common and seldom achieved by direct C−H activation. Depending on the ligand-to-platinum molar ratio, either di- or mononuclear cyclometalated derivatives can be obtained. In the dinuclear species the fourfold deprotonated substituted bipyridine links the platinum atoms through a delocalized system which acts as a 12-electron donor. With an appropriate choice of the ancillary ligand L′, required to fulfill coordination around the metal atom, it is possible to either favor or prevent association between the monomeric units. With a ligand such as CO an insoluble material is obtained, as expected for stacked d^8 planar complexes. In contrast, bulky ligands, e.g. PR$_3$, hamper association, allowing us to obtain soluble derivatives. Soluble species with even higher nuclearity can be synthesized by using bidentate L′ ligands suitable for bridging two monomeric units. The solid-state structure of a tetranuclear complex has been solved by single-crystal X-ray diffraction analysis.

Multiple C−H activation is also achieved with a 1:1 ligand-to-platinum ratio. The mononuclear C,N,C cyclometalates obtained can further react with another "PtR$_2$" fragment to give dinuclear derivatives. This two-step synthetic approach opens up new prospects for assembling species with different environments around each of the platinum atoms and, consequently, different properties.

Overall the results presented herein once again underline the potential of the "Pt(R)$_2$" fragments in the intramolecular activation of C−H bonds. As shown, the synthesis of very

Scheme 3
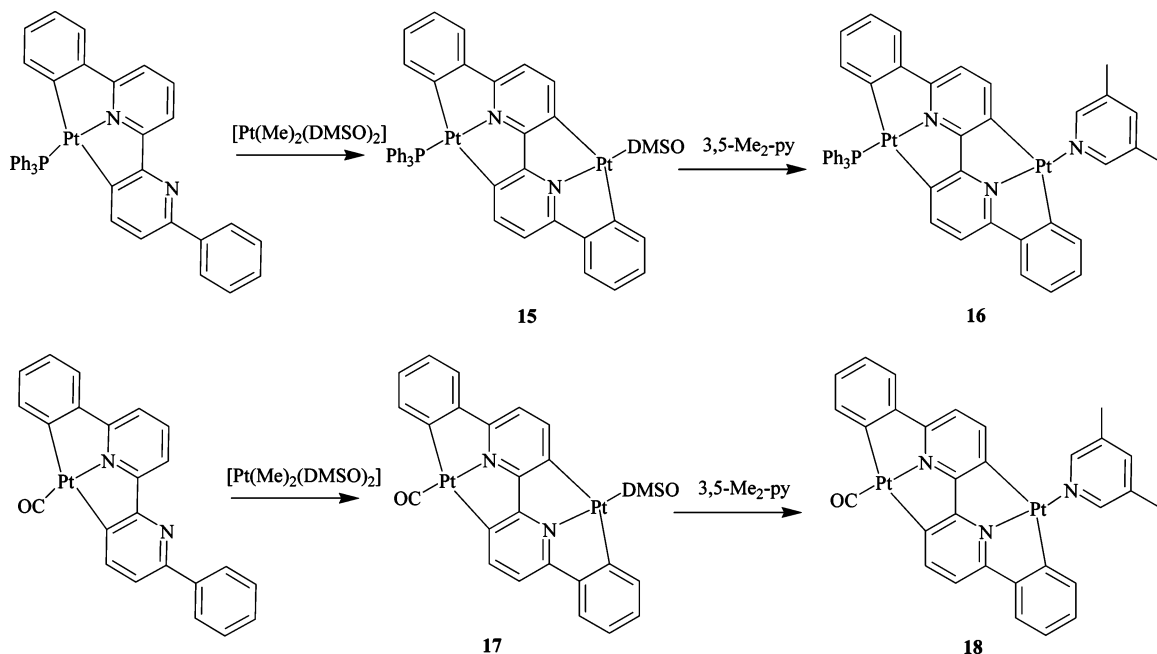
unusual molecules can be achieved whose properties deserve further investigation. It is also worth noting that the reactivity of these fragments is of paramount importance in intermolecular C−H activation.[23]

Experimental Section

The platinum complexes *cis*-[PtR$_2$(DMSO)$_2$] (R = Me, Ph) were prepared according to literature methods.[24] The ligand 6,6′-diphenyl-2,2′-bipyridine was synthesized according to ref 16. All the solvents were purified and dried according to standard procedures.[25] Elemental analyses were performed with a Perkin-Elmer 240B elemental analyzer by Mr. Antonello Canu (Dipartimento di Chimica, Università degli studi di Sassari, Sassari, Italy). Infrared spectra were recorded with a FT-IR Jasco 480P spectrometer using Nujol mulls. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 300.0, 75.4, and 121.4 MHz, respectively. ^{1}H NOE difference spectra and 2D ^{1}H−^{1}H COSY spectra were recorded with a standard pulse sequence. Chemical shifts are given in ppm relative to internal TMS (^{1}H, ^{13}C) and external 85% H$_3$PO$_4$ (^{31}P). The mass spectrometric measurements were performed on a VG 7070EQ instrument, equipped with a PDP 11 250J data system and operating under positive ion fast atom bombardment (FAB) conditions with 3-nitrobenzyl alcohol as the supporting matrix.

