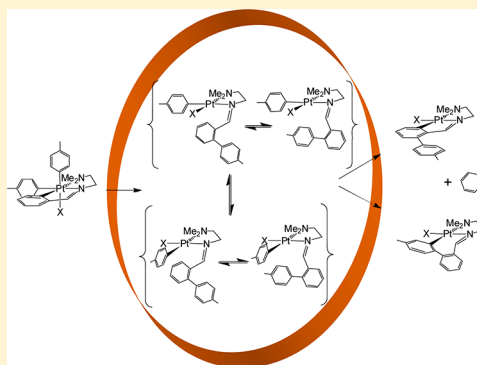


New Insights in the Formation of Five- Versus Seven-Membered Platinacycles: A Kinetic-Mechanistic Study

Paul V. Bernhardt,[†] Teresa Calvet,[‡] Margarita Crespo,^{*,§} Mercè Font-Bardía,^{‡,||} Susanna Jansat,[§] and Manuel Martínez^{*,§}[†]School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane 4072, Australia[‡]Departament de Mineralogia, Cristal·lografia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, E-08028 Barcelona, Spain[§]Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, E0-028 Barcelona, Spain^{||}Unitat de Difracció de RX, Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB), Universitat de Barcelona, Solè i Sabarís 1-3, E-08028 Barcelona, Spain

S Supporting Information

ABSTRACT: The reaction of Pt(IV) organometallic cyclometalated complexes of type $[\text{PtXAr}_2(\text{Ar}'\text{CHNCH}_2\text{CH}_2\text{NMe}_2)]$ to produce 5- and 7-membered Pt(II) metalacycles by a formal C–C reductive elimination/C–H oxidative addition/Ar–H reductive elimination sequence has been studied from a preparative and kinetic-mechanistic perspective. The detection and characterization of key intermediates has also been achieved via the careful selection of reaction conditions, including time, extracted from the kinetic studies. From the data collected, it is clear that a fine-tuning of the reactivity is possible with respect to the formation of the alternative 5- and 7-membered cyclometalated complexes (i.e., $[\text{PtX}(\text{Ar}-\text{Ar}'\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ and $[\text{PtX}(\text{Ar}-\text{Ar}'\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$). In all cases a common reductive elimination reaction occurs to form a non cyclometalated intermediate compound of type $[\text{PtX}(\text{Ar})(\text{Ar}-\text{Ar}'\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$, which leads to the selective formation of the above-mentioned complexes by the actuation of an unexpected equilibrium between its *cis*-(X_2NMe_2) and *trans*-(X_2NMe_2) isomers. While the *cis*-(X_2NMe_2) isomer produces the 7-membered metallacycle, the *trans*-(X_2NMe_2) form leads exclusively to the 5-membered analogue. The isomerization process is dominated by the steric hindrance existing between the Ar–Pt and Ar–Ar'CHN–Pt moieties in the *cis*-(X_2NMe_2) isomer that forces a Z conformation of the imine, thus leading exclusively to the 7-membered ring formation only for the less hindered X = Cl systems.



■ INTRODUCTION

C–C bond formation is one of the most important processes in organic synthesis. Involvement of Pd(II)/Pd(IV), in addition to Pd(0)/Pd(II) systems, plays a decisive role in catalytic processes, and, since Pt(IV) species are more readily accessible, parallel studies with organoplatinum compounds are often useful in providing mechanistic information.¹ In addition, unsymmetrical bidentate ligands containing amine and imine functionalities have been proven to be useful in catalysis.^{2,3} For this type of ligand, it has been observed that geometrical isomerism of square-planar palladium and platinum compounds is controlled by steric effects. The trigonal planar arrangement around the unsaturated N-atom (sp^2) is supposed to be more tolerable to the steric strain than the saturated N-atom (sp^3).⁴ Recently, the great importance of isomerization steps, traditionally overlooked in catalytic cycles, has been shown for Stille coupling.⁵

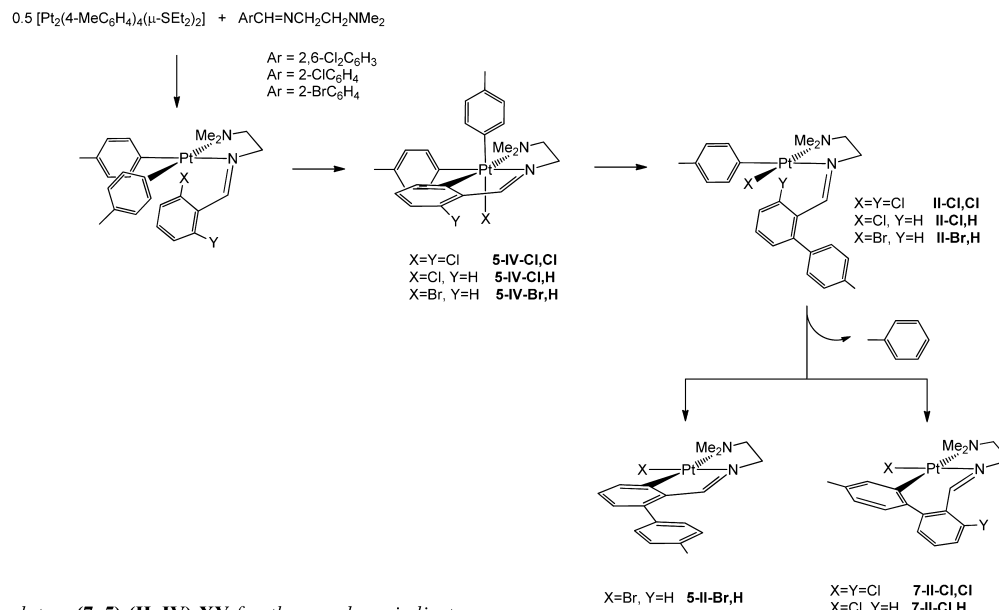
In recent years, we have been involved in studies related to the formation of platinum(II) cyclometalated compounds containing a biaryl moiety from the corresponding platinum-

(IV) cyclometalated compounds $[\text{PtXAr}_2(\text{Ar}'\text{CHNCH}_2\text{CH}_2\text{NMe}_2)]$.^{6–11} For this process, it has been suggested that the first step consists of a reductive elimination to give a platinum(II) compound with a bidentate ligand containing amine and imine functionalities in which a dangling biphenyl moiety is already formed.^{12,13} However, many of these intermediates have never been isolated despite their possible importance in isomerism reactions. Furthermore, the nature of the final compounds of the reaction of $[\text{Pt}^{\text{II}}(\text{Ar})_2(2\text{-XAr}'\text{CHNCH}_2\text{CH}_2\text{NMe}_2)]$ has been found to be extremely dependent on the nature of the X *ortho* substituent on the metalating amino-imino ligand,^{10,14} despite the homogeneity observed in the kinetic-mechanistic studies carried out on similar systems.^{13,15–20} To gain insight into these reactions, a comprehensive kinetic-mechanistic study of the reactions of cyclometalated platinum(IV) compounds of type $[\text{PtXAr}_2(\text{Ar}'\text{CHNCH}_2\text{CH}_2\text{NMe}_2)]$ in toluene solution was undertaken.

Received: October 29, 2012



Scheme 1



Nomenclature (7, 5)-(II, IV)-XY for the complexes indicates:

Number of members of the metallacycle for cyclometallated complexes (7, 5)

Oxidation state of the Platinum centre (II, IV)

Halide ligand attached to the Platinum centre (X)

Substituent in the non-metallated *ortho* position of the $\text{ArCH}=\text{NCH}_2\text{CH}_2\text{NMe}_2$ ligand (Y)

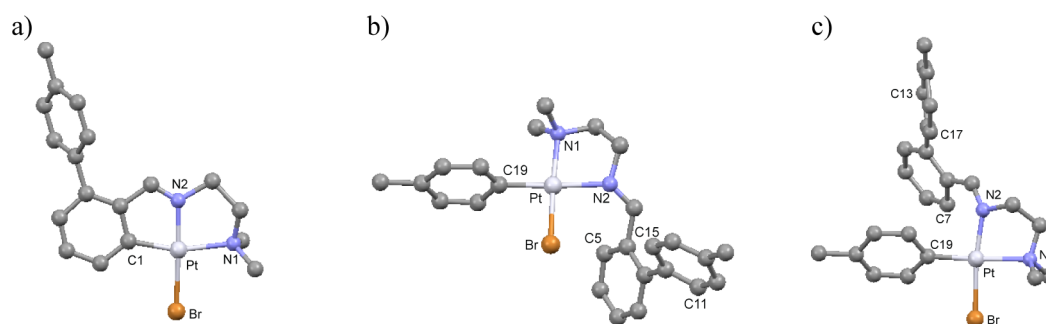


Figure 1. Molecular structure of compounds (a) **5-II-Br,H**, (b) **E-II-Br,H**, and (c) **E-II'-Br,H**.

As will be shown, two distinct geometrical isomers with a dangling biphenyl moiety are formed, and these intermediates lead to either five or seven-membered platinum(II) cyclometalated compounds.

