Carbon-carbon bond formation in cationic aryl-olefin-platinum(II) complexes

Vincenzo De Felice, Augusto De Renzi, Diego Tesauro, and Aldo Vitagliano

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dissolved in nitromethane (5 mL). After 10 days, the solvent was removed under vacuum and the complex $[PtCl(4\text{-}Mepy)(bpy)](BF_4)$ crystallized from CH_2Cl_2/Et_2O (yield: 70%). Selected ^1H NMR data (in CD_3NO_2, CH_3NO_2 as internal standard: 9.48 (d, 1 H), 8.71 (d, H-2,H-6 of Mepy), 7.59 (d, H-3,H-5 of Mepy), 2.60 (s, *M*epy). Anal. Calcd for $C_{16}H_{15}BClF_4N_3Pt$: C, 33.91; H, 2.67; N, 7.42. Found: C, 33.61; H, 2.71; N, 7.21.

By a similar procedure, $[PtCl(4\text{-}Mepy)(phen)](BF_4)$ was obtained starting from **2c**. Selected ^1H NMR data (in CD_3NO_2, CH_3NO_2 as internal standard): 9.62 (d, 1 H), 8.74 (d, H-2,H-6 of Mepy), 7.64 (d, H-3,H-5 of Mepy), 2.64 (s, *M*epy).

Synthesis of $[PtCl(4\text{-}Mepy)(dmphen)](BF_4)$. To a stirred solution of the complex $[PtCl_2(dmphen)]$ (0.030 g, 0.063 mmol) in chloroform (10 mL) was added 0.012 g (0.15 mmol) of 4-Mepy. After 2 h was added at 0 °C the stoichiometric amount of $AgBF_4$ (0.012 g) dissolved in acetone (1.2 mL). After 20 min the suspension was filtered through a thin layer of Celite and the solvent removed under vacuum. The resulting solid was extracted with dichloromethane, and the product precipitated as a white solid by adding diethyl ether (yield: 65%). ^1H NMR (CD_3NO_2, CH_3NO_2 as internal standard): 8.73 (d, 1 H), 8.67 (d, 1 H), 8.30 (d, H-2,H-6 of Mepy), 8.12 (s, 2 H), 7.85 (d, 1 H), 7.73 (d, 1 H), 7.51 (d, H-3,H-5 of Mepy), 3.30 (s, NCMe), 2.58 (s, NCMe), 2.12 (s, 4-*M*epy). Anal. Calcd for $C_{20}H_{19}BClF_4N_3Pt$: C, 38.82; H, 3.10; N, 6.79. Found: C, 38.83; H, 3.18; N, 6.73.

X-ray Structure Determination of $[PtCl(C_2H_4)(C_{14}H_{12}N_2)(NC_5H_5)][CF_3SO_3]$. Crystals suitable for X-ray analysis were obtained with the following procedure. A solution of $AgCF_3SO_3$ (0.068 g, 0.27 mmol) in methyl cyanide (5 mL) was added dropwise under nitrogen to the complex *cis*-$[PtCl_2(py)(ethylene)]$ (0.100 g, 0.27 mmol) dissolved in 20 mL of a 1:1 mixture of CH_2Cl_2/MeCN. After 15 min of stirring at 0 °C the suspension was filtered through a thin layer of Celite and the N-N ligand added to the clear filtrate. The volume of the solution was concentrated to 5 mL, and 1 mL of diethyl ether was added dropwise, producing white crystals, which were isolated after 24 h.

Single-crystal X-ray diffraction data were measured at room temperature on an Enraf-Nonius CAD4 diffractometer. The measured intensities were corrected for crystal decay and reduced to F_0 values. Crystal data and experimental details are summarized in Table V. The structure was solved by direct and Fourier methods[11] and refined by full matrix least-squares calculations. An absorption correction was applied after convergence of the isotropic refinement according to the empirical method by Walker and Stewart.[12]

Anisotropic thermal parameters were used for all non-hydrogen atoms. Aromatic hydrogen atoms were positioned at calculated positions and refined with fixed geometry with respect to their carrier atoms (C–H 1.08 Å). The positions of the hydrogen atoms of the ethylene molecule were found experimentally and refined under the constraints of equal C–H bonds and H···H contacts [C–H$_{av}$ 0.99 (5) Å]. A final difference-Fourier map gave peaks of residual electron density not exceeding 0.8 e Å^{-3}. Fractional positional parameters for the refined atoms are listed in Table VI.

Acknowledgment. We thank the Consiglio Nazionale delle Ricerche and MURST for financial support and the Centro Interdipartimentale di Metodologie Chimico-Fisiche, Università di Napoli "Federico II", for the use of the Varian XL-200 and Bruker AC-270 NMR spectrometers.

Supplementary Material Available: Lists of hydrogen positions and anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

OM920211F

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(11) (a) Sheldrick, G. M. SHELX-86, Program for Crystal Structure Determination. University of Gottingen, FRG, 1986. (b) Sheldrick, G. M. SHELX-76, Crystal Analysis Package. University of Cambridge, U.K., 1976.

(12) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

Carbon–Carbon Bond Formation in Cationic Aryl–Olefin–Platinum(II) Complexes

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Received December 6, 1991

Cationic five-coordinate $[Pt(3\text{-}R^1\text{-}4\text{-}R^2\text{-}C_6H_3)(MeCN)(6\text{-}Me\text{-}py\text{-}2\text{-}CH{=}NPh)(C_2H_4)]^+$ complexes (R^1, R^2 = H, Me, OMe) undergo an unexpected rearrangement at 0 °C in chloroform solution, affording, after treatment with aqueous LiCl, the neutral four-coordinate species $[Pt(2\text{-}Et\text{-}4\text{-}R^1\text{-}5\text{-}R^2\text{-}C_6H_2)Cl(6\text{-}Me\text{-}py\text{-}2\text{-}CH{=}NPh)]$. Pt–C$_{aryl}$ bond breaking and making is involved in the whole process, resulting in a 1,2-shift of the platinum atom to an adjacent position of the benzene ring. The same compound is obtained, together with products deriving from a typical insertion, when an equimolar amount of ethylene is added to a chloroform solution of $[Pt(3\text{-}R^1\text{-}4\text{-}R^2\text{-}C_6H_3)(MeCN)(6\text{-}Me\text{-}py\text{-}2\text{-}CH{=}NPh)]^+$ at 0 °C. When higher (>3) ethylene/Pt ratios are used, only the five-coordinate $[Pt(3\text{-}R^1\text{-}4\text{-}R^2\text{-}C_6H_3CH_2CH_2)Cl(6\text{-}Me\text{-}py\text{-}2\text{-}CH{=}NPh)(C_2H_4)]$ complex is isolated. As the experimental data rule out the possibility of a (2-arylethyl)platinum to (2-ethylaryl)platinum rearrangement, different reaction paths are suggested for the two processes. When the two reactions are combined in a "one-pot" sequence, a regiocontrolled double alkylation of the aryl system can be obtained. The behavior of substrates containing bidentate nitrogen ligands having different five-coordination stabilizing effects is examined, and data concerning the reactions of propene and styrene are reported.