Synthesis of [Pt$_2$(L)(DMSO)$_2$] (1). To a solution of 6,6′-diphenyl-2,2′-bipyridine (L; 200 mg, 0.65 mmol) in anhydrous toluene (20 mL) was added with vigorous stirring 496 mg of *cis*-[PtR$_2$(DMSO)$_2$] (R = Me, Ph; 1.3 mmol): the solution rapidly changed color to orange. The stirred solution, kept under an argon atmosphere, was heated to 80 °C. During the heating, a yellow-green precipitate was formed. After the mixture was cooled, the precipitate was filtered off, washed with toluene and diethyl ether,

and vacuum-pumped to give the analytical sample as a green-yellow solid. Yield: 458 mg, 83%. Mp: >270 °C. Anal. Calcd for C$_{26}$H$_{24}$N$_2$O$_2$Pt$_2$S$_2$: C, 36.71; H, 2.84; N, 3.29. Found: C, 37.43; H, 3.04; N, 3.29. IR (Nujol, cm^{-1}): ν_{max} 1013 (s), 1119 (s).

Synthesis of [Pt$_2$(L)(PPh$_3$)$_2$] (2). To a solution of PPh$_3$ (30.8 mg, 0.117 mmol) in CH$_2$Cl$_2$ (40 mL) was added slowly, with vigorous stirring, 50.0 mg of **1** (0.0588 mmol). The yellow solution that formed was stirred for 1 h and then filtered over Celite, concentrated to a small volume, and treated with diethyl ether. The precipitate that formed was filtered, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 51.4 mg, 72%. Mp: >270 °C. Anal. Calcd for C$_{58}$H$_{42}$N$_2$P$_2$Pt$_2$·H$_2$O: C, 56.31; H, 3.58; N, 2.26. Found: C, 56.30; H, 3.75; N, 2.04. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.82 (d, 2H, H$_4$, H$_4$′, J_{H-H} = 7.7 Hz). $^3J_{Pt-H}$ = 17.8 Hz); 6.21 (d, 2H, H$_3$″. H$_3$‴, J_{H-H} = 7.8 Hz, $^3J_{Pt-H}$ = 80 Hz); 6.51 (td, 2H, H$_4$‴. H$_4$″, J_{H-H} = 7.0, J_{H-H} = 1.4 Hz); 6.59 (dd, 2H, H$_5$. H$_5$′, J_{H-H} = 7.7 Hz, J_{H-H} = 1.4 Hz); 6.78 (t, 2H, H$_5$″. H$_5$‴, J_{H-H} = 7.0 Hz); 7.47 (d, 2H, H$_6$″, H$_6$‴, J_{H-H} = 7.0 Hz); 7.41 (m, 18H, Hm, Hp (PPh$_3$)); 7.82 (m, 12H, Ho (PPh$_3$)). ^{31}P NMR (CD$_2$Cl$_2$): δ 24.9 (s, $^1J_{Pt-P}$ = 3949 Hz).

Synthesis of [Pt$_2$(L)(PCy$_3$)$_2$] (3). Complex **3** was obtained by following the same procedure used for complex **2**, using PCy$_3$ instead of PPh$_3$. Yield: 48%. Mp: >270 °C. Anal. Calcd for C$_{58}$H$_{78}$N$_2$P$_2$Pt$_2$: C, 55.49; H, 6.26; N, 2.23. Found: C, 55.25; H, 6.27; N, 2.43. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.18−1.28 (m, 18H, CH$_2$ (PCy$_3$)); 1.55−1.83 (m, 30H, CH$_2$ (PCy$_3$)); 2.05−2.17 (m, 12H, CH$_2$ (PCy$_3$)); 2.40−2.55 (m, 6H, CH (PCy$_3$)); 6.93−7.04 (m, 6H, H$_5$″, H$_4$″, H$_5$); 7.29 (dd, 2H, H$_3$″, J_{H-H} = 7.1 Hz, J_{H-H} = 1.6 Hz); 7.54 (d, 2H, H$_4$, J_{H-H} = 7.6 Hz); 7.75 (d, 2H, H$_5$″, J_{H-H} = 7.7 Hz). ^{31}P NMR (CDCl$_3$): δ 22.3 (s, $^1J_{Pt-P}$ = 3687 Hz).

Synthesis of [Pt$_2$(L)(P(m-PhSO$_3$Na)$_3$)$_2$] (4). To a solution of P(m-PhSO$_3$Na)$_3$ (117.8 mg) in a 1:1 water/acetone mixture was added with vigorous stirring under an argon atmosphere 70.5 mg of **1** (0.083 mmol). The mixture was stirred at room temperature for 15 h. The yellow solution obtained was filtered, concentrated to small volume, and treated with acetone. The yellow precipitate that formed was filtered off and washed with acetone to give **4** in almost quantitative yield. Mp: >270 °C. Anal. Calcd for C$_{58}$H$_{48}$N$_2$Na$_6$O$_{24}$P$_2$Pt$_2$S$_6$·6H$_2$O: C, 35.92; H, 2.49; N, 1.44; Found: C, 35.86; H, 2.69; N, 1.38. ^{1}H NMR (DMSO-d_6): δ 5.84 (d, 2H, J = 8.0 Hz); 5.99 (d, 2H, J = 7.1 Hz); 6.42 (t, 2H, J = ca. 7.5 Hz); 6.70 (t, 2H, J = ca. 7.5 Hz); 6.77 (d, 2H, J = 8.2 Hz);

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7.34–8.04 (m, 26H). ^{31}P NMR (DMSO-d_6): δ 25.67 (s, $^1J_{Pt-P}$ = 3961 Hz).

