

Unexpected Formal Aryl Insertion in a Cyclometalated Diphenylplatinum(IV) Complex: The First Seven-Membered Cyclometalated Platinum Compound Structurally Characterized

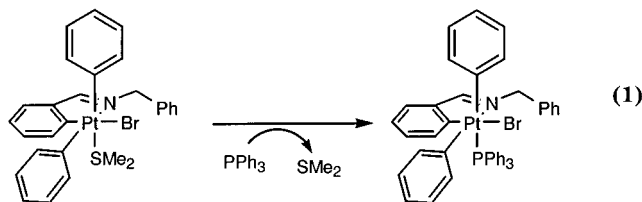
Mercè Font-Bardía,[†] Carlos Gallego,[‡] Manuel Martínez,^{*,‡} and Xavier Solans[†]

Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, E-08028 Barcelona, Spain, and Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona, Spain

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Summary: Cyclometalation of the (2-BrC₆H₄)CHNBzl imine via oxidative addition on [Pt^{II}(Ph)₂(SMe₂)₂] to produce the corresponding [Pt^{IV}Br(Ph)₂(CC₅H₃CHNBzl)(SMe₂)] compound has been achieved, and the X-ray crystal structure of its triphenylphosphine derivative has been determined. The lability of the SMe₂ ligand in this complex enables the reductive elimination of a C₆H₆ molecule and the formal insertion of the other phenyl ligand in the cyclometalated Pt–C bond, producing the first structurally characterized seven-membered cyclometalated platinum complex.

Substitution reactions on inert Werner-type coordination complexes have been studied for a long time and, although a few important challenges still exist,¹ the results seem quite clear as far as the intimate mechanism is concerned. The same sorts of studies on organometallic complexes are much more scarce, even though their inherent interest is evident both from the catalytic point of view and from that of activation processes of organic substrates.² Furthermore, the dissociation reactions on these octahedral complexes have been found to be a key step for the reductive elimination processes.³ According to our interest in the substitution reactions on theoretically inert t_{2g}⁶ Pt(IV) organometallic complexes,⁴ we decided to continue the study of such reactions (eq 1) when much bulkier groups, having a smaller trans influence, are present in the molecule.



For this purpose the reaction of the Pt(II) compound *cis*-[Pt(Ph)₂(SMe₂)₂] with the (2-BrC₆H₄)CHNBzl imine

was carried out according to the already well-established procedures.⁵ After 4 h of reaction, the solution was taken to dryness. The proton NMR spectrum (250 MHz, acetone-*d*₆, room temperature) of the residue showed a set of signals which indicated that the activation of the C–Br bond has taken place, producing the expected cyclometalated compound *cis*-[Pt^{IV}Br(Ph)₂(CC₅H₃CHNBzl)(SMe₂)]. The CH imine proton signal at 8.51 ppm shows a Pt(IV)-indicative coupling constant, *J*_{Pt–H}, of 45.4 Hz;⁵ furthermore, the product reacts with PPh₃ to produce the corresponding triphenylphosphine derivative, characterized by the corresponding proton and phosphorus NMR signals: CH, 7.82 ppm (*J*_{Pt–H} = 46 Hz); CH₂, 3.64 and 5.79 ppm (*J*_{H–H} = 17.6 Hz); PPh₃, –5.93 ppm (*J*_{Pt–P} = 1001.8 Hz). On standing, the acetone solution of the triphenylphosphine complex produced good X-ray-quality crystals that were structurally analyzed.⁶ Figure 1 shows the determined structure for the P(IV) cyclometalated complex. The complex has the well-established⁵ facial arrangement of the three Pt–C bonds observed in complexes of the same family, and the PPh₃ ligand is located in the less hindered available position of the octahedral coordination polyhedron. As a whole, the structure has the same characteristics as those determined for complexes with two methyl ligands instead of the two phenyl groups.^{4,5}

The kinetics of the substitution reaction of SMe₂ by PPh₃ were studied at variable temperature and sulfide and phosphine concentrations, to establish possible differences due to the size and trans influences on the non-cyclometalated organometallic ligands.⁴ The reaction mechanism and rate law found are indicative of the operation of the established limiting dissociative mechanism, which involves the existence, under steady-state conditions, of a pentacoordinated intermediate with no SMe₂ attached. Further reactions of this intermediate with the entering phosphine ligand produce the final complex.⁴ The kinetic and thermal activation param-

[†] Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals.