Introduction

One of the most fascinating topics in organometallic chemistry, for both theoretical and experimental reasons, concerns the insertion of a π-coordinated alkene into a cis metal-bound hydrocarbyl group.[1] Scarce examples of such reactions are found in platinum(II) chemistry, however,[2] and several stable cis hydrocarbyl olefin complexes are

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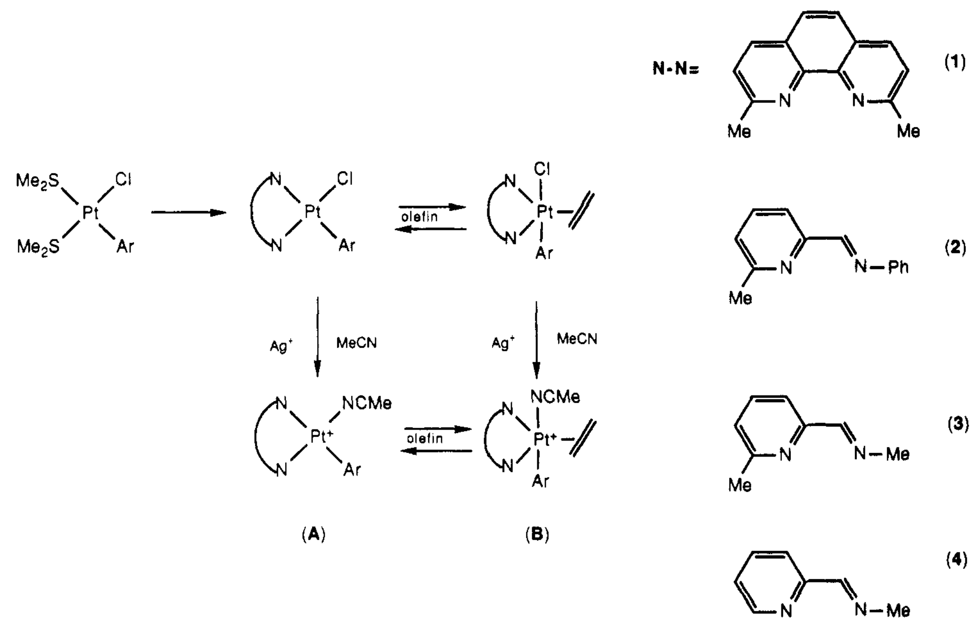
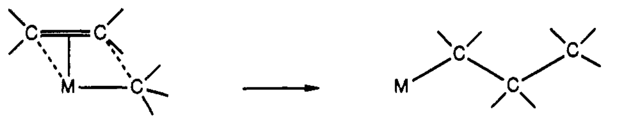
(1) Collmann, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 6.3.

Scheme I

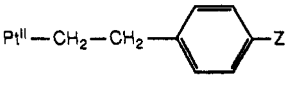


known.[3] Indeed, the proposed reaction mechanism requires a coplanar arrangement of the M–C bond and of the π-coordinated alkene in order to attain the four-center transition state:[4]

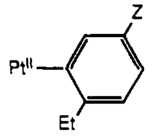


Since in square-planar complexes the direction of the Pt(II)-coordinated double bond is usually perpendicular to the coordination plane, the contribution of the rotational barrier around the Pt–alkene bond may increase the activation energy enough to prevent the insertion process. Such a hypothesis has been recently confirmed by achieving an easy insertion reaction on a square-planar Pt(II) complex containing an "in-plane" coordinated double bond.[2b]

During our studies on five-coordination in Pt(II) chemistry, we isolated several stable complexes of the general formula [PtXCl(N-N)(olefin)] (X = alkyl or aryl group).[5] The coordination polyhedron is a trigonal bipyramid in which the X group occupies an axial position while the olefin lies in the equatorial plane, and these compounds were shown to be inert toward the insertion. Although the related cationic species[6] $[PtX(L)(N\text{-}N)(olefin)]^+$ behaved similarly, a preliminary investigation disclosed a remarkable exception in the case in which X = para-substituted aryl and L = MeCN.[7] Indeed, besides a typical ethylene insertion, leading to a (σ-2-arylethyl)platinum(II) moiety (I), the unusual formation of a (σ-2-ethylaryl)platinum(II) fragment (II) was observed.



I



II

To the best of our knowledge, no analog of the latter reaction has been reported in the literature. We report in this paper our results on the above processes.

Results

Synthesis of the Cationic Complexes. The synthesis of cationic four-coordinate $[PtAr(MeCN)(N\text{-}N)]^+$ (type A) and/or five-coordinate $[PtAr(MeCN)(N\text{-}N)(olefin)]^+$ (type B) complexes (Ar = substituted aryl group, N-N = bidentate nitrogen ligand, olefin = ethylene (a), propene (b), styrene (c)) was performed according to Scheme I as reported in the case of the analogous ethylene–methyl derivatives.[6]

It was previously shown[5] that the stability of the five-coordinate adducts toward the olefin release is mainly dependent on the steric features of the bidentate nitrogen ligand and the electronic properties of the alkene. In addition, comparative measurements[6] involving some neutral and cationic complexes showed a lower pk_{diss} value (at least by 1 order of magnitude) for the latter compounds when the neutral apical ligand is methyl cyanide. Therefore, only by using N-N ligands having high a five-coordination stabilizing effect (e.g. 2,9-dimethyl-1,10-phenanthroline (1)) does the above-reported procedure afford stable (both in the solid state and in solution) cationic adducts with all olefins. When a N-N ligand of minor steric demands (6-Me-py-2-CH=NPh, (2)) was used, only the ethylene complex could be isolated in the solid state and fully characterized in solution (pk_{diss} = ca. 2 at room temperature). When the olefin was propene or styrene, the dissociation equilibrium was largely favorable toward the four-coordinate complexes at room temperature, and cooling to −20 °C was required in order to detect significant amounts of five-coordinate species by ^1H NMR spectroscopy.[8] When N-N ligands having a poor or non-

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[2] (a) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 6, Chapter 39.5, p 563. (b) Rakowsky, M. H.; Woolcock, J. C.; Rettig, M. F.; Wing, R. M. *Organometallics* 1988, 7, 2149 and references therein.