Synthesis of [Pt$_2$(L)(3,5-dimethylpyridine)$_2$] (5). To a suspension of **1** (150 mg, 0.176 mmol) in CHCl$_3$ (30 mL) was added with vigorous stirring 0.40 mL of 3,5-lutidine (d = 0.939 g/mL; 3.53 mmol, 10-fold excess). The mixture was heated to reflux for 5 h. After it was cooled, the mixture was filtered over Celite, concentrated to small volume, and treated with Et$_2$O. The precipitate that formed was filtered, washed with Et$_2$O, and vacuum-pumped to give the analytical sample as an orange solid. Yield: 118 mg, 74%. Mp: >270 °C. Anal. Calcd for C$_{36}$H$_{30}$N$_4$Pt$_2$: C, 47.58; H, 3.33; N, 6.16. Found: C, 47.84; H, 3.28; N, 6.49. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.41 (s, 12H, Me); 6.78 (dd, 2H, J_{H-H} = 7.3 Hz, J_{H-H} = 1.4 Hz, $^3J_{Pt-H}$ = 27 Hz, H$_3''$, H$_3'''$); 6.97 (td, 2H, J_{H-H} = 1.4 Hz, J_{H-H} = 7.3 Hz, H$_5''$, H$_5'''$); 6.99 (d, 2H, J_{H-H} = 7.6 Hz, H$_5$, H$_5'$); 7.05 (td, 2H, J_{H-H} = 1.4 Hz, J_{H-H} = 7.3 Hz, H$_4''$, H$_4'''$); 7.18 (d, 2H, J_{H-H} = 7.6 Hz, $^3J_{Pt-H}$ = 18 Hz, H$_4$, H$_4'$); 7.27 (dd, 2H, J_{H-H} = 7.3 Hz, J_{H-H} = 1.2 Hz, H$_6''$, H$_6'''$); 7.53 (s, 2H, H$_4$ 3,5-dimethylpyridine); 8.69 (s, 4H, $^3J_{Pt-H}$ = 43 Hz, H$_2$ 3,5-dimethylpyridine). ^{13}C NMR (CD$_2$Cl$_2$): δ 18.1 (CH$_3$); 115.9 (CH); 122.6 (CH); 123.8 (CH); 128.6 (CH); 132.6 (CH); 135.5 (C, C$_3$ 3,5-dimethylpyridine); 137.9 (CH); 144.2 (CH); 149.9 (C); 151.1 (CH, C$_2$ 3,5-dimethylpyridine); 158.9 (C); 160.7 (C); 162.9 (C); 178.2 (C). MS–FAB (m/z): 909 [M]$^+$, 802 [M − 3,5-dimethylpyridine]$^+$, 694 [M − 2(3,5-dimethylpyridine)]$^+$, 501 [M − H − 2(3,5-dimethylpyridine) − Pt]$^+$, 307 [L − H]$^+$.

Synthesis of [Pt$_2$(L)(quinoline)$_2$] (6). To a suspension of **1** (50 mg, 0.059 mmol) in CHCl$_3$ (20 mL) was added with vigorous stirring 0.14 mL of quinoline (d = 1.093 g/mL; 1.18 mmol, 10-fold excess). The mixture was heated to reflux for 24 h. After it was cooled, the mixture was filtered over Celite and evaporated to dryness. The orange solid obtained was washed with *n*-hexane and filtered off to give the analytical sample. Yield: 42%. Mp: >270 °C. Anal. Calcd for C$_{40}$H$_{26}$N$_4$Pt$_2$·H$_2$O: C, 49.49; H, 2.91; N, 5.77. Found: C, 49.80; H, 3.02; N, 5.45. ^{1}H NMR (CDCl$_3$): δ 6.47 (dd, 2H, J_{H-H} = 6.1 Hz, J_{H-H} not resolved); 6.75−7.05 (m, 6H); 7.22 (dd, 2H, J_{H-H} = 6.7 Hz, J_{H-H} not resolved); 7.40−8.20 (m, 10H); 8.42 (d, 2H, J_{H-H} = 8.0 Hz); 9.32 (dd, 2H, J_{H-H} = 8.1 Hz, J_{H-H} = 5.6 Hz); 9.55 (d, 2H, J_{H-H} = 5.6 Hz).

Synthesis of [Pt$_2$(L)(dppm)]$_2$ (7). To a solution of dppm (22.6 mg, 0.059 mmol) in acetone (30 mL) was added slowly with stirring 50.0 mg of **1** (0.059 mmol). The orange suspension was stirred for 1 h at room temperature and then filtered to give [Pt$_2$(L)(dppm)]$_2$ (**7**) as a reddish solid (36.0 mg); a second crop (11.0 mg) was obtained from the mother liquor by concentration to small volume followed by precipitation with diethyl ether and filtration. Total yield: 47.0 mg, 74%. Mp: >270 °C. Anal. Calcd for C$_{95}$H$_{70}$N$_4$P$_4$Pt$_4$: C, 52.32; H, 3.18; N, 2.60. Found: C, 52.60; H, 3.19; N, 3.04. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.30 (m, 4H, $^4J_{Pt-H}$ = ca. 30 Hz, CH$_2$); 5.15 (dd, 4H, J_{H-H} = 7.8 Hz, H$_5$ or H$_4$); 5.22 (d, 4H, J_{H-H} = 7.8 Hz, H$_5$ or H$_4$); 6.40 (d, 4H, H$_3''$, J_{H-H} = 7.3 Hz); 6.60 (td, 4H, H$_4''$, J_{H-H} = 7.3 Hz, J_{H-H} = 1.4 Hz); 6.78 (t, 4H, J_{H-H} = 7.8 Hz, H$_5''$); 6.82 (dd, 4H, H$_6''$, J_{H-H} = 7.6 Hz, J_{H-H} = 1.4 Hz); 7.30 (m, 24H, Hm, Hp (PPh)); 7.35 (m, 8H, Ho (PPh)); 8.05 (m, 8H, Ho (PPh)). ^{31}P NMR (CD$_2$Cl$_2$): δ 12.70 (s, $^1J_{Pt-P}$ = 4045 Hz, $^2J_{P-P}$ = 30 Hz, $^3J_{Pt-P}$ = 72 Hz).