[‡] Departament de Química Inorgànica.

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(6) Anal. Calcd (found) for PtC₄₄H₃₇BrNP: C, 59.7 (59.7); H, 4.2 (4.3); N, 1.6 (1.3). X-ray data: *M*_r = 885.72, space group *P*1̄, triclinic, *a* = 10.1980(10) Å, *b* = 11.5200(10) Å, *c* = 17.6330(10) Å, α = 71.85°, β = 86.43°, γ = 67.70°, *V* = 1817.3(6) Å³, *T* = 293(2) K, *Z* = 2, μ(Mo Kα) = 5.035 mm^{−1}, 10 761 reflections measured, 6719 unique reflections (*R*_{int} = 0.0317) which were used in all calculations, final *R*_w(*F*²) = 0.1447 (all data).

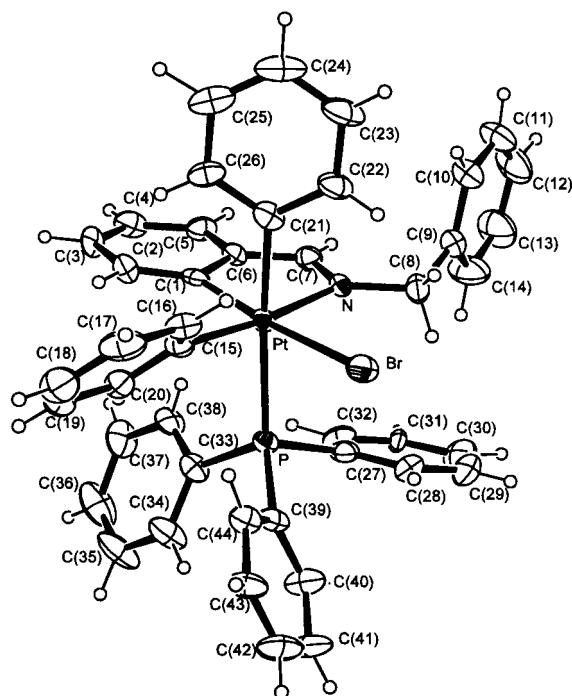


Figure 1. View of the X-ray structure of the cyclometalated platinum(IV) compound prepared, $[\text{Pt}^{\text{IV}}\text{Br}(\text{Ph})_2(\text{CC}_5\text{H}_4\text{CH/NBz})(\text{PPh}_3)]$ (ellipsoids indicate 20% probability). Relevant distances (Å): Pt–C(1), 2.067(8); Pt–C(15), 2.045(7); Pt–C(21), 2.095(8); Pt–N, 2.181(6); Pt–P, 2.4888(18); Pt–Br, 2.5547(10). Relevant angles (deg): C(1)–Pt–N, 80.5(3); C(1)–Pt–C(15), 93.4(3); C(1)–Pt–C(21), 86.1(3); C(1)–Pt–P, 97.69(174); C(1)–Pt–Br, 174.21(18).

eters found for the process, that is, the sulfide ligand dissociation ($k_1^{293} = 0.12 \text{ s}^{-1}$, $\Delta H^\ddagger = 60 \pm 3 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -58 \pm 11 \text{ J K}^{-1}\text{mol}^{-1}$), agree with the substitution mechanisms proposed and are of the same order as those found for systems with methyl ligands.⁴ The negative activation entropy can be related to the existence of a highly ordered dissociative transition state, produced by the steric relief occurring on partial decoordination of the leaving sulfide ligand. Nevertheless, the existence of any other sort of ordered interaction in the molecule following this partial decoordination would produce the same effect (see below).