RESULTS AND DISCUSSION

Formation of Five- Versus Seven-Membered Platina-cycles Containing Biphenyl Moieties: Characterization of Intermediates. Previous studies indicated that the reactions of $[\text{Pt}_2(4\text{-MeC}_6\text{H}_4)_4(\mu\text{-SEt}_2)_2]$ with bidentate N-donor ligands $2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2$ and $2\text{-XC}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2$ ($\text{X} = \text{Cl}$ or Br) lead to coordination of the ligand followed by intramolecular C-X ($\text{X} = \text{Cl}$ or Br) oxidative addition. The process produces the cyclometalated platinum(IV) compounds of type **5-IV** shown in Scheme 1. Further reaction of these compounds in refluxing toluene gives the seven-membered cyclometalated platinum(II) compounds $[\text{PtCl}(4\text{-MeC}_6\text{H}_4)_2(2\text{-ClC}_6\text{H}_3\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ (**7-II-Cl,Cl**)¹⁰ and $[\text{PtCl}(4\text{-MeC}_6\text{H}_4)_2(2\text{-BrC}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ (**7-II-Cl,H**)²¹ in a process involving formation of a C–C bond between two aryl rings and release of a toluene molecule. In contrast, the reactivity of

the more inert bromido analogue $[\text{PtBr}(4\text{-MeC}_6\text{H}_4)_2(\text{CC}_3\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ has not been studied so far. An initial attempt to produce an analogous seven-membered platinacycle was carried out in refluxing toluene following the procedure reported for the chlorinated compounds.¹⁴ In this case, though, a complex mixture of compounds resulted in which the major component was a five-membered platinacycle with an “*exo* C_{aryl}–C_{aryl}” bond (**5-II-Br,H**). As a first glance, a general picture of the observed processes should consist of: (i) C_{aryl}–C_{aryl} reductive elimination from the platinum(IV) compounds of type **5-IV** to give platinum(II) compounds of type **II** containing a biphenyl; (ii) C–H activation at either a distal or a proximal position of the biphenyl moiety leading, respectively, to seven (**7-II**) or five-membered (**5-II**) platinacycles with elimination of a toluene molecule.

To prove the validity of this common mechanism as well as to understand the factors governing the formation of either five or seven-membered platinacycles, attempts to isolate and characterize the proposed intermediates **II** were carried out. Preliminary time-resolved experiments were conducted at different temperatures to ascertain the best set of conditions

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Structures Determined for Compounds **5-II-Br,H**, **E-II-Br,H**, and **E-II'-Br,H** with Estimated Standard Deviations

| 5-II-Br,H | | E-II-Br,H | | E-II'-Br,H | |
|------------------|----------|------------------|----------|-------------------|----------|
| Pt–C(1) | 1.979(9) | Pt–C(19) | 1.999(5) | Pt–C(19) | 1.97(1) |
| Pt–N(1) | 2.167(7) | Pt–N(1) | 2.065(4) | Pt–N(1) | 2.21(1) |
| Pt–N(2) | 1.931(5) | Pt–N(2) | 2.108(5) | Pt–N(2) | 1.98(1) |
| Pt–Br | 2.438(1) | Pt–Br | 2.426(9) | Pt–Br | 2.417(2) |
| C(1)–Pt–N(2) | 78.9(3) | C(19)–Pt–N(1) | 95.8(2) | C(19)–Pt–N(2) | 95.6(6) |
| N(1)–Pt–N(2) | 85.5(2) | N(1)–Pt–N(2) | 81.6(2) | N(1)–Pt–N(2) | 81.3(5) |
| C(1)–Pt–Br | 99.2(3) | C(19)–Pt–Br | 87.3(1) | C(19)–Pt–Br | 91.7(4) |
| N(1)–Pt–Br | 96.3(2) | N(2)–Pt–Br | 95.3(1) | N(1)–Pt–Br | 95.3(1) |

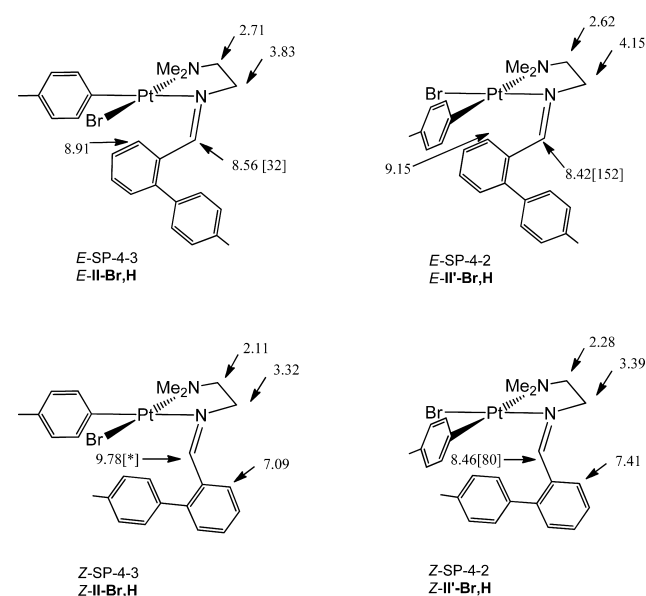
where each of the species was present in representative amounts (see following sections). For example, the reactions of **5-IV-Cl,Cl** and **5-IV-Cl,H** in toluene at 70 °C were sampled and monitored by ¹H NMR spectra at different times. While for **5-IV-Cl,Cl**, resonances assigned to an intermediate **II-Cl,Cl** were only observed at the very beginning of the process, for **5-IV-Cl,H**, formation and build up of intermediate **II-Cl,H** was clearly observed.

In view of the higher complexity of the behavior of species **5-IV-Br,H** ($[\text{PtBr}(4\text{-MeC}_6\text{H}_4)_2(\text{CC}_5\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$), its solution reactivity was studied more thoroughly. The complex was dissolved in a 1:1 mixture of toluene-methanol, and the mixture was heated at 45 °C. After 24 h, the ¹H NMR spectra reveals that the solution contains 70% of compound **II-Br,H** and 20% of compound **5-II-Br,H**, along with other minor components; crystals of **II-Br,H** suitable for X-ray analysis could be obtained directly from this reaction mixture. In another experiment, compound **5-IV-Br,H** was dissolved in toluene and warmed at 60 °C for 36 h, under these conditions the presence of **5-II-Br,H**, along with two isomeric forms of **II-Br,H** (later identified as *Z*- and *E*-SP-4-2) were detected in solution. Orange crystals of compound **5-II-Br,H** were obtained from the mixture and crystallographically characterized. The X-ray diffraction (XRD) studies on compound **5-II-Br,H** (Figure 1a, Table 1) show the presence of a fused [5,5,6] tricyclic system formed by a five-membered platinacycle, a [N,N'] chelate and a phenyl group of the biaryl moiety. As found in related systems, the Pt-amine bond is longer than the corresponding Pt-imine (2.167(7) Å vs 1.931(5) Å), and the smallest angles around the platinum are those involving the chelate and the metalacycle (N(1)–Pt–N(2) = 85.5(2) ° and N(2)–Pt–C(1) = 78.9(3) °). The results clearly indicate that compound **II-Br,H** is formed from **5-IV-Br,H** in a reductive elimination process, leading to formation of a biphenyl moiety, while compound **5-II-Br,H** could be formed in a subsequent process involving intramolecular C–H activation, leading to a five-membered platinacycle concurrent with toluene elimination.

As stated, complex **II-Br,H** formed in a reductive elimination process from **5-IV-Br,H** has been unequivocally characterized by crystallography (Figure 1b, Table 1). As expected, a biphenyl fragment is formed involving a *para*-tolyl ligand and the aryl ring of the nitrogen ligand. The amine-imine ligand is bidentate, and the square planar coordination around the platinum is completed with a bromido, trans to the dimethyl-amine moiety, and a *para*-tolyl ligand. The arrangement around the imine fragment is *E*, which is the most favored to produce a five-membered platinacycle through metalation at C(5). The distance Pt···C(5) is 3.607 Å, in the range reported for formation of this type of metalacycle^{22,23} and considerably

shorter than the distance to the carbon atoms available for formation of seven membered platinacycles (Pt···C(15) = 4.880 Å and Pt···C(11) = 6.695 Å) which confirms the suitability of **II-Br,H** as a precursor of five-membered cyclometalated compound **5-II-Br,H**. It is interesting to note that the NMR data obtained for compound **II-Br,H** in solution are in good agreement with the *E*-SP-4-3 arrangement determined by XRD. In particular, the value of *J*(HC=N–Pt) is characteristic of both an *E* conformation of the imine and the presence of a C-donor ligand trans to the same group, while the biphenyl hydrogen closest to the platinum center (C(5)-H) appears as a downfield shifted doublet.²⁴ Because of the presence of the chelate amine-imine ligand, only isomers SP-4-3 and SP-4-2 are possible; furthermore, a similar stability can be expected for them based on the similar trans influence of amine and imine ligands.⁴ Additionally, the imine group may adopt an *E* or a *Z* conformation, thus producing four possible isomers, as shown in Chart 1. Moreover, the dangling biaryl moiety may adopt different rotational arrangements to reduce the steric hindrance of these highly crowded complexes.

From the final reaction mixture obtained in toluene at 95 °C, the *E*-SP-4-2 form of the **II-Br,H** species (**II'-Br,H**) depicted in

Chart 1. Four Possible Isomers of the Compound Formed in the Reductive Elimination Process from **5-IV-Br,H**^a

^a¹H NMR data (CDCl₃, δ in ppm; *J*(H–Pt) [in brackets] in hertz (Hz), * not observed) for the imine, the methylene and the doublet, at lowest field in the aromatic region, included.