[3] *Dictionary of Organometallic Compounds*; Chapmann and Hall: London, England, 1990.

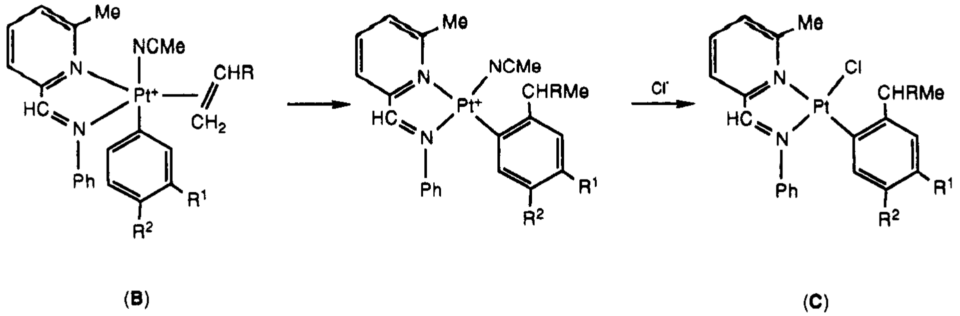
[4] Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

[5] (a) Albano, V. G.; Braga, D.; De Felice, V.; Panunzi, A.; Vitagliano, A. *Organometallics* **1987**, *6*, 517. (b) Cucciolito, M. E.; De Felice, V.; Panunzi, A.; Vitagliano, A. *Organometallics* **1989**, *8*, 1180.

[6] Sanchez, A.; Castellari, C.; Panunzi, A.; Vitagliano, A.; De Felice, V. *J. Organomet. Chem.* **1990**, *388*, 243.

[7] De Felice, V.; De Renzi, A.; Panunzi, A.; Vitagliano, A. *Abstracts of Papers*; XIII International Conference on Organometallic Chemistry, Torino, Italy, Sept 1988; Abstract 309.

Scheme II



R = H, Me, Ph
$R^1 = R^2 = H$
$R^1 = H$ $R^2 = OMe$
$R^1 = OMe$ $R^2 = H$
$R^1 = H$ $R^2 = Me$
$R^1 = Me$ $R^2 = H$

existent five-coordination stabilizing effect were used (6-Me-py-2-CH=NMe (3) or py-2-CH=NMe (4)), no appreciable amount of adduct could be detected by ^{1}H NMR spectroscopy even when the olefin was ethylene.

Reactivity of the Complexes. When the cationic $[PtAr(MeCN)(6\text{-Me-py-2-CH=NPh})(C_2H_4)]^+$ (type B) complexes (Ar = C_6H_5, 3- and 4-MeC_6H_4, 3- and 4-$MeOC_6H_4$) were allowed to stand in chloroform solution at 0 °C, thus reducing the ethylene release, a slow intramolecular process took place and after 24 h four-coordinate (2-ethylaryl)–Pt(II) compounds were isolated in good yields by treating the reaction mixture with LiCl (Scheme II).

The para-substituted aryl derivatives were more reactive than the meta species, and the presence of a methyl was more effective than that of a methoxy group. In fact, the *p*-tolyl derivative quantitatively transformed even at −20 °C, while a 50% conversion was obtained with the *m*-anisyl species after 2 days at room temperature. The reactivity of the complex containing the unsubstituted phenyl lies between those of the two *p*-substituted aryls.

The type C products were characterized by usual procedures, i.e. elemental analysis and ^{1}H and ^{13}C NMR spectroscopy. The geometric isomer containing the Pt σ-bound aryl group cis to the iminic nitrogen, as indicated by the high value of the coupling constant of the CH=N proton with ^{195}Pt ($^3J_{\text{Pt-H}}$ = 90–100 Hz),[5a] was the only product in any case. The ^{195}Pt–C(1)$_{\text{aryl}}$ coupling constant could not be evaluated, as the satellite bands were not detected.[9] Protolysis of the Pt–C σ bond with gaseous HCl allowed us to isolate the ethyl-substituted arenes.

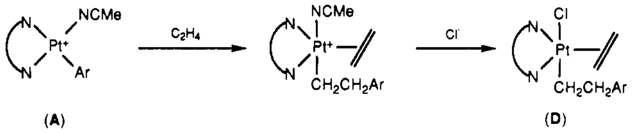
The conditions leading to good yields for the above reaction are rather precise, and the following observations are crucial for inferring a reasonable mechanism.

(i) The reaction is strongly inhibited by an excess of free MeCN, as well as by the use of a more strongly bound neutral ligand such as aniline or by the presence of other coordinating species such as diethyl ether or THF.

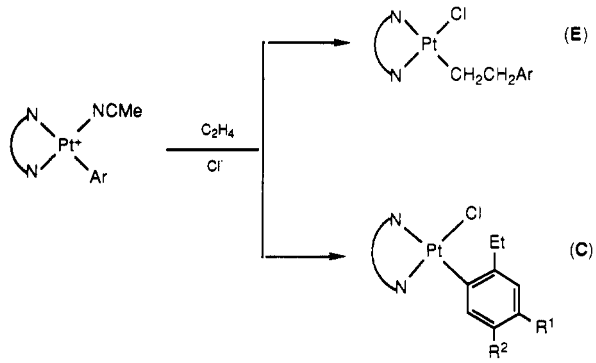
(ii) The reaction is strongly inhibited by using a N-N ligand (2,9-dimethyl-1,10-phenanthroline), which greatly stabilizes the five-coordinate species.

(iii) If an excess of free ethylene is introduced, the reaction is overwhelmed by a different process, leading to the typical insertion product (type I hydrocarbyl derivative).

Scheme III



Scheme IV



(iv) Increasing the temperature affords mixtures of type I and type II hydrocarbyl derivatives.

In order to get more information on the above reaction, we attempted to react the cationic four-coordinate $[PtAr(MeCN)(N\text{-}N)]^+$ (N-N = 2, type A) compounds with ethylene (saturated chloroform solution at 0 °C and atmospheric pressure), which is an alternative route to the synthesis of cationic five-coordinate species in the case of methyl derivatives. In fact, in the presence of free methyl cyanide, the five-coordinate complexes $[PtArCl(6\text{-Me-py-2-CH=NPh})(C_2H_4)]$ were obtained after treatment of the reaction mixture with LiCl. In the absence of excess MeCN, a typical insertion reaction ensued and the same treatment allowed the isolation of $[Pt(ArCH_2CH_2)Cl(6\text{-Me-py-2-CH=NPh})(C_2H_4)]$ (type D) complexes in good yields (Scheme III).