When the substitution process was studied with platinum complex solutions that were not freshly prepared, the absorbance–time traces showed a consistent complex behavior. Furthermore, the solutions of the dimethyl sulfide complex showed, on standing, sets of new signals in the ^1H NMR spectrum that correspond to a new Pt(II) cyclometalated compound, as indicated by the much larger platinum coupling constant of the CH proton (now at 8.79 ppm), 122.2 Hz; after long periods all Pt(IV) complex signals disappear. These results would be expected if a reductive elimination has taken place on the quasi-labile Pt(IV) organometallic complex;⁷ in any case the simple process would require the elimination of a biphenyl molecule that could not be easily detected by the proton NMR spectrum.

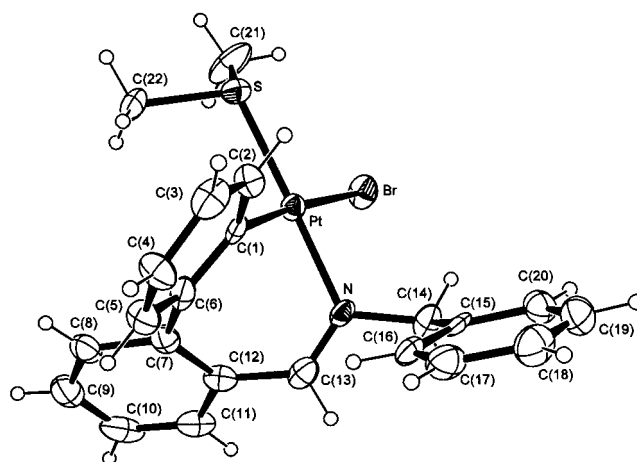


Figure 2. View of the X-ray structure of the seven-membered cyclometalated platinum(II) compound prepared, $[\text{Pt}^{\text{II}}\text{Br}(\text{CC}_5\text{H}_4\text{C}_6\text{H}_4\text{CH/NBz})(\text{SMe}_2)]$ (ellipsoids indicate 20% probability). Relevant distances (Å): Pt–C(1), 2.021(5); Pt–N, 2.044(4); Pt–S, 2.2528(14); Pt–Br, 2.5254(5). Relevant angles (deg): C(1)–Pt–N, 87.40(14); C(1)–Pt–S, 89.04(11); M–Pt–S, 176.39(10); C(1–6)–C(7–12), 577(3).

On standing, the solutions of the aforementioned Pt(IV) dimethyl sulfide complexes produced, to our knowledge, the first structurally characterized seven-membered cyclometalated platinumacycle, $[\text{Pt}^{\text{II}}\text{Br}(\text{CC}_5\text{H}_4\text{C}_6\text{H}_4\text{CH/NBz})(\text{SMe}_2)]$. From these solutions X-ray-quality crystals could be collected and analyzed.⁸ The structure (Figure 2) shows a highly hindered Pt(II) center, due to the extreme steric demands of the aryl groups of the cyclometalated ligand. In this respect all attempts to carry out an oxidative addition on the complex with MeI failed; only the starting material was recovered. Reaction with excess triphenylphosphine of this compound leads to the substitution of the SMe_2 on the Pt(II) complex (^{31}P NMR signal at 17.8 ppm, $J_{\text{Pt-P}} = 1889 \text{ Hz}$); no further opening of the cyclometalated ring is observed, as opposed to other cases.⁹