Synthesis of [Pt$_2$(L)(dppe)]$_2$ (8). Complex **8** was obtained by following the same procedure used for complex **7**, using dppe instead of dppm. Total yield: 96%. Mp: >270 °C. Anal. Calcd for C$_{96}$H$_{72}$N$_4$P$_4$Pt$_4$: C, 52.98; H, 3.35; N, 2.55. Found: C, 52.81; H, 3.56; N, 2.34. ^{1}H NMR (CD$_2$Cl$_2$): δ 3.60 (m, 4H, CH$_2$); 3.75 (m, 4H, CH$_2$); 5.69 (dd, 4H, J_{H-H} = 7.8 Hz, J_{H-H} not resolved, H$_5$); 5.78 (d, 4H, J_{H-H} = 7.8 Hz, H$_4$); 6.20 (d, 4H, J_{H-H} = 7.3 Hz, $^3J_{Pt-H}$ = ca. 30 Hz, Hz, H$_3''$); 6.52 (d, 4H; J_{H-H} = 7.3 Hz, J_{H-H} = 1.4 Hz, H$_4''$); 6.72 (td, 4H, J_{H-H} = 7.3 Hz, J_{H-H} not resolved, H$_5''$); 6.82 (dd, 4H, J_{H-H} = 7.3 Hz, J_{H-H} = 1.3 Hz, H$_6''$); 7.20 (m, 12H, Hm + Hp (PPh)); 7.46 (m, 12H, Hm + Hp (PPh)); 7.76 (m, 8H,

Ho (PPh)); 7.88 (m, 8H, Ho (PPh)). ^{31}P NMR (CD$_2$Cl$_2$): δ 23.95 (s, $^1J_{Pt-P}$ = 4010 Hz, $^3J_{P-P}$ = 35.9 Hz). MALDI-TOF: m/z 1093 [Pt$_2$(L)(dppe)]$^+$.

Synthesis of [Pt$_2$(L)(dppp)]$_2$ (9). Complex **9** was obtained by following the same procedure used for complex **7**, using dppp instead of dppm. Total yield: 89%. Mp: >270 °C. Anal. Calcd for C$_{98}$H$_{76}$N$_4$P$_4$Pt$_4$: C, 53.17; H, 3.46; N, 2.53. Found: C, 53.51; H, 3.63; N, 2.53. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.72−2.88 (m, 8H, CH$_2$); 3.18−3.34 (m, 4H, CH$_2$); 5.92 (d, 4H, J_{H-H} = 7.8 Hz, H$_5$); 6.12 (dd, 4H, J_{H-H} = 7.8 Hz, J_{H-H} = 1.6 Hz, H$_4$); 6.43 (d, 4H, J_{H-H} = 7.3 Hz, 4H, H$_3''$); 6.60 (td, 4H, J_{H-H} = 7.3 Hz, J_{H-H} = 1.4 Hz, H$_4''$); 6.79 (td, 4H, J_{H-H} = 7.3 Hz, J_{H-H} not resolved, H$_5''$); 6.88 (dd, 4H, J_{H-H} = 7.3 Hz, J_{H-H} not resolved, H$_6''$); 7.27 (m, 12H, Hm, Hp (dppp)); 7.38 (m, 12H, Hm, Hp (dppp)); 7.50 (m, 8H, Ho (dppp)); 7.82 (m, 8H, Ho (dppp)). ^{31}P NMR (CD$_2$Cl$_2$): δ 15.15 (s, $^1J_{Pt-P}$ = 3922 Hz).

Synthesis of [Pt$_2$(L)(CO)$_2$] (10). Method 1. In an acetone suspension of **1** (50.0 mg, 0.0588 mmol) carbon monoxide was bubbled with stirring at atmospheric pressure and room temperature. The color of the mixture changed slowly from yellow-green to red. After 1.5 h the red suspension was filtered and washed with diethyl ether to give the analytical sample. Yield: 77%. Mp: >270 °C. Anal. Calcd for C$_{24}$H$_{12}$N$_2$O$_2$Pt$_2$·3H$_2$O: C, 35.79; H, 2.24; N, 3.48. Found: C, 35.47; H, 1.97; N, 3.49. IR (Nujol, ν_{max}/cm^{-1}): 2063 (vs).

Method 2. In a dichloromethane solution of **5** (50.2 mg, 0.055 mmol) CO was bubbled with stirring at atmospheric pressure and room temperature. After 1 h the suspension that formed was filtered and washed with diethyl ether to give the analytical sample. Yield: 35.5 mg, 85.5%.

Complex **10** is obtained also by passing a stream of CO over a solid sample of compound **1** at room temperature.

Synthesis of [Pt$_2$(L)(PPh$_3$)$_2$] from [Pt$_2$(L)(CO)$_2$]. To a suspension of **10** (7.5 mg, 0.01 mmol) in CHCl$_3$ (20 mL) was added with vigorous stirring 5.2 mg of PPh$_3$ (0.02 mmol). The yellow solution that formed was stirred for 1 h and then filtered over Celite, concentrated to small volume, and treated with diethyl ether. The precipitate that formed was filtered, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 10.4 mg, 86.2%.