Small amounts of styrenes and Pt–ethyl derivatives were also detected by ^{1}H NMR spectroscopy in the crude reaction mixture, reasonably as a consequence of a β-elimination on the initially formed (2-arylethyl)platinum species and subsequent insertion of ethylene into the Pt–H bond.

The type D five-coordinate complex reported in Scheme III was the main reaction product at high ethylene concentration. Otherwise, if the starting ethylene/Pt ratio was reduced, the four-coordinate type C complex was also formed. By using the stoichiometric amount of ethylene, a mixture of four compounds was obtained (as an example,

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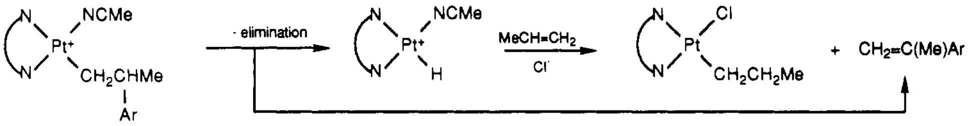
[8] In the last two cases different stereoisomers were formed owing to the hindered rotation of the prochiral alkene and to the presence of a stereogenic metal center.

[9] Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* 1978, 357.

Scheme V



35% C, 22% D, 25% unreacted A as the chloride form, and 18% four-coordinate species E deriving from D by ethylene release, in the case of R^1 = H and R^2 = OMe).

When a N-N ligand having a poor five-coordination-stabilizing effect (6-Me-py-2-CH=NMe (**3**)) was used, similar C—C bond formation processes were observed (Scheme IV). In this case, however, the four-coordinate type E complex was always the main reaction product. As a limiting case, with the N-N ligand py-2-CH=NMe (**4**), only the square-planar $[Pt(ArCH_2CH_2)Cl(py\text{-}2\text{-}CH{=}NMe)]$ (type E) complex was isolated, and no type C product was obtained. In addition, in this latter case the presence of free MeCN had only a moderate slowing effect on the reaction rate.

A possible explanation of this dependence on the ethylene concentration could take into account the rearrangement to Pt-Ar-2-CH_2CH_3 of an initially formed Pt-CH_2CH_2Ar fragment, in the absence of ligands ensuring a coordinative saturation. We have not found reports of similar processes in the Pt(II) chemistry. However, Lehmkuhl et al.[10] described a migratory insertion of ethylene on thermally unstable 18e $[NiAr(X)(C_2H_4)]$ complexes (X = η^5-cyclopentadienyl or η^5-pentamethylcyclopentadienyl). This afforded, at −30 °C in the presence of excess ethylene, the corresponding $[Ni(ArCH_2CH_2)(X)(C_2H_4)]$ compounds. In the absence of free ethylene a ((1,2,7-η^3)-methylbenzyl)Ni species was detected in solution and a mechanism involving a reversible β-elimination was postulated for its formation.[10]

In our case, we have no evidence for the presence of similar species in solution. In addition, the isolated $[Pt(ArCH_2CH_2)Cl(6\text{-}Me\text{-}py\text{-}2\text{-}CH{=}NPh)(C_2H_4)]$ compounds (vide supra) were transformed into the corresponding four-coordinate species by thermal ethylene release and, after chloride removal by $AgBF_4$ treatment, allowed to stand in chloroform solution at 0 °C. No rearrangement was observed at all. Moreover, the reaction performed on the $[PtC_6D_5(MeCN)(6\text{-}Me\text{-}py\text{-}2\text{-}CH{=}NPh)(C_2H_4)]^+$ complex gave a type C product containing the exclusively deuterated $-CH_2CH_2D$ group. A rearrangement via a π-allylic intermediate should afford a $-CHDCH_3$ group. By inspection of the ^1H and ^{13}C NMR spectra of the isolated complex and of the ethylbenzene obtained by gaseous HCl treatment, a nearly quantitative label retention was observed on the methyl group. This should imply a hydrogen transfer from the Pt σ-bound aryl to the coordinated ethylene without the intermediacy of other species, such as water in the solvent or protic impurities. We wish to note that label loss can be observed instead on the aromatic ring when the crude type C product is purified by column chromatography on Florisil or silica. In this case, variable amounts of the type C geometrical isomer (i.e. the one containing the σ-bound aryl trans to the iminic nitrogen) are also formed. As it is known that platinum compounds promote H-D isotopic exchange on aromatic rings in acidic media,[11] the properties of the stationary phase used in the chromatographic purification could explain both of the reported observations.

Attempts were made to use olefins different from ethylene as substrates in the described process. Four-coordinate cationic $[PtAr(MeCN)(N\text{-}N)]^+$ species (N-N = **2**) were treated at −20 °C with propene in chloroform solution and in the presence of MeCN. After excess propene and MeCN removal, the rearrangement at −20 °C of the five-coordinate adduct gave good yields of type C products (Scheme II). We note that both possible geometrical isomers were identified in the crude reaction mixture and separated by column chromatography. When propene was simply added, at −20 °C, to a solution of type A complexes, a mixture of type C compounds and a Pt-*n*-propyl derivative was obtained, while β-methylstyrenes were found in solution. The formation of this latter species agrees with a β-elimination on the intermediate deriving from a propene insertion into the Pt-aryl σ bond, followed by a successive propene insertion into the Pt-H bond (Scheme V).

Similar results were obtained by using styrene as substrate. No attempts were made to isolate and fully characterize the metal complexes formed. However, when we started from $[PtC_6D_5(MeCN)(6\text{-}Me\text{-}py\text{-}2\text{-}CH{=}NPh)]^+$ and styrene in a 1:1 molar ratio at −20 °C, HCl treatment of the crude reaction product allowed us to get $C_6D_4H\text{-}CH(Ph)\text{-}CH_2D$ as the main organic product, thus indicating a behavior identical with that reported above in the case of ethylene and propene.

We wish to note that, from a synthetic point of view, the protolysis of the Pt-C bond in both type I and II hydrocarbyl derivatives gives rise to the same organic product. However, if excess ethylene is added to an aged (24 h) chloroform solution of $[Pt(4\text{-}MeC_6H_4)(MeCN)(6\text{-}Me\text{-}py\text{-}2\text{-}CH{=}NPh)(C_2H_4)]^+$, HCl treatment of the reaction product allows us to isolate 1,2-diethyl-4-methylbenzene resulting from a subsequent insertion reaction on a previous type II hydrocarbyl derivative. Addition of propene to an aged chloroform solution of the corresponding *p*-methoxy complex affords 1-ethyl-2-isopropyl-4-methoxybenzene (Scheme VI). This "one-pot" procedure could be useful for synthetic applications.