Scheme 2

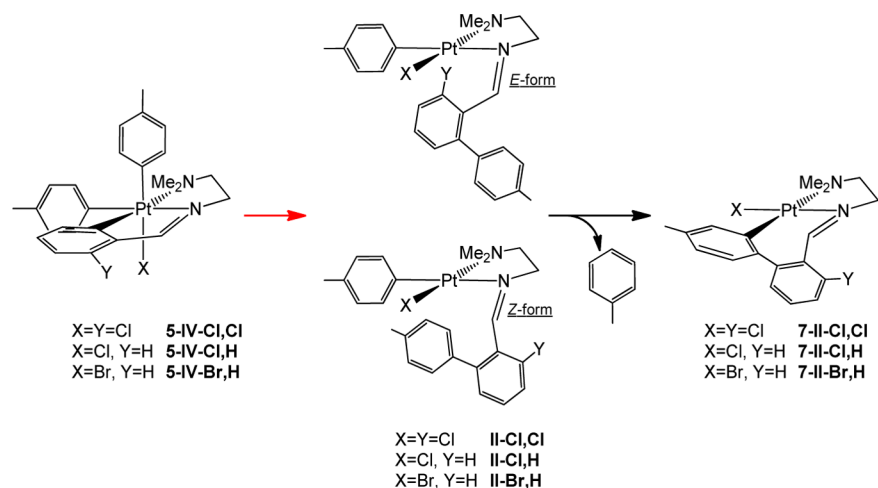


Chart 1 could also be isolated and identified in solution given the high value of $J(HC=N-Pt) = 152$ Hz observed for the imine proton, as well as for the doublet at $\delta = 9.15$ ppm, assigned to an aromatic proton vicinal to the platinum. Similarly, Z-SP-4-2 form of the same species could also be isolated and characterized by 1H NMR, with a much smaller $J(HC=N-Pt)$ (80 Hz) value; the NOESY $^1H-^1H$ spectra revealing cross-peaks between methylene and aromatic protons support the Z conformation of the imine. From the solutions of complex **II'-Br,H** good quality crystals could be isolated and the corresponding XRD studies were conducted; Figure 1c and Table 1 collect the structural data for the complex. As expected, this compound is a geometrical isomer of compound **II-Br,H** (E-SP-4-3, Chart 1) in which a *para*-tolyl ligand is trans to the dimethylamine moiety, and the arrangement around the imine fragment is *E*. As for isomer E-SP-4-3 discussed above, for E-SP-4-2 the shorter distance of the platinum center to the proximal C-H bond [$Pt \cdots C(7) = 3.500$ Å] than to the distal C-H bonds of the biphenyl [$Pt \cdots C(17) = 5.485$ Å and $Pt \cdots C(13) = 7.012$ Å] indicates its suitability to act as a precursor of five- rather than seven membered cyclometalated compounds. While for E-SP-4-2, the Pt-imine bond length (1.975(11) Å) is shorter than the Pt-amine distance (2.223(14) Å) in agreement with the lower coordinating ability of amine versus imine nitrogen atom, the reverse trend is observed for compound E-SP-4-3, in which the Pt-imine (2.108(5) Å) is slightly longer than the Pt-amine (2.066(5) Å) distance. This result can be related to the larger trans influence of the *para*-tolyl versus the bromido ligand. It is important to note that neat solutions of E-SP-4-2 or Z-SP-4-2 in $CDCl_3$ at room temperature evolve in a few days to mixtures of both isomers, the predominant species having a Z conformation, which suggest a facile isomerization process favoring the less hindered species.

As indicated above, all the isomers shown in Chart 1 can be readily identified by 1H NMR spectroscopy, since previous studies carried out for compounds $[PtCl_2(ArCH=NCH_2CH_2NMe_2)]$ or $[PtPh_2(ArCH=NCH_2CH_2NMe_2)]$ indicate that larger $J(HC=N-Pt)$ values are expected for (i) imine moieties trans to a halido ligand versus trans to a C-donor ligand, and (ii) *E* versus *Z* conformation of the imine.^{17,24,25} In addition, for these compounds, the aromatic hydrogen which is close to the platinum atom in the *E* isomers appears as a doublet shifted downfield, and for the *Z* isomers the methylene

protons appear upfield because of their proximity to the biaryl system.

From the general view of Chart 1, we can speculate that for the isomers with a Z arrangement around the imine the distal hydrogen atoms of the biaryl are closer to the platinum center and, therefore, formation of a seven-membered platinacycle should arise from these isomers. For the detection of these proposed intermediates with a Z configuration, harsher conditions were tested. After reacting for 2 h at 95 °C a toluene solution of compound **5-IV-Br,H** a complex mixture of compounds was formed. The major component of the mixture corresponds to the E-SP-4-2 form of compound **II-Br,H**, while the five-membered cyclometalated compound **5-II-Br,H** was also present in significant quantities. Only small amounts of the Z-SP-4-2 form of **II-Br,H** were present as well as the new seven-membered platinacycle **7-II-Br,H**. Longer reaction times under the same conditions led to reaction mixtures with decreasing proportions of *E*- and *Z*-SP-4-2 and increasing amounts of both **5-II-Br,H** and **7-II-Br,H**. To attempt the isolation of compound **7-II-Br,H**, the reaction of $[Pt_2(4-MeC_6H_4)_4(\mu-SEt_2)_2]$ with imine $2-BrC_6H_4CH=NCH_2CH_2NMe_2$ was carried out in refluxing toluene. After 6 h, workup of the reaction mixture gave, in addition to compound **5-II-Br,H**, a light yellow solid showing a 1H NMR spectrum consistent with that expected for the Z-SP-4-3 isomeric form depicted in Chart 1. On increasing the reaction time up to 16 h, a five-, **5-II-Br,H**, and seven-membered platinacycle **7-II-Br,H** mixture was detected by 1H NMR, the **5-II-Br,H**:**7-II-Br,H** ratio being 4:1. Compound **7-II-Br,H** could not be isolated from these mixtures and was only characterized in solution according to the data available for analogous seven-membered platinacycles.^{10,21}

Thus, the observed preparative results suggest that formation of seven-membered platinacycles require both the SP-4-3/SP-4-2 isomerization at the platinum center and *E/Z* rearrangement to produce the required precursor. In contrast, formation of a five-membered platinacycle can take place under milder conditions from the E-SP-4-3 isomer formed on reductive elimination from compounds of type **5-IV**. In this respect it is interesting to point out that a seven-membered platinacycle is formed readily upon reaction of imine $2-BrC_6H_4CH=NCH_2(4-ClC_6H_4)$ with $[Pt_2(4-MeC_6H_4)_4(\mu-SEt_2)_2]$,¹⁰ which suggests that the required isomer is more easily formed for imines containing just one nitrogen donor atom.

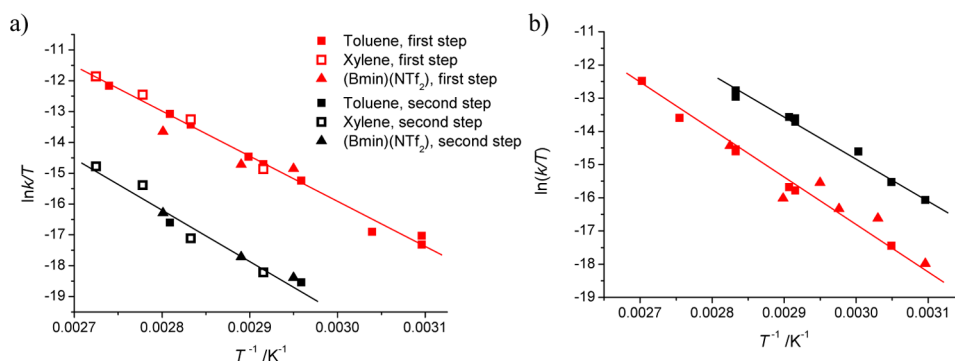


Figure 2. Eyring plots for the reactions observed by UV–vis monitoring of the two step process occurring on solution of 5-IV-Cl,H (a) and 5-IV-Cl,Cl (b) in different solvents and temperatures.

Table 2. Kinetic and Thermal Activation Parameters for the Two Reaction Steps Observed for the Reaction of 5-IV-Cl,H, 5-IV-Cl,Cl, and 5-IV-Br,H Leading to 7-II-Cl,H, 7-II-Cl,Cl, and 5-II-Br,H, Respectively

| Reaction | Step | Assignment ^a | $10^5 \times {}^{340}k$ /s ⁻¹ | ΔH^\ddagger /kJ mol ⁻¹ | ΔS^\ddagger /J K ⁻¹ mol ⁻¹ |
|-------------------------|------|---|---|--|---|
| 5-IV-Cl,H → 7-II-Cl,H | Fast | Biphenyl reductive elimination | 9.1 | 122±5 | 33±13 |
| | Slow | Distal C-H biphenyl oxidative addition | 0.29 | 141±15 | 60±44 |
| 5-IV-Cl,Cl → 7-II-Cl,Cl | Fast | Distal C-H biphenyl oxidative addition | 29 | 102±5 | -16±15 |
| | Slow | Biphenyl reductive elimination | 3.4 | 118±5 | 13±13 |
| 5-IV-Br,H → 5-II-Br,H | Fast | Biphenyl reductive elimination | 240 | 97±4 | -13±11 |
| | Slow | Proximal C-H biphenyl oxidative addition | 30 | 86±7 | -63±20 |
| | | SP-4-3 ⇌ SP-4-2 isomerisation equilibrium | 150 | 42±5 | -179±15 |

^aSee text.