Synthesis of [Pt(H$_2$L)(DMSO)] (11). To a solution of 6,6′-diphenyl-2,2′-bipyridine (75.0 mg, 0.243 mmol) in toluene (50 mL) was added with vigorous stirring 61.8 mg of [Pt(Me)$_2$(DMSO)$_2$] (0.162 mmol). The solution was heated to 80 °C for 8 h, during which time a small quantity of precipitate was formed. After the mixture was cooled, the precipitate was filtered off and washed with diethyl ether to give 14.8 mg of compound **1** as a green-yellow solid. The filtered solution was concentrated to small volume and treated with *n*-hexane. The precipitate that formed was filtered, washed with *n*-hexane, and vacuum-pumped to give **11** as an orange solid. Yield: 54%. Mp: dec at 210 °C. Anal. Calcd for C$_{24}$H$_{20}$N$_2$OPtS: C, 49.74; H, 3.48; N, 4.83. Found: C, 50.19; H, 2.99; N, 4.39. ^{1}H NMR (CD$_2$Cl$_2$): δ 3.68 (s, 6H, $^3J_{Pt-H}$ = 26.8 Hz, CH$_3$ (DMSO)); 7.16 (td, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.2 Hz, H$_5''$); 7.29 (td, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.2 Hz, H$_4''$); 7.42 (t, 1H, J_{H-H} = ca. 7.5 Hz, H$_4'''$); 7.44 (1H, H$_3$ (overlapping)); 7.47 (t, 2H, J_{H-H} = ca. 7.5 Hz, H$_3'''$, H$_5'''$); 7.54 (dd, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.2 Hz, H$_6''$); 7.60 (d, 1H, J_{H-H} = 7.9 Hz, H$_5'$); 7.62 (dd, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.2 Hz, J_{Pt-H} not resolved, H$_3''$); 7.74 (t, 1H, J_{H-H} = 7.5 Hz, H$_4$); 7.89 (dd, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.0 Hz, $^4J_{Pt-H}$ = 9 Hz, H$_5$); 8.07 (d, 2H, J_{H-H} = 7.5 Hz, H$_2'''$, H$_6'''$); 8.27 (d, 1H, J_{H-H} = 7.9 Hz, $^3J_{Pt-H}$ = 18 Hz, H$_4'$). IR (Nujol, ν_{max}/cm^{-1}): 1013 (s), 1119 (s),

Synthesis of [Pt(H$_2$L)(CO)] (12). In a dichloromethane solution of **11** (28.3 mg, 0.049 mmol) carbon monoxide was bubbled with stirring at atmospheric pressure and room temperature for 1.5 h. The red-orange solution obtained was concentrated to small volume

and treated with *n*-hexane. The precipitate that formed was filtered, washed with *n*-hexane, and vacuum-pumped to give the analytical sample as an orange solid in almost quantitative yield. Mp: dec at 235 °C. Anal. Calcd for $C_{23}H_{14}N_2OPt$: C, 52.18; H, 2.67; N, 5.29. Found: C, 52.04; H, 2.95; N, 5.12. ^1H NMR (CDCl$_3$): δ 7.15 (td, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.4 Hz, H$_5$″ or H$_4$″); 7.24 (td, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.4 Hz, H$_5$″ Hz,or H$_4$″); 7.31 (dd, 1H, J_{H-H} = 7.7 Hz, J_{H-H} = 1.4 Hz, H$_3$); 7.38−7.53 (m, 5H, H$_5$′, H$_3$‴, H$_4$‴, H$_5$‴, H$_3$″, or H$_6$″); 7.64 (dd, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.4 Hz, H$_3$″ or H$_6$″); 7.69 (t, 1H, J_{H-H} = 7.7 Hz, H$_4$); 7.75 (dd, 1H, J_{H-H} = 7.7 Hz, J_{H-H} = 1.4 Hz, H$_5$); 7.91 (d, 1H, J_{H-H} = 7.7 Hz, $^3J_{Pt-H}$ = 29 Hz, H$_4$′); 8.05 (m, 2H, H$_2$‴, H$_6$‴). ^1H NMR (CD$_2$Cl$_2$): δ 7.17 (td, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.4 Hz, H$_5$″ or H$_4$″); 7.25 (td, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.4 Hz, H$_5$″ or H$_4$″); 7.35−7.52 (m, 5H, H$_3$, H$_3$‴, H$_4$‴, H$_5$‴, H$_3$″, or H$_6$″); 7.57 (d, 1H, J_{H-H} = 7.7 Hz, $^4J_{Pt-H}$ = 7 Hz, H$_5$′); 7.63 (dd, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.4 Hz, $^3J_{Pt-H}$ = 35 Hz, H$_3$″ or H$_6$″); 7.76 (m, 2H, H$_4$, H$_5$); 7.94 (d, 1H, J_{H-H} = 7.7 Hz, $^3J_{Pt-H}$ = 29 Hz, H$_4$′); 8.09 (m, 2H, H$_2$‴, H$_6$‴). IR (Nujol, ν_{max}/cm^{-1}): 2063 (vs).

Synthesis of [Pt(H$_2$L)(PPh$_3$)] (13). To a solution of **11** (71.9 mg, 0.124 mmol) in 20 mL of CH$_2$Cl$_2$ was added, with vigorous stirring, 65.1 mg of PPh$_3$ (0.248 mmol). The orange solution was stirred at room temperature for 1 h, the solvent was evaporated in vacuo, and the solid was washed with *n*-hexane, filtered off, and vacuum-pumped, to give the analytical sample as an orange solid. Yield: 73.4 mg, 77.5%. Mp: dec at 265 °C. Anal. Calcd for $C_{40}H_{29}N_2PPt \cdot H_2O$: C, 61.46; H, 4.00; N, 3.58. Found: C, 61.51; H, 3.33; N, 3.52. ^1H NMR (CDCl$_3$): δ 6.29 (d, broad, 1H, J_{H-H} = 7.4 Hz, H$_3$″); 6.40 (d, 1H, J_{H-H} = 7.9 Hz, H4′); 6.70 (td, 1H, J_{H-H} = 7.4 Hz, J_{H-H} = 1.3 Hz, H$_4$″ or H$_5$″); 6.95 (td, 1H, J_{H-H} = 7.4 Hz, J_{H-H} = 1.2 Hz, H$_4$″ or H$_5$″); 7.04 (d, 1H, J_{H-H} = 7.9 Hz, J_{Pt-H} = ca. 8 Hz, H$_5$′); 7.30−7.51 (m, 14H, H$_2$‴-H$_6$‴, Hm + Hp PPh$_3$); 7.71 (t, 1H, J_{H-H} = 7.8 Hz, H$_4$); 7.82−7.94 (m, 7H, Ho PPh$_3$, H$_6$″); 8.02 (m, 2H, H$_3$ + H$_5$). ^{31}P NMR (CDCl$_3$): δ 28.58 ($^1J_{Pt-P}$ = 4066 Hz).