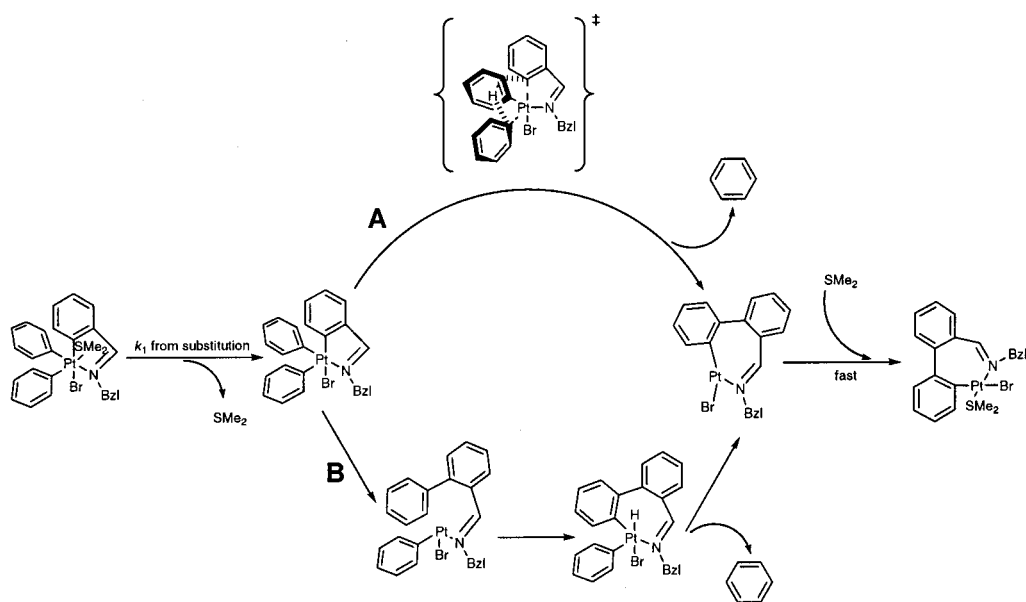
The reductive process from the Pt(IV) compound to produce the new seven-membered cyclometalated Pt(II) complex is not straightforward. It is clear from the stoichiometry that a reductive elimination of benzene has taken place, but a simultaneous formal phenyl insertion into the Pt–C(cyclometalated) bond has also had to occur. Preliminary kinetic observations indicate that the overall reaction is quite clean, with no buildup of intermediates, even at low temperature. The reaction rate observed is inversely dependent both on the concentration of the platinum compound and on that of added SMe_2 , which suggests that the well-established easy dissociation of dimethyl sulfide on these types of complexes, as measured, plays a crucial role in the process.^{3,4,10} Both sequences of reactions indicated in Scheme 1 agree with the stoichiometric process observed.

(8) Anal. Calcd (found) for $\text{PtC}_{22}\text{H}_{22}\text{BrNS}$: C, 42.5 (43.5); H, 4.4 (3.7); N, 2.4 (2.3). X-ray data: $M_r = 607.47$, space group $P2_1/c$, monoclinic, $a = 10.2770(10) \text{ Å}$, $b = 11.0820(10) \text{ Å}$, $c = 18.6390(10) \text{ Å}$, $\beta = 96.45^\circ$, $V = 2109(4) \text{ Å}^3$; $T = 293(2) \text{ K}$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 8.651 \text{ mm}^{-1}$, 10 918 reflections measured, 4430 unique reflections ($R_{\text{int}} = 0.0432$) which were used in all calculations, final $R_w(F^2) = 0.0786$ (all data).

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Scheme 1



On one hand, sequence **A** involves a real C_6H_4 insertion reaction into the Pt–C bond with a concerted shift of a hydrogen to the reductive eliminating benzene. Although insertion reactions in Pt–C bonds are rare and limited,^{11,12} the transition state proposed involves a hydrogen shift that could facilitate the reaction via a concerted reductive elimination of benzene.¹³ This one-step mechanism should be facilitated by a certain degree of Pt–H interaction in the transition state, given the important degree of positive charge density of the Pt(IV) center.¹⁴ On the other hand, sequence **B** seems, in principle, much more feasible. After the reductive elimination reaction of an imine-attached diphenyl group, further oxidative addition of a C–H bond to the Pt(II) center, followed by a fast reductive elimination of benzene, produced the final compound.¹⁵ Nevertheless, such a C–H activation process does not seem very likely, given the lack of planarity/aromaticity of the final metallacycle formed. Only oxidative addition of C–H bonds having the above-mentioned planarity/aromaticity characteristics have been observed on these complexes, even when the C–H bond has been further activated by the presence of a fluorine in an ortho position.⁵ Furthermore, the absence of any intermediate Pt(II) species in solution that could be detected by low-