Kinetico-Mechanistic Studies on the Formation of Seven-Membered 7-II-Cl,Cl and 7-II-Cl,H Metallacycles. It is thus clear that a distinct reactivity is observed arising from the Pt(IV) five-membered cyclometalated complexes [PtCl(4-MeC₆H₄)₂(2-ClCC₅H₃CH=NCH₂CH₂NMe₂)], [PtCl(4-MeC₆H₄)₂(CC₅H₄CH=NCH₂CH₂NMe₂)], and [PtBr(4-MeC₆H₄)₂(CC₅H₄CH=NCH₂CH₂NMe₂)] (Scheme 2). The formation of these platinum(IV) compounds from the corresponding Pt(II) [Pt(4-MeC₆H₄)₂(2-X,YC₆H₃CH=NCH₂CH₂NMe₂)] (X = Y = Cl; X = Cl, Y = H; X = Br, Y = H) precursors has been recently studied kinetico-mechanistically,¹⁵ and a detailed mechanistic study of the reactivity of the final Pt(IV) cyclometalated complexes has been now pursued.

As indicated in the previous section, only compounds 5-IV-Cl,Cl and 5-IV-Cl,H produced the expected seven-membered cyclometalated complexes via the straightforward reductive elimination/oxidative addition/reductive elimination reaction sequence indicated in Scheme 2.^{8,10,21} As the reactivity of compound 5-IV-Br,H was much more complex, initial studies were conducted on the chloro analogues. Initial time-resolved UV–vis spectroscopy of toluene solutions of complexes 5-IV-Cl,Cl and 5-IV-Cl,H indicated that the process involves a sequence with significant differences between the two compounds. Although UV–vis spectral changes could be associated with a two step process using SPECFIT for both compounds,²⁶ only for compound 5-IV-Cl,H could the build up of an intermediate be detected spectroscopically; for compound 5-IV-Cl,Cl only a small induction period could be

quantified. Figure 2 collects the Eyring plots derived for the studies carried out for the two systems at different temperatures. In the figure the data of the reactions measured in ionic liquid (Bmim)(NTf₂) solvent is also included; the perfect alignment with the data in toluene or xylene indicates the expected absence of polar components in the transition states involved in the process.^{27,28} Table 2 collects the relevant kinetic and thermal activation parameters determined for the two steps indicated.

The difference between the two systems is noticeable, especially with reference to the slow step observed, as assigned in Figure 2 and Table 2. If the fast reaction step corresponds to the first reaction from the sequence indicated in Scheme 2, the build up of the intermediate species in the 5-IV-X,Y → 7-II-X,Y reaction should be seen which is only in agreement with the spectroscopic data for the 5-IV-Cl,H → 7-II-Cl,H process. For the reaction of the 5-IV-Cl,Cl the lack of an observable intermediate indicates that a fast step is occurring after the first slower process has started. Nevertheless, the detection of the two processes indicates that the difference in rate constants should not be very large, as effectively indicated in Table 2. To confirm the above suppositions, as well as the probable II-X,Y nature of the intermediate compound, parallel ¹H NMR monitoring of the reaction was conducted. For the 5-IV-Cl,H → 7-II-Cl,H process at 70 °C, sampling of the medium showed the presence of II-Cl,H in its *E* form in the reaction medium immediately after the reaction had started. On standing, species 7-II-Cl,H begins to appear in the reaction medium, and a

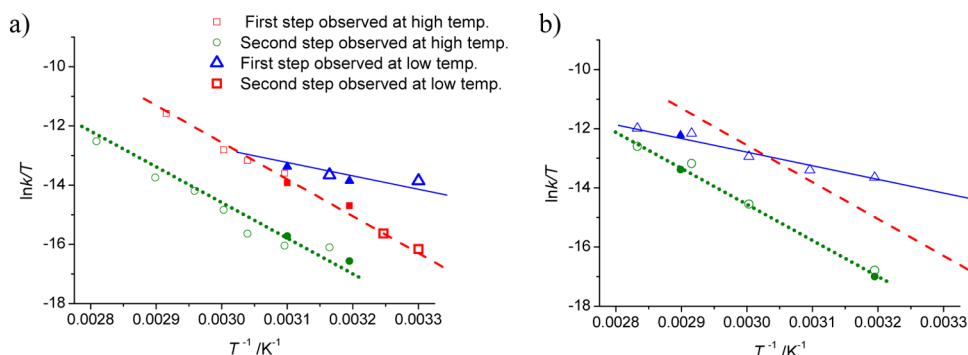


Figure 3. Eyring plots for the reactions observed by UV–vis monitoring of the sequential process occurring on (a) solution of **5-IV-Br,H** and (b) solution of **II-Br,H**. Empty points toluene/xylene solutions, full points (Bmim)(NTf₂) solution.

progressive disappearance of **E-II-Cl,H** occurs once the initial **5-IV-Cl,H** complex has been totally consumed. However, monitoring of the **5-IV-Cl,Cl** → **7-II-Cl,Cl** process indicates no build up of the equivalent **II-Cl,Cl** complex, and the reaction medium only ever shows the presence of the initial **5-IV-Cl,Cl** and final **7-II-Cl,Cl** compounds.

As a whole the general **5-IV-X,Y** → **7-II-X,Y** process seems to occur in a rather different rate sequence despite the common reactivity observed. For the **Cl,H** system the process is triggered by a concerted reductive elimination of a biphenyl moiety followed by a rate limiting distal C–H oxidative addition reaction, and a fast reductive elimination of toluene from the Pt(IV) hydride species formed.^{6,7} The absence of differences in the reaction rates with the use of the (Bmim)(NTf₂) ionic liquid as the solvent confirms the expected concerted nature of the processes occurring upon decoordination of the -NMe₂ moiety to form the 14/16 electron intermediates required by the microreversibility principle.^{15,17,20} The values determined for ΔH^\ddagger and ΔS^\ddagger agree with such mechanism given the need of a Pt(IV/II)-NMe₂ bond dissociation in both steps, when compared with the more facile loss of a SMe₂ ligand.^{12,29,30} For the analogous **Cl,Cl** complex system the initial reductive elimination of the biphenyl moiety is the slower reaction in the process, being rate limiting. The distal C–H oxidative addition reaction (and consequent rapid reductive elimination of toluene from the Pt(IV) hydride species formed) represents a faster process (see Table 2). It is clear that the change from Y = H to Y = Cl produces dramatic differences in the relative rates of the processes observed, as well as in the general rate of the full process (see Table 2). The most plausible explanation for the facts observed are related to the already indicated intramolecular hydrogen bonding possibility between the -N=CH-hydrogen and the Y = Cl substituent in complex **5-IV-Cl,Cl**,^{15,17,31} not possible for Y = H. Thus for this species the biphenyl reductive elimination reaction should be somehow hampered when compared with that occurring on the **5-IV-Cl,H** compound (3.4×10^{-5} versus 9.1×10^{-5} s⁻¹ at 67 °C, Table 2). Furthermore, if the structure of the two possible **II-Cl,Y** intermediates (*E* and *Z*) are compared, steric factors should produce a much higher effective concentration of the correctly positioned *Z*-form species indicated at the bottom of Scheme 2 for Y = Cl with respect to that for Y = H, thus producing a higher biphenyl C–H oxidative addition rate (29×10^{-5} versus 0.29×10^{-5} s⁻¹ at 67 °C, Table 2). It should also be taken into account that the *Z* ⇌ *E* isomerization process should be rather fast under the conditions of the reactions studied,

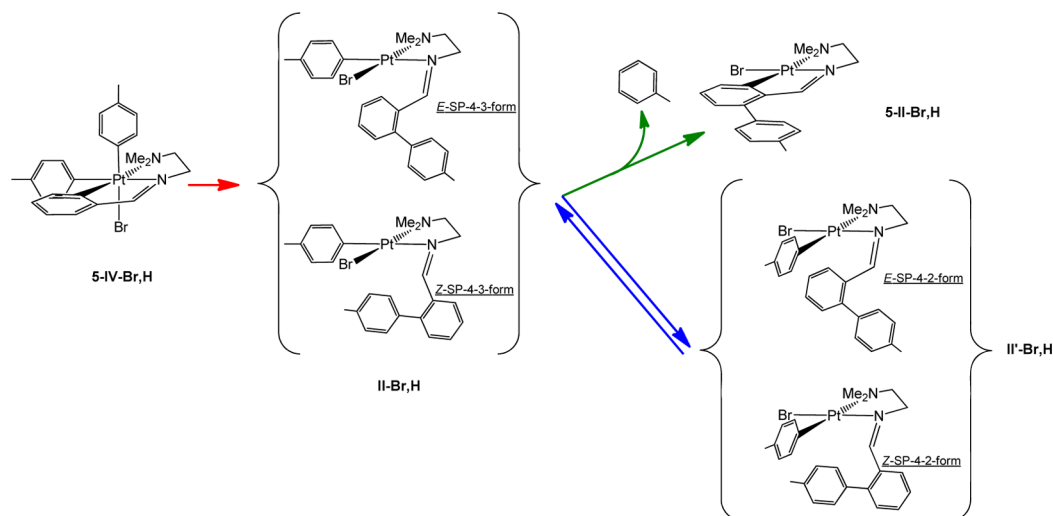
thus not being rate determining in any case.^{2,17,32} The same reasoning applies for the equivalent compounds where the relative position of the X and tolyl ligands is reversed in the square planar complex (see below).

Kinetic-Mechanistic Studies on the Spontaneous Reaction of the Five-Membered **5-IV-Br,H** Metallacycle.