Discussion

The formation of the C-C bond in the process transforming an olefin-aryl-Pt(II) five-coordinate complex into a (2-substituted-aryl)-Pt(II) four-coordinate derivative (Scheme II) seems to involve a breaking of the starting Pt-C_{aryl} σ bond and the slipping of the aromatic ring so that a novel Pt-C bond is made with an adjacent carbon. From our experimental data, the reaction does not occur when the N-N bidentate ligand strongly stabilizes the five-coordination (e.g. **1**) and/or the fifth coordinative position is occupied by an anionic ligand (e.g. a halogen). In addition, a low reaction rate is observed when the fifth neutral ligand is less labile than methyl cyanide (e.g. an amine) or when an excess of methyl cyanide is present. Thus, a preliminary dissociative step, affording a four-coordinate $[PtAr(olefin)(N\text{-}N)]^+$ intermediate (F, Scheme VII), is suggested. The occurrence of a typical migratory insertion on this intermediate could be hindered owing to the restricted rotation of the olefin, which would not allow

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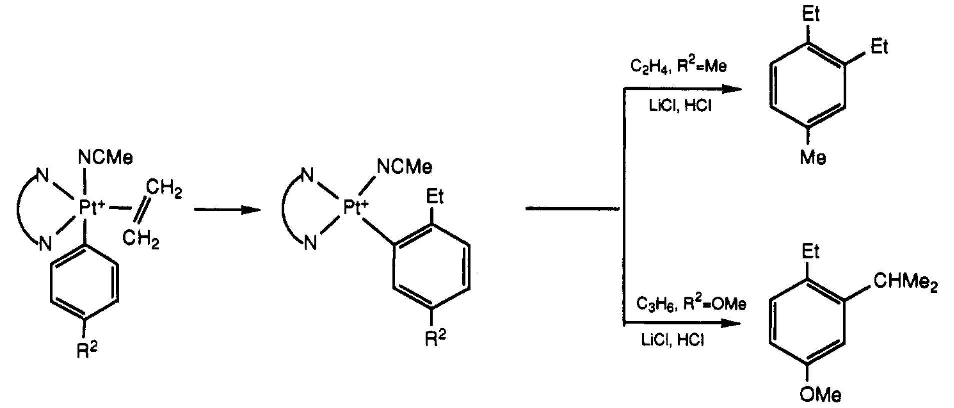
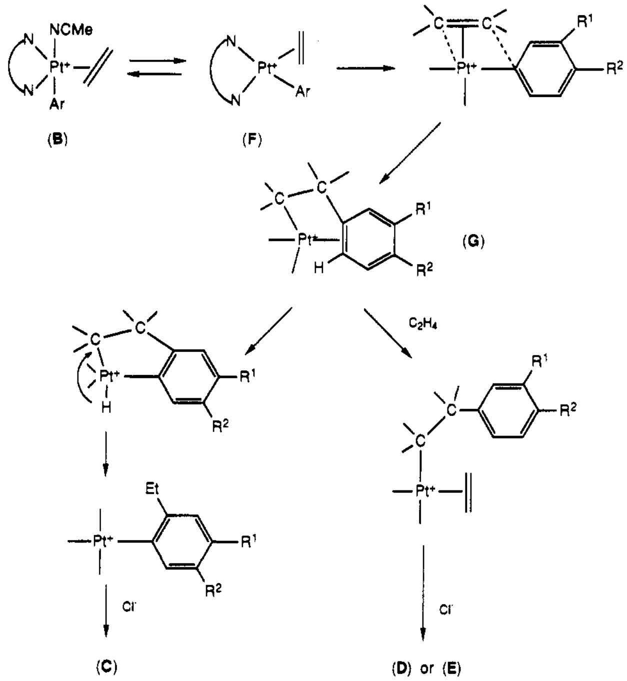
[10] Lehmkuhl, H.; Keil, T.; Benn, R.; Rufińska, A.; Kruger, C.; Poplawska, J.; Bellenbaum, M. *Chem. Ber.* **1988**, *121*, 1931.

[11] Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 6, Chapter 39.6, p 607.

Scheme VI

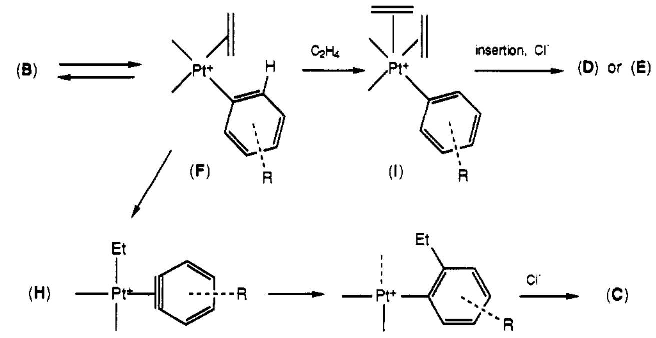


Scheme VII



an easy attainment of a coplanar arrangement of the double bond and the Pt–C bond. Moreover, as reported in the previous section, we have no evidence of the formation of type C products by a rearrangement of the ionic precursor of the insertion compound E or D. In contrast, these latter species are the reaction products in the presence of excess olefin. Nevertheless, a reaction path involving a typical preliminary insertion could be devised if the first step is supposed to afford a Pt–C–C–Ar fragment (G) with the aromatic ring η^2 bound to the metal.[12] From this hypothesis, in the presence of free ethylene, displacement would occur, pushing the aromatic ring away from the platinum and drawing the insertion process to completion (final products E or D according to the five-coordination stabilizing effect of the N-N ligand). In the absence of free ethylene, an ortho metalation could ensue via oxidative addition of the H–C$_{aryl}$ bond and reductive elimination of the H–C$_{alkyl}$ group, affording the final product C. However, as reported in the previous section, when [PtAr(MeCN)(N-N)]$^+$ (type A) species are reacted with ethylene at a low alkene/Pt ratio, type C products are obtained only when the N-N ligands have fairly good five-coordination stabilizing effects, such as **2** and, to a less extent, **3**. The formation of C was never observed with N-N ligand **4** or 2,2′-bipyridine. Although this does not rule out the above mechanism, to us it seems very hard to explain why the use of the latter ligands should prevent the formation of an intermediate such as G. In fact, G might as well be formed from species B and from species A, while the preliminary attainment of a tbp geometry, with an axial aryl group and an equatorial olefin, from which the other axial neutral ligand is released, seems to be a necessary condition for the obtainment of type C products.