Synthesis of [Pt(H$_2$L)(3,5-dimethylpyridine)] (14). To a solution of **11** (70.0 mg, 0.12 mmol) in 15 mL of CHCl$_3$ was added, with vigorous stirring, 0.14 mL of 3,5-lutidine (1.21 mmol, 10-fold excess). The solution was refluxed for 12 h, the solvent was evaporated in vacuo, and the solid was washed with *n*-hexane, filtered off, and dried in vacuo to give the analytical sample as an orange solid. Yield: 68.5 mg, 93%. Mp: dec at 216 °C. Anal. Calcd for $C_{29}H_{23}N_3Pt \cdot H_2O$: C, 55.59; H, 4.02; N, 6.71. Found: C, 55.56; H, 3.39; N, 6.15. ^1H NMR (CDCl$_3$): δ 2.42 (s, 6H, CH$_3$ 3,5-dimethylpyridine); 6.95 (dd, 1H, J_{H-H} = 7.1 Hz, J_{H-H} = 1.2 Hz, H$_3$″); 7.09 (td, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.4 Hz, H$_4$″ or H$_5$″); 7.23 (td, 1H, J_{H-H} = 7.1 Hz, J_{H-H} = 1.2 Hz, H$_4$″ or H$_5$″); 7.34−7.46 (m, 5H, H$_2$‴-H$_6$‴); 7.36 (d, overlapping, 1H, J_{H-H} = 7.6 Hz, H$_4$′); 7.50 (s, broad, overlapping, 1H, H$_4$ 3,5-dimethylpyridine); 7.55 (d, partially overlapping, 1H, J_{H-H} = 7.5 Hz, H$_5$′); 7.66 (t, 1H, J_{H-H} = 7.9 Hz, H$_4$); 7.82 (dd, 1H, J_{H-H} = 7.8 Hz, J_{H-H} = 1.2 Hz, H$_6$″); 8.07 (m, 2H, H$_3$ + H$_5$); 8.74 (s, broad, 2H, J_{Pt-H} = ca. 45 Hz, H$_2$ 3,5-dimethylpyridine).

Synthesis of [Pt$_2$(L)(PPh$_3$)(3,5-dimethylpyridine)] (16). To a solution of **13** (65.0 mg, 0.085 mmol) in toluene (20 mL) were added under vigorous stirring 32.4 mg of [Pt(Me)$_2$(DMSO)$_2$] (0.085 mmol). The solution was stirred at 80 °C for 14 h. The precipitate that formed was filtered off, washed with diethyl ether (compound **15**, 42 mg), and taken up with chloroform (20 mL). After addition of 3,5-dimethylpyridine (0.3 mL, d = 0.939 g/mL; 2.65 mmol) the suspension was refluxed for 14 h. The suspension was cooled and filtered. The filtered solution was concentrated to small volume and treated with diethyl ether. The dark yellow precipitate that formed was filtered off, washed with diethyl ether, and dried in vacuo to give the analytical sample as a dark yellow solid. Yield 14.1 mg. Mp: >260 °C. Anal. Calcd for $C_{47}H_{36}N_3PPt_2 \cdot H_2O$: C, 52.17; H, 3.54; N, 3.88. Found: C, 52.02; H, 3.01; N, 3.52. ^1H

NMR (CDCl$_3$): δ 2.39 (s, 6H, CH$_3$); 5.86 (d, 1H, J_{H-H} = 7.9 Hz); 6.13 (d, 1H, J_{H-H} = 7.6 Hz); 6.50−6.58 (m, 2H); 6.74−6.80 (m, 2H); 6.91−7.19 (m, 6H); 7.39−7.44 (m, 10H, H$_4$ dimethylpyridine+ Hm + Hp PPh$_3$); 7.82−7.89 (m, 6H, Ho PPh$_3$); 8.72 (s, 2H, J_{Pt-H} = ca. 42 Hz, H$_2$ dimethylpyridine).

Synthesis of [Pt$_2$(L)(DMSO)(CO)] (17). To a solution of **12** (40.0 mg, 0.0755 mmol) in toluene (20 mL) was added with vigorous stirring 28.8 mg of [Pt(Me)$_2$(DMSO)$_2$] (0.0755 mmol). The solution was stirred at 80 °C for 10 h. The precipitate that formed was filtered off and washed with diethyl ether to give compound **17** as a dark red solid. Yield: 34 mg, 56%. Mp: >260 °C. IR (Nujol, cm^{-1}) ν_{max} 2053 (s). Anal. Calcd for $C_{25}H_{18}N_2O_2SPt_2 \cdot 2H_2O$: C, 35.89; H, 2.65; N, 3.35. Found: C, 35.25; H, 2.20; N, 3.02.