As indicated in the sections above, as well as in previously carried out studies,¹⁵ the spontaneous reaction of **5-IV-Br,H** in toluene solution, under the same conditions used for the reaction of compounds **5-IV-Cl,Cl** and **5-IV-Cl,H**, showed a rather different behavior. The UV–vis spectral monitoring of the changes indicated a series of reaction steps that could be properly evaluated once the correct temperature conditions had been established. SPECFIT²⁶ fitting of these spectral changes to a series of three consecutive processes produced a set of coherent spectral changes and rate constants. Figure 3a collects the Eyring plots corresponding to the data collected in toluene and (Bmim)(NTf₂) solution. It should be noted that the initial observation of these separate reactions steps, as well as their optimal temperature and time conditions, have allowed the isolation of the intermediate/dead end complexes indicated in the above preparative section on this report. When the reaction has been carried out using the isolated **E-II-Br,H**, indicated in the previous sections (from mild reaction conditions), the results have been very revealing as to the assignment of one of the three steps appearing in Figure 3a. Figure 3b shows the good agreement of the data from the spontaneous reaction of this isolated **E-II-Br,H** in toluene or (Bmim)(NTf₂) solution. From the data it is clear that the reaction leading to the reductively eliminated biphenyl ligand complex from **5-IV-Br,H** corresponds to the red squares/dashed line in Figure 3.

As for the reactions indicated in the same figure by the blue and green line/symbols, the application of more forcing reaction conditions on **5-IV-Br,H** or **E-II-Br,H** showed the presence of two compounds in all cases, even at very long reaction times. It is thus clear that a consecutive fast+slow reaction step sequence does not apply for the process observed. The alternative slow+fast consecutive sequence can also be discarded given the observation of both steps at low temperature; the difference between the rates of the two processes being too large for the kinetic measurement of an induction period (1.5×10^{-5} versus 3.7×10^{-4} s⁻¹ at 40 °C).^{33,34} The operation of two parallel processes is the only possible explanation for the facts observed. A careful choice of reaction conditions (as indicated in the first section of this report) allowed the isolation from the reaction medium of the new 5-membered cyclometalated Pt(II) complex, **5-II-Br,H**, as

Scheme 3



well as the new *E*-II'-Br,H compound differing from *E*-II-Br,H in Scheme 2 by the relative trans Br/tolyl position in the square planar environment of the Pt(II) (see Chart 1). Given the fact that compound 5-II-Br,H is a dead-end, as far as the formation of *E*-II'-Br,H is concerned, the process leading to this proximal cyclometalated derivative should correspond to the slower step of the set observed (green circles/dotted line). The reaction indicated by the blue triangles/solid line corresponds then to the II-Br,H \rightleftharpoons II'-Br,H isomerization equilibrium process. Table 2 collects the kinetic and thermal activation parameters corresponding to the C–H bond activation related processes, and Scheme 3 summarizes the reactivity observed for this system (considering that the *Z* \rightleftharpoons *E* isomerization process should be rather fast under the conditions of the reactions studied).

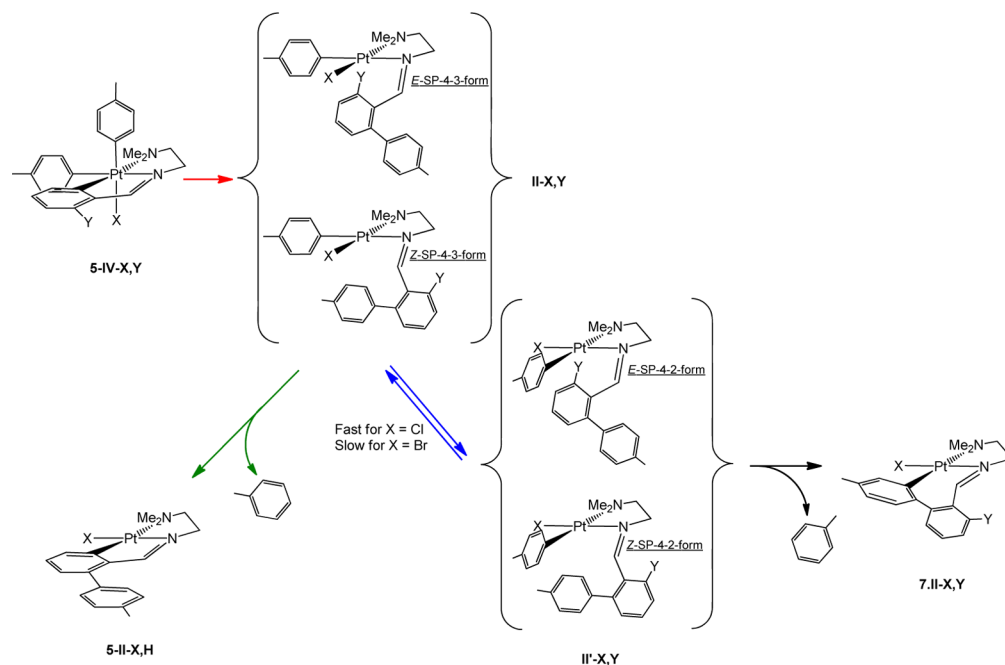
It seems that under these conditions, as stated, the activation of the proximal C–H bond of compound *E*-II-Br,H producing 5-II-Br,H is preferred to that of the distal activation, in the *Z* form, leading to a possible 7-II-Br,H. The relatively facile II-Br,H \rightleftharpoons II'-Br,H isomerization equilibrium process can only be held responsible for this fact if the *Z*-II'-Br,H form is also less reactive in the formation of the 7-II-Br,H species. The kinetic and thermal activation parameters collected in Table 2 indicate that while the values determined for the ΔH^\ddagger and ΔS^\ddagger corresponding to the reductive elimination process are in line of those found for the other two systems in the previous section, those for the proximal C–H bond activation to form the new 5-II-Br,H show an activation enthalpy more favorable, despite the higher degree of ordering needed for the process to take place (as expected). As for the values of the activation parameters determined for the II-Br,H \rightleftharpoons II'-Br,H isomerization process, collected in Table 2, it is clear that the reaction is not related to a rate limiting highly dissociative sequence.³⁵ The very negative value determined for ΔS^\ddagger , as well as the low activation enthalpy, indicate a highly ordered transition state that does not correlate with a limiting dissociation of the ancillary -NMe₂ group,³⁶ followed by the reorganization of the 14 electron species formed has been established for Pd(II) complexes.^{37,38} The alternative dissociation of the bromido ligand adds up the improbable formation of ionic species in toluene to the above-mentioned factors.

The fact that compound II'-Br,H could be isolated from the reaction mixtures, and that at high temperatures the II-Br,H \rightleftharpoons

II'-Br,H isomerization process appears to be slowed down considerably (isokinetic temperature for the 5-IV-Br,H \rightarrow 5-II-Br,H and II-Br,H \rightleftharpoons II'-Br,H being ca. 90–95 °C, Figure 3), led us to the study of the reaction of the isolated II'-Br,H complex under much harsher conditions. Effectively, the previously indicated preparative procedures show that compound 7-II-Br,H can be obtained from toluene solutions of 5-IV-Br,H after 6 h in refluxing toluene.

It seems thus clear that under conditions where the back isomerization from the SP-4-2 II'-Br,H to the SP-4-3 II-Br,H analogue is slow enough, the seven-membered Pt(II) cyclometalated 7-II-Br,H compound (Scheme 2) is formed, thus indicating that this reaction occurs on the *Z*-SP-4-2 isomers of this complex. The distinct reactivity of the family of complexes studied (i.e., 5-IV-Cl,Cl, 5-IV-Cl,H, and 5-IV-Br,H) can then be solely related to the feasibility of a favorable SP-4-3 to SP-4-2 isomerization for II-Cl,Cl and II-Cl,H complexes, as already reported for some Pd(II) complexes,⁵ that allows the formation of the 7-II-X,Y compounds without the appearance of the 5-II-Cl,H species formed from the proximal C–H bond activation, when X = Cl and Y = H. Scheme 4 summarizes the complete reactivity observed for the compounds studied. The distinct isomerization reactivity from 5-IV-Cl,H and 5-IV-Br,H remains the only point that still needs some explanation. The evaluation of the relative trans influence of the chlorido and bromido ligands³⁹ indicates that the weakening of the Pt–NMe₂ cannot be held responsible for the facts. This observation is in line with the thermal activation parameters indicated in Table 2 plus the fact that dissociation of this ancillary group should lead to the C–H bond activation process.^{13,15,20,40,41} An alternative associative triggered isomerization mechanism would be much more in line with the activation parameters obtained, as well as with the fact that only a Pt–C bond exists in the complex, thus disfavoring a dissociatively activated general substitution reactivity of the complexes.^{42,43,43,44} A possible C–H...Pt agostic interaction of a correctly positioned phenyl ring (see Scheme 3) in the empty axial position could generate a transient pentacoordinated species capable of undergoing a rotation and establishing the SP-4-3 \rightleftharpoons SP-4-2 equilibrium observed under the reaction conditions.^{45,46} Clearly the presence of a more sterically demanding bromido ligand should produce a hampering of the process with respect to X = Cl,

Scheme 4



thus slowing down the reaction and enabling the direct $\text{II-Br,H} \rightarrow \text{5-II-Br,H}$ metalation reaction.