Scheme VIII



A different pathway to C can be considered (Scheme VIII) involving a metal-mediated hydrogen transfer in the four-coordinate intermediate [PtAr(N-N)(olefin)]$^+$ (F) and affording a [Pt(alkyl)(benzyne)(N-N)]$^+$ species (H). Subsequent alkyl and Pt addition on the triple bond can account for the resulting type C complex. On these grounds, the inhibition caused by the presence of free olefin or other donors can be attributed to their coordination to F with consequent crowding of the coordination environment and hindering of the hydrogen transfer. It is also conceivable that the addition of this olefin ligand promotes an olefin–aryl arrangement (I) that favors the typical insertion.

However, we observe that the same benzyne species H should be formed independently from the location of the substituent on the starting σ-bound aryl (we note that a triple-bond formation involving the C1 and C2 carbon atoms in 3-substituted aryls can be excluded on the basis of the derivatives obtained). Accordingly, the same C complex should be obtained irrespective of the presence in the starting B of a 3- or 4-substituted aryl. In contrast, strict regiochemical control was found in the reaction products, pointing away from a true benzyne intermediate and suggesting a concerted mechanism passing through some transition state (K), during which a "memory" is kept of the original binding site of the platinum atom.

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[12] A similar palladium(II) complex was recently characterized: Li, Chen-Shun; Cheng, Chien-Hong; Liao, Fen-Ling; Wang, Sue-Lein. *J. Chem. Soc., Chem. Commun.* **1991**, 710.

Table I. ^{1}H NMR Data (Selected ^{13}C Data (δ) in Brackets) for [Pt(2-Et-4-R^1-5-R^2-C_6H_2)Cl(N–N)] Complexes[a]

N-N	R^1	R^2	CH_2CH_3	CH═N	MeC-(Het)	Ar–Pt	others
2[b]	H	OMe	3.0 (m, 1 H), 2.6 (m, 1 H), 1.13 (t, 3 H)	9.20 (95)	3.30	6.62 (s, 1 H, 46), 6.40 (d, 1 H), 6.17 (d, 1 H)	3.60 (OMe)
			[31.3 (CH_2, 48), 15.3 (CH_3)]	[167.5]	[26.2]	[155.2 (C5, 70), 125.6 (C3, 52), 120.8, 109.3 (C4 and C6)]	[55.2 (OMe)]
2[b]	OMe	H	3.0 (m, 1 H), 2.6 (m, 1 H), 1.14 (t, 3 H)	9.20 (95)	3.32	6.95 (d, 1 H[c]), 6.2 (m, 2 H)	3.65 (OMe)
2[b]	H	Me	3.0 (m, 1 H), 2.5 (m, 1 H), 1.13 (t, 3 H)	9.19 (97)	3.28	1H,[d] 6.35 (m, 2 H)	1.98 (Me)
			[31.5 (CH_2, 49), 15.2 (CH_3)]	[167.5]	[26.1]	[143.3 (C2), 137.0 (C6), 135.8 (C1), 132.4 (C5, 53), 125 (C3, 47)]	[21.2 (Me)]
2[b]	Me	H	3.0 (m, 1 H), 2.6 (m, 1 H), 1.13 (t, 3 H)	9.20 (97)	3.31	6.9 (d, 1 H[c]), 6.42 (d, 1 H), 6.34 (s, 1 H)	2.11 (Me)
			[31.5 (CH_2, 50), 15.1 (CH_3)]	[167.3]	[26.1]	[145.9 (C2), 135.6 (C6), 131.6 (C1 or C4), 126.4 (44), 124.9 (50) (C3 and C5)]	[20.3 (Me)]
2[b]	D[e]	D	3.0 (m, 1 H), 2.6 (m, 1 H), 1.13 (t, 2 H, CH_2D)	9.20 (95)	3.33		
			[32.0 (CH_2[c]), 14.8 (t, CH_2D, J_D = 19 Hz)]	[167.1]	[26.3]		
3[f]	H	OMe	3.05 (m, 2 H), 1.24 (t, 3 H)	9.00 (100)	3.23	6.95 (s, 1 H, 50), 6.80 (m, 1 H), 6.48 (d, 1 H)	3.75 (OMe), 3.41 (NMe)
3[f]	H	Me	3.05 (m, 2 H), 1.27 (t, 3 H)	9.00 (102)	3.21	7.20 (s, 1 H[c]), 7.05 (d, 1 H), 6.70 (d, 1 H)	2.22 (Me), 3.38 (NMe)

[a] Spectra recorded in $CDCl_3$ (reference δ 7.26, $CHCl_3$ [δ 77.0, $^{13}CDCl_3$]); the coupling constants with ^{195}Pt (Hz) are reported in parentheses. Abbreviations: s (singlet), d (doublet), t (triplet), m (multiplet); the symbols described the multiplicity of the signals referring to the Pt σ-bound aryl ignore the eventual coupling with the meta protons (0–3 Hz). [b] The chemical shifts of the heteroaromatic 6-Me-pyridine protons are centered at approximately δ 7.9 (t, 1 H), 7.7 (d, 1 H), and 7.65 (d, 1 H) [^{13}C δ 166 (C6, 17), 154 (C2, 53), 138.5 (C4), 125–130 (C3, C5)]. The *N*-phenyl protons gave signals in the range δ 7.1–7.0 (m, 3 H) and 6.9–6.8 (m, 2 H) [^{13}C δ 148 (N–C, 64)]. [c] Coupling constant with ^{195}Pt not evaluable. [d] Obscured by other signals. [e] Perdeuterated Pt–Ar complex. [f] The chemical shifts of the heteroaromatic 6-Me-pyridine protons are centered at approximately δ 7.9 (t, 1 H) and 7.6–7.5 (2 d, 2 H).

As depicted on the right side of Scheme IX, when the olefin is added (J) to a four-coordinate type A species, containing a N-N ligand unable to stabilize five-coordination, the typical insertion ensues, irrespective of the olefin/Pt ratio used. Otherwise, fast attainment of an equilibrium with a tbp arrangement of the ligands can open the route toward type C products. It must be point out that a dissociative step as one goes from I or J to L may be required.[4]

As noted in the previous section, under conditions favoring the typical insertion, significant amounts of Pt(II)–alkyl complexes and free styrenes are always found. The formation of these byproducts is very likely the consequence of β-elimination processes (Scheme V) undergone by the cationic species $[Pt(ArCHRCH_2)(MeCN)(N\text{-}N)]^+$, while the corresponding neutral chloride complexes are stable in solution.