Synthesis of [Pt$_2$(L)(3,5-dimethylpyridine)(CO)] (18). To a suspension of **17** (30.0 mg, 0.0375 mmol) in CHCl$_3$ (15 mL) was added with vigorous stirring 0.04 mL of 3,5-dimethylpyridine (0.375 mmol). The suspension was heated to reflux for 8 h. After it was cooled, the mixture was filtered. The solution obtained was concentrated to small volume and treated with diethyl ether. The precipitate that formed was filtered off, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a brick red solid. Yield: 50.4% (15.7 mg). Mp: dec at 245 °C. IR (Nujol, cm^{-1}): ν_{max} 2052 (s). Anal. Calcd for $C_{30}H_{21}N_3OPt_2 \cdot H_2O$: C, 42.50; H, 2.71; N, 4.95. Found: C, 42.49; H, 2.65; N, 4.33. ^1H NMR (CD$_2$Cl$_2$): δ 2.38 (s, 6H, CH$_3$); 6.78 (dd, 1H, J_{H-H} = 7.1 Hz, J_{H-H} not resolved, H3″, see numbering scheme in Chart 2); 6.70−7.12 (m, 6H, aromatics); 7.25−7.30 (m, 3H, aromatics), 7.45 (dd, 1H, J_{H-H} = 1.6 Hz, J_{H-H} = 7.1 Hz, H3‴, see numbering scheme in Chart 2); 7.51−7.56 (m, 2H, aromatics); 8.64 (s, broad, J_{Pt-H} = 43 Hz, H$_2$ 3,5-dimethylpyridine).

Single-Crystal X-ray Data Collections and Structure Determinations. Crystal data are summarized in Table 1. The diffraction experiments were carried out on a Bruker SMART CCD area-detector diffractometer at 150 K, using Mo Kα radiation (λ = 0.710 73 Å) with a graphite crystal monochromator in the incident beam. No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,[26] and an empirical absorption correction was applied (SADABS)[27] to the collected reflections. The calculations were performed using the Personal Structure Determination Package[28] and the physical constants tabulated therein.[29] The structures were solved by direct methods (SHELXS)[30] and refined by full-matrix least squares using all reflections and minimizing the function $\sum w(F_o^2 - kF_c^2)^2$ (refinement on F^2). In **5**·2CHCl$_3$ the chloroform molecule is partially disordered, with the carbon atom and one Cl atom ordered, while the other two Cl atoms are split into four half-atoms with occupancy factors of 0.50 each. In **8**·1.5CHCl$_3$·H$_2$O there is a disordered chloroform half-molecule, with an occupancy factor of 0.50, and two disordered water half-molecules, with occupancy factors of 0.50 each. All the non-hydrogen atoms were refined with anisotropic thermal factors. The hydrogen atoms of the disordered solvent molecules were ignored. All the other hydrogen atoms were placed in their ideal positions (C−H = 0.97 Å), with the thermal parameter B 1.10 times that of the carbon atom to which they are attached, and were not refined. In the final Fourier maps the maximum residuals were as follows: for **5**·2CHCl$_3$, 2.63(48) e Å^{-3} at 0.91 Å from Pt; for **8**·1.5CHCl$_3$·H$_2$O 2.72(70) e Å^{-3} at 1.36 Å from Pt(4). For noncentrosymmetric

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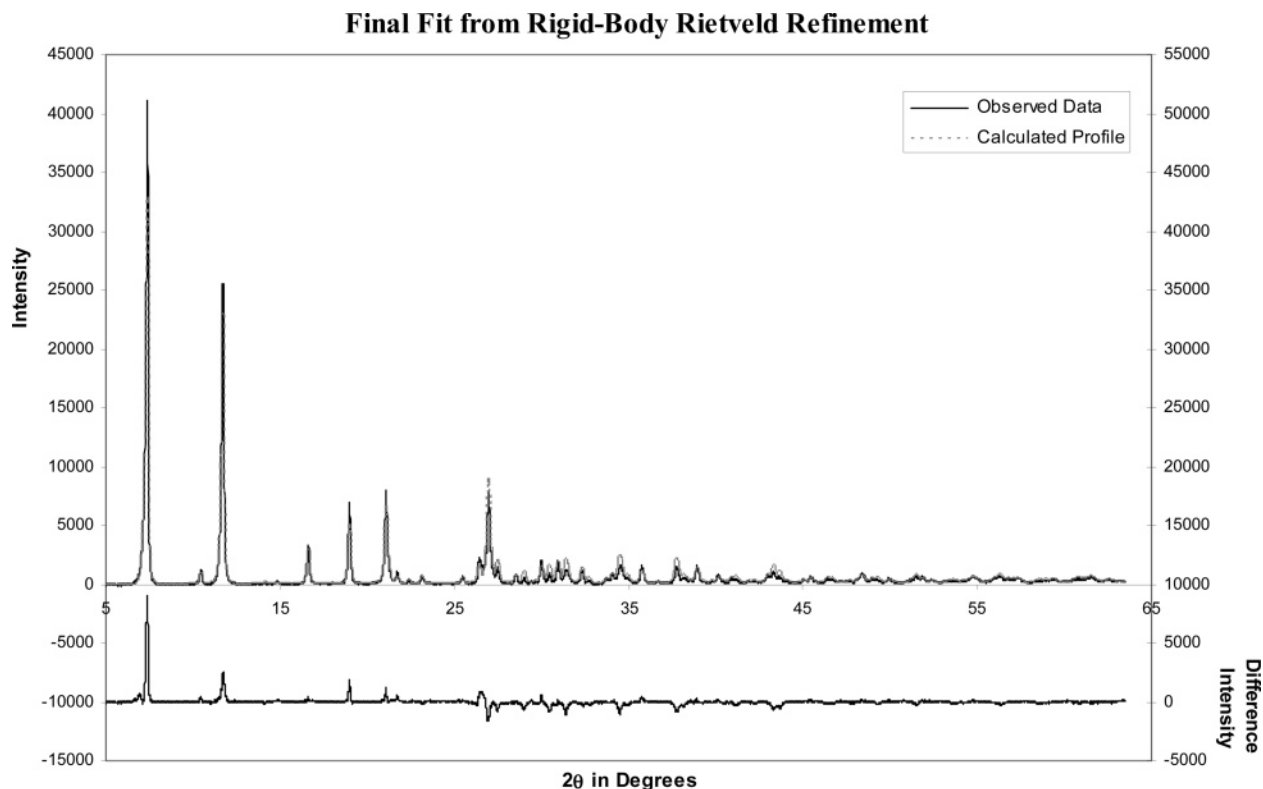
Final Fit from Rigid-Body Rietveld Refinement