Finally the regioselective formation of seven-membered metallacycles from complexes II'-X,Y also needs some explanation, given the fact that the expected preferential formation of five-membered compounds has been observed in this work from II-Br,H , as well as in previous reports with similar complexes.⁷ The overall results indicate that the Z-SP-4-2 form of the series of complexes $[\text{PtX}(\text{Ar})(\text{Ar-Ar'CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ (Scheme 4) is the only reacting form producing such seven-membered compounds; the much more hindered nature of this isomeric form forces the biphenyl ligand to adopt a Z positioning, thus facilitating the formation of 7-II type metallacycles observed. The only five-membered biphenyl compounds are obtained in situations where the SP-4-3 arrangement is favored.

CONCLUSIONS

From the data collected on the solution behavior of complexes 5-IV-X,Y (Scheme 4) it is clear that a rather fine-tuning of the reactivity occurs with respect to the formation of the alternative 7-II,X,Y or 5-II,X,H complexes. A common reductive elimination reaction occurs to form compounds E-II-X,Y, which should lead to the formation of complexes 5-II-X,Y (as observed for 5-II-Br,H), since the facile equilibration reaction to Z-II-X,H leading directly to complexes 7-II-X,H does not occur. Nevertheless, the actuation of a fast $\text{SP-4-3} \rightleftharpoons \text{SP-4-2}$ ($\text{II-X,Y} \rightleftharpoons \text{II'-X,Y}$) isomerization process for $\text{X} = \text{Cl}$ prevents this 5-II-X,Y formation process. In this case the rapidly equilibrated II'-X,Y compounds establish a $\text{E} \rightleftharpoons \text{Z}$ equilibrium, and the Z form (the major component detected in the preparative procedures) produces exclusively the final 7-II-X,Y compounds.

EXPERIMENTAL SECTION

General Information. Microanalyses were performed at the Serveis Científic-Tècnics (Universitat de Barcelona). Electrospray mass spectra were performed at the Servei d'Espectrometria de Masses

(Universitat de Barcelona) in a LC/MSD-TOF spectrometer using $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ 1:1 to introduce the sample. NMR spectra were performed at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using a Mercury-400 spectrometer and referenced to SiMe_4 . δ values are given in ppm and J values in Hz. Abbreviations used: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. For numbering used for NMR spectra assignments, see Chart 2.

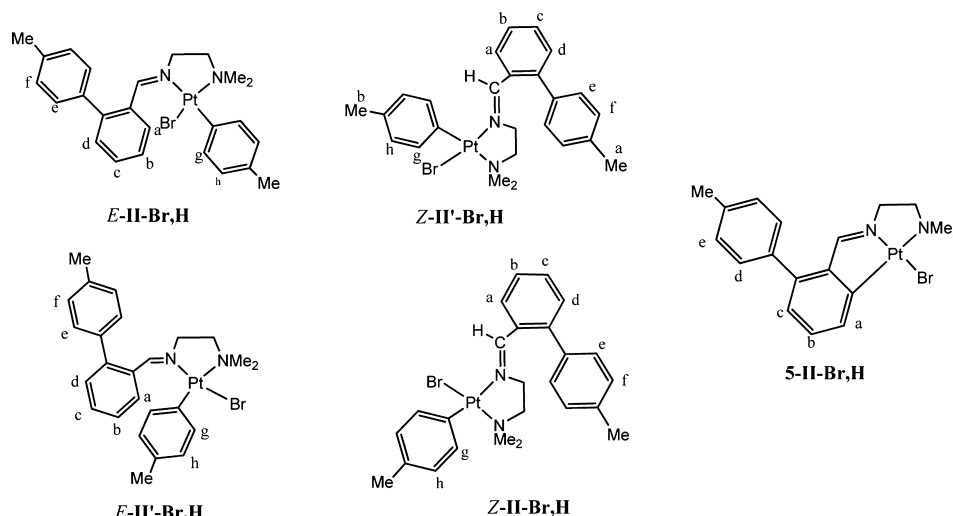
Compounds. Compounds $\text{cis-}[\text{Pt}(\text{4-MeC}_6\text{H}_4)_2(\mu\text{-SEt}_2)]_2$,⁴⁷ 5-IV-Cl,Cl, 5-IV-Cl,H, 5-IV-Br,H, 7-II-Cl,Cl, and 7-II-Cl,H were prepared as reported elsewhere.^{10,15,21}

II-Cl,Cl (E-SP-4-3-[PtCl(4-MeC₆H₄){2-(4-MeC₆H₄)6-ClC₆H₃CH=NCH₂CH₂NMe₂}]₂). This compound was detected in solution when the reaction of compound 5-IV-Cl,Cl to produce 7-II-Cl,Cl carried out in toluene at 70 °C was monitored by ¹H NMR. ¹H NMR (CDCl₃, 400 MHz): δ = 8.75 [s, br, 1H, CHN]; 8.05 [dd, ³J(H-H) = 8.0, ⁴J(H-H) = 2.0, 1H]; 8.03 [dd, ³J(H-H) = 7.6, ⁴J(H-H) = 1.2, 1H]; 7.30–7.32 [m, 1H]; 7.28 [d, ³J(H-H) = 7.6, 2H]; 7.15 [d, ³J(H-H) = 7.2, 2H]; 2.77 [s, 6H, NMe₂]; 2.39 [s, 3H, Me]; 2.25 [s, 3H, Me].

II-Cl,H (E-SP-4-3-[PtCl(4-MeC₆H₄){2-(4-MeC₆H₄)C₆H₄CH=NCH₂CH₂NMe₂}]₂). A 50 mg portion of [Pt(4-MeC₆H₄)₂(2-ClC₆H₄CHNCH₂CH₂NMe₂)] were dissolved in toluene (10 mL) and the solution was heated at 70 °C for 2 h. After this time, 20 mg of 7-II-Cl,H were filtered off, and the toluene was concentrated to half-volume. Crystals of II-Cl,H, slightly unpurified with 7-II-Cl,H, were formed. The solution was concentrated to dryness and a ¹H NMR in CDCl₃ was taken showing the presence of isomers E-SP-4-3, E-SP-4-2 and Z-SP-4-2. ¹H NMR (CDCl₃, 400 MHz): (E-SP-4-3): δ = 9.01 [d, ³J(H-H) = 7.2, 1H]; 8.56 [s, ³J(H-Pt) = 32.0, 1H, CHN]; 7.54 [t, ³J(H-H) = 8.0, 1H]; 7.52 [t, ³J(H-H) = 8.0, 1H]; 7.35 [d, ³J(H-H) = 8.0, 4H]; 7.24 [d, ³J(H-H) = 8.0, 2H]; 7.18–7.14 [m, 1H]; 6.83 [d, ³J(H-H) = 8.0, 2H]; 3.81 [t, ²J(H-H) = 5.0, 2H]; 2.85 [s, 6H, NMe₂]; 2.70 [m, 2H]; 2.41 [s, 3H, Me]; 2.25 [s, 3H, Me]. (E-SP-4-2): δ = 9.22 [d, ³J(H-H) = 8.0]; 8.33 [s, ³J(H-Pt) = 146]. (Z-SP-4-2): δ = 8.69 [s].

II-Br,H (E-SP-4-3-[PtBr(4-MeC₆H₄){2-(4-MeC₆H₄)C₆H₄CH=NCH₂CH₂NMe₂}]₂). A 200 mg portion (0.31 mmol) of 5-IV-Br,H was dissolved in 60 mL of a 1:1 mixture of toluene-methanol, and the final solution was heated at 46 °C for 36 h. The solution was concentrated at low pressure and the solid precipitated by adding 15 mL of ether. Recrystallization in acetone at room temperature affords 56 mg of compound II-Br,H. ¹H NMR (CDCl₃, 400 MHz): δ = 8.91 [d, ³J(H-

Chart 2. Numbering Used for NMR Spectra Assignments



H) = 8.0, 1H, H^a]; 8.56 [s, ³J(H–Pt) = 32.0, 1H, CHN]; 7.53 [t, ³J(H–H) = 8.0, 1H, H^b or c]; 7.46 [t, ³J(H–H) = 8.0, 1H, H^b or c]; 7.38 [d, ³J(H–H) = 8.0, 2H]; 7.36–7.25 [m, 5H]; 6.81 [d, ³J(H–H) = 8.0, 2H]; 3.83 [t, ³J(H–H) = 4.0, 2H, CH₂]; 2.85 [s, ³J(H–Pt) = 24.0, 6H, NMe₂]; 2.71 [t, ³J(H–H) = 4.0, 2H, CH₂]; 2.41 [s, 3H, Me]; 2.25 [s, 3H, Me]. ESI(+)-MS, *m/z*: 650 [M + NH₄]; 541 [M + PhMe]; 460 [M – PhMe–Br].

II'-Br,H (*Z*-SP-4-2-[PtBr(4-MeC₆H₄){2-(4-MeC₆H₄)C₆H₄CH=NCH₂CH₂NMe₂}]₂). A 50 mg portion of **5-IV-Br,H** was dissolved in toluene and heated at 95 °C for 2 h. The solvent was removed, and the residue was crystallized in CH₂Cl₂-MeOH, leading to a first crop of compound **5-II-Br,H**, followed by a second crop of **II'-Br,H**. ¹H NMR (CDCl₃, 400 MHz): δ = 8.46 [s, ³J(H–Pt) = 80.0, 1H, CHN]; 7.51 [t, ³J(H–H) = 8.0, 1H, H^b or c]; 7.41 [d, ³J(H–H) = 8.0, 1H, H^a or d]; 7.35 [t, ³J(H–H) = 8.0, 1H, H^b or c]; 7.34 [d, ³J(H–H) = 8.0, 2H, H^f]; 7.23 [d, ³J(H–H) = 8.0, 1H, H^a or d]; 7.09 [d, ³J(H–H) = 8.0, 4H, H^g]; 6.71 [d, ³J(H–H) = 8.0, 2H, H^b]; 3.39 [td, ²J(H–H) = 12.0, ³J(H–H) = 4.0, 2H, CH₂]; 2.77 [s, 6H, NMe₂]; 2.47 [s, 3H, Me^a]; 2.28 [t, ³J(H–H) = 4.0, 2H, CH₂]; 2.20 [s, 3H, Me^b]. ESI(+)-MS, *m/z*: 1282.26 [2 M + NH₄]; 654.00 [M + Na]; 650.15 [M + NH₄].