Experimental Section

^{1}H NMR spectra were recorded at 270 or 200 MHz on a Bruker AC-270 or a Varian XL-200 spectrometer, respectively. $CDCl_3$, CD_3NO_2, or a mixture of both was used as solvent and $CHCl_3$ (δ 7.26) or CHD_2NO_2 (δ 4.33) as internal standard. Solvents and reagents were of AnalaR grade and, unless otherwise stated, were used without further purification. N-N ligands were prepared and stored under nitrogen. Unless otherwise stated, platinum complexes were prepared and stored in air. Elemental analyses are reported in the supplementary material (Table 1/S).

Materials. Ligand 1 is commercially available. Ligands 2–4 were prepared according to a previously described general method.[13] **[PtArCl(Me_2S)$_2$]** complexes were obtained by properly adapting a reported procedure.[5b] The same method was used to synthesize **[Pt(C_6D_5)Cl(Me_2S)$_2$]** from [(COD)$PtCl_2$] and C_6D_5-MgBr. The neutral complexes **[PtArCl(N-N)]** and **[PtArCl(N-N)(olefin)]** were obtained by adapting known procedures,[5] and their ^{1}H NMR parameters are reported in the supplementary material (Tables 2/S and 3/S, respectively).

Synthesis of [PtAr(MeCN)(N-N)]BF_4 Complexes (N-N = 2, 3, 4; Type A). To a solution of 0.5 mmol of the corresponding neutral complex in 30 mL of a CH_2Cl_2/CH_3CN mixture (5:1 v/v) is added dropwise an equimolar amount of $AgBF_4$ dissolved in 5 mL of CH_3CN at 0 °C. After 20 min of stirring the mixture is filtered through Celite and evaporated to dryness. Recrystallization is achieved by dissolving the glassy solid in chloroform and adding diethyl ether. Red crystals are obtained in 80–90% yield. The ^{1}H NMR data are reported in the supplementary material (Table 4/S).

Synthesis of [PtAc(MeCN)(N-N)(olefin)]BF_4 Complexes (N-N = 1, olefin = a–c; N-N = 2, olefin = a; Type B). To a solution of 0.5 mmol of the corresponding neutral complex in 10 mL of a CH_2Cl_2/CH_3CN mixture (1:1 v/v) is added dropwise an equimolar amount of $AgBF_4$ dissolved in 5 mL of CH_3CN at 0 °C. After 20 min of stirring the mixture is filtered through Celite and evaporated to dryness. In the case of ethylene complexes recrystallization is achieved by dissolving the glassy solid in chloroform and adding diethyl ether. White crystals were obtained in 80–90% yield. The ^{1}H NMR data are reported in the supplementary material (Table 5/S).

Rearrangement of [PtAr(MeCN)(6-Me-py-2-CH═NPh)(C_2H_4)]BF_4 to Type C Complexes. Samples of the title compounds (0.2 mmol) are dissolved in 5 mL of chloroform at 0 °C and allowed to stand at this temperature 24–48 h. A saturated aqueous solution of LiCl (5 mL) is then added and the mixture vigorously shaken. The organic phase is separated and dried on Na_2SO_4. Evaporation of the solvent gives red microcrystalline solids in 70–80% yield as crude products, the major impurity being represented by the four-coordinate complex **[PtArCl(6-Me-py-2-CH═NPh)]**. Satisfactory elemental analyses could be obtained after chromatographic purification on Florisil by eluting with methylene chloride. When Ar = *m*-anisyl, a 72-h reaction time was required to obtain a 50% yield. ^{1}H and ^{13}C NMR data are reported in Table I.

Reaction between [PtAr(MeCN)(N-N)]BF_4 Complexes and Ethylene. A 0.2-mmol sample of the appropriate complex is dissolved in 5 mL of a $CHCl_3/CH_3NO_2$ mixture (10:1 v/v) in a 25-mL Schlenk type flask. The solution is cooled to 0 °C and saturated with ethylene at atmospheric pressure (ethylene/Pt ratio > 10:1). By the same procedure described above, orange microcrystals of the corresponding five-coordinate **[Pt($ArCH_2CH_2$)Cl(N-N)(C_2H_4)]** (type D) complexes are obtained in 80–90% yield, in the case of N-N = 2. For the *m*-anisyl derivative a lower (ca. 40%) yield is observed.

When N-N = 3 and 4, the four-coordinate **[Pt($ArCH_2CH_2$)Cl(N-N)]** (type E) complexes are isolated in similar yield. The ^{1}H and ^{13}C NMR data are reported in Tables II and III, respectively.

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(13) van der Poel, H.; van Koten, G. *Inorg. Chem.* 1981, *20*, 2950.

Table II. ^{1}H NMR Data [Selected ^{13}C Data (δ) in Brackets] for [Pt(3-R^1-4-R^2-$C_6H_3CH_2CH_2$)Cl(6-Me-py-2-CH=NPh)(C_2H_4)] Complexes[a]

R^1	R^2	CH_2CH_2	olefin[b]	CH=N	MeC-(Het)	Ar–Pt	others
H	OMe	1.8 (m, 2 H), 0.9 (m, 2 H[b])	3.1 (m, 2 H), 2.2 (m, 2 H)	9.20 (33)	3.08	6.65 (m, 4 H)	3.68 (OMe)
		[36.4 (26), 10.4 (667)]	[31.6, 33.6 (388)]	[159.9]	[27.4]	[157.3 (C4), 135.5 (C1, 58), 128.4 (C2, C6), 113.4 (C3, C5)]	[55.1 (OMe)]
OMe	H	1.9 (m, 2 H), 0.9 (m, 2 H[b])	3.1 (m, 2 H), 2.4 (m, 2 H)	9.11 (35)	3.09	7.00 (t, 1 H), 6.6 (m, 1 H), 6.3 (m, 2 H)	3.66 (OMe)
H	Me	1.9 (m, 2 H), 0.9 (m, 2 H[b])	3.1 (m, 2 H), 2.2 (m, 2 H)	9.18 (33)	3.09	6.65 (d, 2 H), 6.89 (d, 2 H)	2.18 (Me)
		[36.9,[b] 10.3 (670)]	[31.7, 33.7 (388)]	[159.8]	[27.4]	[140.3 (C1, 60), 134.7 (C4), 128.7, 126.4 (C2, C6–C3, C5)]	[20.8 (Me)]
Me	H	1.9 (m, 2 H), 0.9 (m, 2 H[b])	3.1 (m, 2 H), 2.3 (m, 2 H)	9.15 (33)	3.10	6.96 (t, 1 H), 6.83 (d, 1 H), 6.55 (m, 2 H)	2.17 (Me)
		[37.5 (25), 10.0 (674)]	[31.7, 33.7 (330)]	[160.0]	[27.5]	[143.0 (C1, 55), 137.5 (C3)]	[21.0 (Me)]