temperature NMR measurements indicates that the C–H bond activation should be relatively fast.

From the results, and the images in Figure 1 and Scheme 1, it is clear that, if SMe_2 does not previously dissociate, the structure is too rigid for such a sterically demanding transition state. The fact that the corresponding phosphine derivative $[\text{Pt}^{\text{IV}}\text{Br}(\text{Ph})_2(\text{CC}_5\text{H}_3\text{CH}/\text{NBzl})(\text{PPh}_3)]$ does not evolve in the same direction is a clear indication that the feasibility of the dissociation of the sixth ligand is fundamental for the process.³ Further studies are under way in order to ascertain the mechanism of the reaction observed; some degree of interaction with the leaving hydrogen atom on the complex, in a way that could be considered as having a certain degree of hydride character, has been observed.¹⁶ The existence of this sort of interaction can also account for the negative values found for the activation entropy for the sulfide by the phosphine substitution reactions studied (see above).

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Supporting Information Available: Listings of observed rate constants for the substitution process studied, the mechanism and rate law operating for the reaction, and the crystal structure data for the compounds $[\text{Pt}^{\text{IV}}\text{Br}(\text{Ph})_2(\text{CC}_5\text{H}_3\text{CH}/\text{NBzl})(\text{PPh}_3)]$ and $[\text{Pt}^{\text{II}}\text{Br}(\text{CC}_5\text{H}_4\text{C}_6\text{H}_4\text{CH}/\text{NBzl})(\text{SMe}_2)]$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(10) Values of the observed rate constants are 2.7×10^{-4} , 5.9×10^{-4} , and $9.8 \times 10^{-4} \text{ s}^{-1}$ for $[\text{Pt}^{\text{IV}}] = 2.5 \times 10^{-4} \text{ M}$ and $[\text{SMe}_2] = 2.0 \times 10^{-3}$, 1.0×10^{-3} , and $5.0 \times 10^{-4} \text{ M}$, respectively; and 2.0×10^{-3} , 1.5×10^{-3} , and $1.2 \times 10^{-3} \text{ s}^{-1}$ for $[\text{Pt}^{\text{IV}}] = 2.5 \times 10^{-4}$, 7.5×10^{-4} , and $12.5 \times 10^{-4} \text{ M}$, respectively, with no SMe_2 added.

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(16) The preparation of $[\text{Pt}^{\text{II}}\text{Ph}(\text{CC}_5\text{H}_4\text{CH}/\text{NBzl})(\text{SMe}_2)]$ was carried out in order to establish the possible insertion of the phenyl ring into the $\text{Pt}^{\text{II}}\text{--C}(\text{cyclometalated})$ bond on addition of LiBr to the solution medium. Neither in chloroform nor in acetone solution was evolution of the compound to the possible $[\text{Pt}^{\text{II}}\text{Ph}(\text{CC}_5\text{H}_4\text{C}_6\text{H}_4\text{CH}/\text{NBzl})(\text{SMe}_2)]$ observed. Nevertheless, the proton NMR spectrum of the complex $[\text{Pt}^{\text{II}}\text{Ph}(\text{CC}_5\text{H}_4\text{CH}/\text{NBzl})(\text{SMe}_2)]$ showed a signal at 9.41 ppm (dd, $J_{\text{H--H}} = 1.5$, 7.4 Hz) indicative of a certain through-space interaction between the two platinum-bound aromatic rings.