II'-Br,H (*E*-SP-4-2-[PtBr(4-MeC₆H₄){2-(4-MeC₆H₄)C₆H₄CH=NCH₂CH₂NMe₂}]₂). A 50 mg portion of **5-IV-Br,H** was dissolved in toluene and heated at 95 °C for 2 h. The solvent was partially removed, and the solution was cooled. Light yellow crystals of **II'-Br,H** were formed. ¹H NMR (CDCl₃, 400 MHz): δ = 9.15 [d, ³J(H–H) = 8.0, 1H, H^a]; 8.42 [s, ³J(H–Pt) = 152.0, 1H, CHN]; 7.33 [td, ³J(H–H) = 7.2, ⁴J(H–H) = 1.6, 1H, H^b or c]; 7.26 [d, ³J(H–H) = 8.0, 2H]; 7.18 [td, ³J(H–H) = 7.6, ⁴J(H–H) = 1.2, 1H, H^b or c]; 7.15 [d, ³J(H–H) = 8.0, 2H]; 7.05 [dd, ³J(H–H) = 7.6, ⁴J(H–H) = 1.2, 1H, H^d]; 6.92 [d, ³J(H–H) = 8.0, 2H]; 6.34 [d, ³J(H–H) = 8.0, 2H]; 4.15 [t, ³J(H–H) = 4.0, 2H, CH₂]; 2.98 [s, 6H, NMe₂]; 2.62 [t, ³J(H–H) = 4.0, 2H, CH₂]; 2.42 [s, 3H, Me]; 1.91 [s, 3H, Me]. ESI(+)-MS, *m/z*: 1282.26 [2 M + NH₄]; 650.15 [M + NH₄]. Anal. Calc. for: C₂₅H₂₉BrN₂Pt: C: 47.47; H: 4.62; N: 4.43%. Found: C: 47.24; H: 4.54; N: 4.39%.

II-Br,H (*Z*-SP-4-3-[PtBr(4-MeC₆H₄){2-(4-MeC₆H₄)C₆H₄CH=NCH₂CH₂NMe₂}]₂). A 50 mg portion of **5-IV-Br,H** was dissolved in 20 mL of toluene, and the solution was refluxed for 6 h. The solvent was removed, and the residue was crystallized in CH₂Cl₂-MeOH, leading to a first crop of compound **5-II-Br,H**, followed by a second crop of **II-Br,H** as pale yellow solid (15 mg). ¹H NMR (CDCl₃, 400 MHz): δ = 9.78 [s, 1H, CHN]; 7.59 [td, ³J(H–H) = 7.6, ⁴J(H–H) = 1.2, 1H, H^b or c]; 7.52 [d, ³J(H–H) = 8.0, 2H]; 7.45 [td, ³J(H–H) = 8.0, ⁴J(H–H) = 1.2, 1H, H^b or c]; 7.38 [d, ³J(H–H) = 7.2, 2H]; 7.34 [d, ³J(H–H) = 8.0, 2H]; 7.18 [d, ³J(H–H) = 8.0, 2H]; 7.09 [d, ³J(H–H) = 8.0, 1H, H^a or d]; 6.71 [d, ³J(H–H) = 8.0, 1H, H^a or d]; 3.32 [t,

³J(H–H) = 4.0, 2H, CH₂]; 2.98 [s, 6H, NMe₂]; 2.42 [s, 3H, Me]; 2.11 [t, ³J(H–H) = 4.0, 2H, CH₂]; 1.26 [s, 3H, Me].

5-II-Br,H. A solution of **5-IV-Br,H** (190 mg, 0.3 mmol) in 16 mL of toluene was heated at 60 °C for 36 h. After this time, the solution was concentrated at low pressure and analyzed by ¹H NMR showing the presence of species **5-II-Br,H**, and **II'-Br,H** (*Z* and *E* isomers). Recrystallization allows isolation of orange crystals of **5-II-Br,H**. ¹H NMR (CDCl₃, 400 MHz): δ = 8.37 [s, ³J(H–Pt) = 148.0, 1H, CHN]; 7.92 [d, ³J(H–H) = 8.0, ³J(H–Pt) = 40.0, 1H, H^a]; 7.26 [m, 1H, H^b]; 7.22 [s, 4H, H^d]; 6.90 [d, ³J(H–H) = 8.0, 1H, H^c]; 4.00 [t, ³J(H–H) = 4.0, ³J(H–Pt) = 36, 2H, CH₂]; 3.07 [t, ³J(H–H) = 4.0, 2H, CH₂]; 2.93 [s, ³J(H–Pt) = 12.0, 6H, NMe₂]; 2.40 [s, 3H, Me]. ESI(+)-MS, 541.0 [M+H], 501.2 [M-Br+CH₃CN], 460.0 [M-Br]. Anal. Calc. for: C₁₈H₂₁BrN₂Pt: C: 40.01; H: 3.92; N: 5.18%. Found: C: 39.94; H: 4.04; N: 4.87%.

7-II-Br,H. This compound was characterized by ¹H NMR in the reaction mixture obtained when **5-IV-Br,H** (20 mg) were heated in refluxing toluene for 16 h. ¹H NMR (CDCl₃, 400 MHz): δ = 8.74 [s, ³J(H–Pt) = 156.0, 1H, CHN]; 7.61 [td, ³J(H–H) = 7.6, ⁴J(H–H) = 1.6, 1H]; 7.55 [s, 1H]; 7.50 [d, ³J(H–H) = 7.6, 1H]; 6.80 [m, 2H]; 4.47 [td, ³J(H–H) = 12; 4.0, 1H, CH₂]; 3.81 [dd, ³J(H–H) = 12; 4.0, 1H, CH₂]; 3.02 [s, 3H, NMe₂]; 2.74 [s, 3H, NMe₂]; 2.57 [dd, ³J(H–H) = 12.0; 4.0, 2H, CH₂]; 2.30 [s, 3H, Me].

Kinetics. The kinetic profiles for the reactions were followed by UV–vis spectroscopy in the 700–300 nm range on HP8452A or Cary50 instruments equipped with thermostatted multicell transports. Observed rate constants were derived from absorbance versus time traces at the wavelengths where a maximum increase and/or decrease of absorbance were observed. The calculation of the observed rate constants from the absorbance versus time monitoring of reactions, studied under second or first order concentration conditions, were carried out using the SPECFIT software.²⁶ The general kinetic technique is that previously described.^{6,15,48} Supporting Information, Table S1 collects all the obtained *k*_{obs} values for all the systems studied as a function of the starting complex, process studied, and temperature. All post-run fittings were carried out by the standard available commercial programs.

X-ray Structure Analysis. Prismatic crystals were selected and mounted on a MAR345 diffractometer with an image plate detector (**E-II-Br,H** and **5-II-Br,H**) or on an Oxford Diffraction Gemini CCD diffractometer employing an Oxford Cryosystems Series 600 Cryostream Cooler (**E-II'-Br,H**). The structures were solved by direct methods using the SHELXS computer program and refined by the full-matrix least-squares method, with the SHELXL97 computer program.^{49,50} All hydrogen atom positional parameters were computed and refined using a riding model, with an isotropic temperature factor

Table 3. Crystallographic and Refinement Data for Compounds 5-II-Br₂H, E-II-Br₂H, and E-II'-Br₂H

| | 5-II-Br ₂ H | E-II-Br ₂ H | E-II'-Br ₂ H |
|---|---|---|---|
| formula | C ₁₈ H ₂₁ BrN ₂ Pt | 2C ₂₅ H ₂₉ BrN ₂ Pt·CH ₃ OH | C ₂₅ H ₂₉ BrN ₂ Pt |
| Fw | 540.37 | 1297.05 | 632.50 |
| temp, K | 173(2) | 293(2) | 173(2) |
| wavelength, Å | 0.71073 | 0.71073 | 1.54180 |
| crystal system | orthorhombic | monoclinic | tetragonal |
| space group | <i>P</i> 2 ₁ <i>cn</i> | <i>C</i> 2/ <i>c</i> | <i>I</i> 4 ₁ / <i>a</i> |
| <i>a</i> , Å | 9.734(5) | 27.778(11) | 21.655(4) |
| <i>b</i> , Å | 14.922(6) | 15.491(5) | |
| <i>c</i> , Å | 12.734(5) | 13.504(3) | 20.826(7) |
| β , deg | | 109.51(2) | |
| <i>V</i> , Å ³ ; <i>Z</i> | 1850(1); 4 | 5477(3); 4 | 9767 (4); 16 |
| <i>d</i> (calcd), Mg/m ³ | 1.941 | 1.573 | 1.721 |
| abs coeff, mm ⁻¹ | 9.745 | 6.597 | 12.747 |
| <i>F</i> (000) | 1024 | 2520 | 4896 |
| rfins coll./ unique | 16733/4767 | 26357/7970 | 11220/3875 |
| | [<i>R</i> (int) = 0.0603] | [<i>R</i> (int) = 0.0888] | [<i>R</i> (int) = 0.0457] |
| data/restraint/parameter | 4767/4/200 | 7970/4/283 | 3875/0/266 |
| GOF on <i>F</i> ² | 1.089 | 1.115 | 1.036 |
| final <i>R</i> [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> ₁ = 0.0495 | <i>R</i> ₁ = 0.0514 | <i>R</i> ₁ = 0.0622 |
| | <i>wR</i> ₂ = 0.1308 | <i>wR</i> ₂ = 0.1545 | <i>wR</i> ₂ = 0.1658 |
| <i>R</i> (all data) | <i>R</i> ₁ = 0.0529 | <i>R</i> ₁ = 0.0591 | <i>R</i> ₁ = 0.0914 |
| | <i>wR</i> ₂ = 0.1357 | <i>wR</i> ₂ = 0.1623 | <i>wR</i> ₂ = 0.1962 |
| peak and hole, e Å ⁻³ | 1.521 and -3.182 | 2.571 and -2.077 | 2.692 and -1.361 |
| CCDC reference no. | 904051 | 904052 | 901843 |

equal to 1.2 times the equivalent temperature factor of the atom to which they are linked; further details are given in Table 3.