Figure 6. Fit between the observed (solid line) and calculated (dotted line) powder X-ray diffraction patterns and difference plot from the rigid-body Rietveld refinement on compound **10**.

8·1.5CHCl$_3$·H$_2$O full refinement of the correct enantiomer led to $R_2 = 0.051$ and $R_{2w} = 0.066$, full refinement of the wrong enantiomer led to $R_2 = 0.069$ and $R_{2w} = 0.101$. Supplementary crystallographic data for this paper have been submitted as Supporting Information and have been deposited with the CCDC.

Powder X-ray Diffraction Structure Determination. Data collection was carried out on a sample of complex **10** in a 0.4 mm diameter borosilicate glass capillary on a Bruker D8 ADVANCE diffractometer in Debye−Scherrer geometry equipped with a copper X-ray source and Göebel mirrors. Data were collected twice, in steps of 0.01° ($5° \leq 2\theta \leq 63.5°$), for 10 s/step in the first instance and 29.8 s/step in the second. These two runs were added together in DIFFRAC^{plus} EVA[31] to give the final dataset.

The data were indexed in Treor90,[32] which is part of the Crysfire[33] suite. The unit cell obtained was tetragonal with $a = 16.8251$ Å and $c = 6.7371$ Å. The unit cell volume (1907.2 Å^3) and symmetry indicated that the asymmetric unit (ASU) comprises half the molecule ($Z' = 0.5$). The space group was identified as $P\bar{4}2_1c$ using the program Extinction Symbol.[34] Integrated intensities were extracted from the observed data by a Pawley refinement procedure (the χ^2 value was 4.70).[35]

A model of the molecule was made by geometry optimization at the DFT/B3LYP level[36] in GAUSSIAN 03.[37] Effective core potentials (ECP) were used to represent the innermost electrons of the platinum atoms,[38] while a standard double-ζ LANL2DZ basis

set described the valence electrons.[37] For all other atoms the 6-31G basis set was used.[39] The resulting model was symmetric about a 2-fold rotation axis at the molecular center of mass, and thus the model of the ASU used during structure solution was one of the symmetrically equivalent halves.

Structure solution was carried out using the Dash[19] program, by a global optimization technique employing a simulated annealing (SA) algorithm[40] to determine the position, orientation, and conformation, within the unit cell, of the ASU model. Each variation of these parameters gives rise to a trial structure, and powder diffraction patterns generated from the trial structures are compared with the observed data using the intensity χ^2 factor, defined as

$$\chi^2 = \sum_h \sum_k [(I_h - c|F_h|^2)(V^{-1})_{hk}(I_k - c|F_k|^2)]$$

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where $I_{h,k}$ values are the integrated intensities extracted from the observed data and V_{hk} is the covariance matrix, both determined from the Pawley refinement, c is the scale factor, and $F_{h,k}$ values are structure factors calculated from the trial structure. The success of a SA run can be monitored by use of a profile χ^2 factor. The consistency of the solutions obtained from several runs gives a further indication of success.

Solutions from initial SA runs were all highly consistent. In all cases the molecule was formed successfully from two ASU's, which were arranged symmetrically about a twofold rotation axis. Thus, in subsequent SA runs the molecular center of mass was fixed on the special position related to this axis and the resulting structural solutions were all identical with one another and extremely similar to those from the initial runs. The intensity and profile χ^2 values from the best run were 539.01 and 27.23, respectively.

A rigid-body Rietveld refinement[20,41] was carried out in Dash in which the background, profile shape, zero point, and unit cell parameters ($a = 16.8067$ Å and $c = 6.7323$ Å) from the Pawley refinement were used. The refined parameters were as follows: a global isotropic temperature factor, the single variable torsion angle of the ASU, ASU orientation parameters, and the positional parameter z. The molecular center of mass was held fixed on the special position, and thus x and y were not refined. The resulting intensity and profile χ^2 values were 327.95 and 28.03, respectively. The final fit between the observed data and the powder diffraction pattern calculated from the refined solution is shown in Figure 6. Although the overall fit is good, the first peak is not well described. An excellent fit can only be obtained if it is described as two overlapping peaks at 7.07 and 7.41° 2θ, but indexing is only possible when only the largest peak at 7.41° is included. This indicates that the minor peak at 7.07° arises from an impurity in the sample.

The unit cell parameters were subjected to a Rietveld refinement in GSAS.[42] The background, the profile shape (pseudo-Voigt), the particle size and microstrain, the scale factor, and θ_0 were the refined parameters. The final unit cell parameters are $a = 16.799(1)$ Å and $c = 6.7283(4)$ Å, values that are very close to those obtained from Pawley refinement.

Supporting Information Available: Figures and a table giving additional information on crystal structures and CIF files giving crystal data for **5**, **8**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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