■ ASSOCIATED CONTENT

■ Supporting Information

Table S1 with values of *k*_{obs} for all the systems studied as a function of temperature and solvent. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: margarita.crespo@qi.ub.edu (M.C.), manel.martinez@qi.ub.edu (M.M.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from projects CTQ2012-37821-C02-01 and CTQ2009-11501 from the Spanish Ministerio de Ciencia e Innovación is acknowledged.

■ REFERENCES

- (1) Canty, A. J. *Dalton Trans.* **2009**, 10409–10417.
- (2) Favier, I.; Gómez, M.; Granell, J.; Martínez, M.; Font-Bardía, M.; Solans, X. *Dalton Trans.* **2005**, 123–132.
- (3) Brito, J. A.; Gómez, M.; Muller, G.; Teruel, H.; Clinet, J. C.; Duñach, E.; Maestro, M. A. *Eur. J. Inorg. Chem.* **2004**, 4278–4285.
- (4) Lee, J. J.; Yang, F. Z.; Lin, Y. F.; Chang, Y. C.; Yu, K. H.; Chang, M. C.; Lee, G. H.; Liu, Y. H.; Wang, Y.; Liu, S. T.; Chen, J. T. *Dalton Trans.* **2008**, 5945–5956.
- (5) Pérez-Temprano, M. H.; Gallego, A. M.; Casares, J. A.; Espinet, P. *Organometallics* **2011**, 30, 611–617.
- (6) Font-Bardía, M.; Gallego, C.; Martínez, M.; Solans, X. *Organometallics* **2002**, 21, 3305–3307.
- (7) Gallego, C.; Martínez, M.; Safont, V. S. *Organometallics* **2007**, 26, 527–537.

- (8) Crespo, M.; Font-Bardía, M.; Calvet, T. *Dalton Trans.* **2011**, 40, 9431–9438.
- (9) Crespo, M.; Calvet, T.; Font-Bardía, M. *Dalton Trans.* **2010**, 39, 6936–6938.
- (10) Martín, R.; Crespo, M.; Font-Bardía, M.; Calvet, T. *Organometallics* **2009**, 28, 587–597.
- (11) Crespo, M.; Font-Bardía, M.; Solans, X. *Organometallics* **2004**, 23, 1708–1713.
- (12) Crespo, M.; Anderson, C. M.; Kfoury, N.; Font-Bardía, M.; Calvet, T. *Organometallics* **2012**, 31, 4401–4404.
- (13) Calvet, T.; Crespo, M.; Font-Bardía, M.; Gómez, K.; González, G.; Martínez, M. *Organometallics* **2009**, 28, 5096–5106.
- (14) Albert, J.; Bosque, R.; Crespo, M.; Granell, J.; Rodríguez, J.; Zafrilla, J. *Organometallics* **2010**, 29, 4619–4627.
- (15) Calvet, T.; Crespo, M.; Font-Bardía, M.; Jansat, S.; Martínez, M. *Organometallics* **2012**, 31, 4367–4373.
- (16) Granell, J.; Martínez, M. *Dalton Trans.* **2012**, 41, 11243–11258.
- (17) Crespo, M.; Font-Bardía, M.; Granell, J.; Martínez, M.; Solans, X. *Dalton Trans.* **2003**, 3763–3769.
- (18) Crespo, M.; Martínez, M.; de Pablo, E. *J. Chem. Soc., Dalton Trans.* **1997**, 1231–1235.
- (19) Crespo, M.; Martínez, M.; Sales, J. *Organometallics* **1993**, 12, 4297–4304.
- (20) Crespo, M.; Martínez, M.; Sales, J.; Solans, X.; Font-Bardía, M. *Organometallics* **1992**, 11, 1288–1295.
- (21) Cortés, R.; Crespo, M.; Davin, L.; Martín, R.; Quirante, J.; Ruiz, D.; Messegue, R.; Calvis, C.; Baldomà, L.; Badia, J.; Font-Bardía, M.; Calvet, T.; Cascante, M. *Eur. J. Med. Chem.* **2012**, 54, 557–566.
- (22) Otto, S.; Chanda, A.; Samuleev, P. V.; Ryabov, A. D. *Eur. J. Inorg. Chem.* **2006**, 2561–2565.
- (23) Crespo, M.; Martín, R.; Calvet, T.; Font-Bardía, M.; Solans, X. *Polyhedron* **2008**, 27, 2603–2611.
- (24) Crespo, M.; Anderson, C. M.; Tanski, J. M. *Can. J. Chem.* **2009**, 80–87.
- (25) Crespo, M.; Font-Bardía, M.; Solans, X. *J. Organomet. Chem.* **2006**, 691, 1897–1906.
- (26) Binstead, R. A.; Zuberbuhler, A. D.; Jung, B. *SPECFIT32*, [3.0.34]; Spectrum Software Associates: Marlborough, MA, 2005.

- (27) Aviles, T.; Jansat, S.; Martínez, M.; Montilla, F.; Rodríguez, C. *Organometallics* **2011**, *30*, 3919–3922.
- (28) Hubbard, C. D.; Illner, P.; van Eldik, R. *Chem. Soc. Rev.* **2011**, *40*, 272–290.
- (29) Bernhardt, P. V.; Gallego, C.; Martínez, M. *Organometallics* **2000**, *19*, 4862–4869.
- (30) Esteban, J.; Font-Bardia, M.; Gallego, C.; González, G.; Martínez, M.; Solans, X. *Inorg. Chim. Acta* **2003**, *351*, 269–277.
- (31) Crespo, M.; Granell, J.; Solans, X.; Font-Bardia, M. *Organometallics* **2002**, *21*, 5140–5143.
- (32) Bernhardt, P. V.; Martínez, M.; Rodríguez, C.; Vazquez, M. *Dalton Trans.* **2012**, *41*, 2122–2130.
- (33) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981.
- (34) Tobe, M. L.; Burgess, J. *Inorganic Reaction Mechanisms*; Longman: Harlow, U.K., 1999.
- (35) Minniti, D. *J. Chem. Soc., Dalton Trans.* **1993**, 1343–1345.
- (36) Faraone, G.; Ricevuto, V.; Romeo, R.; Trozzi, M. *J. Chem. Soc. A* **1971**, 1877–1881.
- (37) Moncho, S.; Ujaque, G.; Lledós, A.; Espinet, P. *Chem.—Eur. J.* **2008**, *14*, 8986–8994.
- (38) Salas, G.; Casas, J. M.; Espinet, P. *Dalton Trans.* **2009**, 8413–8420.
- (39) Anastasi, A.; Deeth, R. J. *J. Chem. Theory Comput.* **2009**, *5*, 2339–2352.
- (40) Crumpton, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442–9456.
- (41) Luedtke, A. T.; Goldberg, K. I. *Inorg. Chem.* **2007**, *46*, 8496–8498.
- (42) Frey, U.; Helm, L.; Merbach, A. E.; Romeo, R. *J. Am. Chem. Soc.* **1989**, *111*, 8161–8165.
- (43) Alibrandi, G.; Bruno, G.; Lanza, S.; Minniti, D.; Romeo, R.; Tobe, M. L. *Inorg. Chem.* **1987**, *26*, 185–190.
- (44) Romeo, R.; Plutino, M. R.; Scolaro, L. M.; Stoccoro, S.; Minghetti, G. *Inorg. Chem.* **2000**, *39*, 4749–4755.
- (45) Wilkins, R. G. *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*; VCH: New York, 1991.
- (46) Font-Bardía, M.; Gallego, C.; González, G.; Martínez, M.; Merbach, A. E.; Solans, X. *Dalton Trans.* **2003**, 1106–1113.
- (47) Steele, B. R.; Vrieze, K. *Transition Met. Chem.* **1977**, *2*, 169–174.
- (48) Roiban, G. D.; Serrano, E.; Soler, T.; Aullón, G.; Grosu, I.; Cativiela, C.; Martínez, M.; Urriolabeitia, E. P. *Inorg. Chem.* **2011**, *50*, 8132–8143.
- (49) Sheldrick, G. M. *SHELXS*; Universität of Göttingen: Göttingen, Germany, 1997.
- (50) Sheldrick, G. M. *SHELX97-Programs for Crystal Structure Analysis* (Release 97-2); Universität of Göttingen: Göttingen, Germany, 1998.