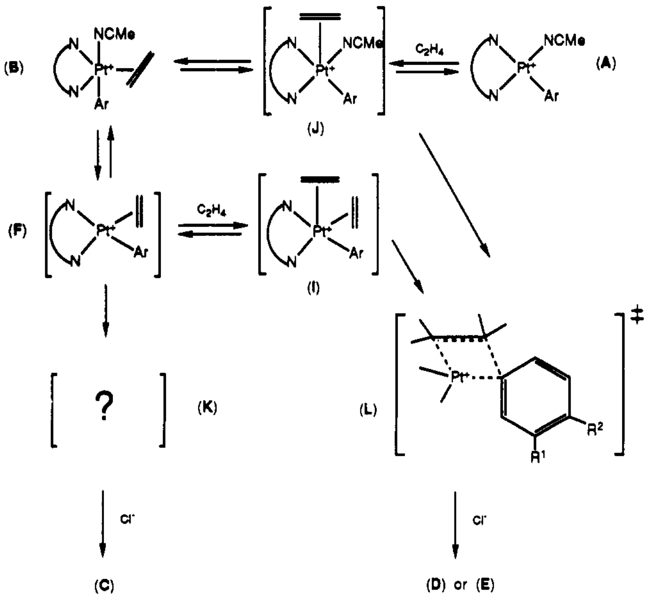
[a] Spectra recorded in $CDCl_3$ (reference δ 7.26, $CHCl_3$ [77.0 $^{13}CDCl_3$]); the coupling constants with ^{195}Pt (Hz) are reported in parentheses. Abbreviations: s (singlet), d (doublet), t (triplet), m (multiplet); the symbols describing the multiplicity of the signals referring to the Pt σ-bound aryl ignore the eventual coupling with the meta protons (0–3 Hz). The chemical shifts of the heteroaromatic 6–Me–pyridine protons are in the range δ 8.0–7.9 (d, 2 H) and 7.80–7.70 (t, 1 H) [^{13}C δ 161 (C6, 32), 152 (C2), 138.5 (C4), 125–130 (C3, C5)]. The *N*-phenyl protons give signals in the range δ 7.8–7.7 (m, 1 H) and 7.55–7.35 (m, 4 H) [^{13}C δ 147 (N–C, 31)]. [b] Coupling constant with ^{195}Pt not evaluable.

Table III. ^{1}H NMR Data [Selected ^{13}C Data (δ) in Brackets] for [Pt(3-R^1-4-R^2-$C_6H_3CH_2CH_2$)Cl(N-N)] Complexes[a]

N-N	R^1	R^2	CH_2CH_2	CH=N	MeC-(Het)	Ar–Pt	others
2	H	OMe	2.4 (m, 2 H), 1.95 (m, 2 H, 80)	9.31 (100)	3.22	6.6 (m, 4 H)	3.66 (OMe)
3	H	OMe	2.72 (t, 2 H), 2.45 (dd, 2 H, 86)	9.10 (102)	3.18	7.26 (d, 2 H), 6.80 (d, 2 H)	3.79 (OMe), 3.90 (NMe, 48)
3	OMe	H	2.77 (t, 2 H), 2.44 (dd, 2 H, 86)	9.10 (102)	3.16	7.16 (t, 1 H), 6.92 (d, 1 H), 6.91 (s, 1 H), 6.68 (d, 1 H)	3.78 (OMe), 3.90 (NMe, 48)
			[39.1 (26), 7.6 (745)]	[168.4]	[26.2]	[159.4 (C3), 146.6 (C1), 128.9 (C5), 120.7 (C6), 113.7, 110.4 (C2 and C4)]	[55.1 (OMe), 48.8 (NMe)]
3	H	Me	2.7 (m, 2 H), 2.45 (m, 2 H[c])	9.10 (100)	3.15	7.05 (d, 2 H), 6.80 (d, 2 H)	2.30 (Me), 3.90 (NMe, 48)
3	Me	H	2.75 (m, 2 H), 2.4 (m, 2 H[c])	9.10 (100)	3.14	7.10 (m, 3 H), 6.95 (m, 1 H)	2.22 (Me), 3.90 (NMe, 48)
4[b]	H	OMe	2.71 (t, 2 H), 2.44 (dd, 2 H, 84)	9.02 (105)	3.76	7.22 (d, 2 H), 6.67 (d, 2 H)	3.86 (OMe), 3.74 (NMe, 48)
			[38.3 (24), 7.0 (750)]	[167.6]		[157.0 (C4), 138.4 (C1, 68), 129.0 (C2, C6), 113.4 (C3, C5)]	[55.2 (OMe), 48.8 (NMe)]

[a] Spectra recorded in $CDCl_3$ (reference δ 7.26, $CHCl_3$); the coupling constants with ^{195}Pt (Hz) are reported in parentheses. Abbreviations: s (singlet), d (doublet), t (triplet), m (multiplet); the symbols describing the multiplicity of the signals referring to the Pt σ-bound aryl ignore the eventual coupling with the meta protons (0–3 Hz). The chemical shifts of the heteroaromatic 6-Me-pyridine protons are centered at approximately δ 8.85 (t, 1 H) and 7.6 (d, 2 H) [^{13}C δ 165 (C6), 154 (C2), 138 (C4), 130.5 and 124 (C3 and C5)]. [b] The chemical shifts of the heteroaromatic 6-H pyridine protons are δ 9.37 (d, 1 H), 8.00 (t, 1 H), 7.76 (d, 1 H), and 7.72 (d, 1 H) [^{13}C δ 154 (C2), 148 (C6), 138.5 (C4), 128 and 126 (C3 and C5)]. [c] coupling constant with ^{195}Pt not evaluable.

Scheme IX



At a lower ethylene/Pt ratio (ca. 3:1), mixtures of type C and D (N-N = **2**) or type C and E (N-N = **3**) complexes are obtained. A partial separation can be achieved by eluting the crude reaction product on Florisil with methylene chloride. Type C complexes migrate slower, thus allowing the isolation of two enriched fractions.

Attempted Rearrangement of Insertion Products to Type C Complexes. [Pt(4-$MeOC_6H_4CH_2CH_2$)Cl(C_2H_4)(6-Me-py-2-CH=NPh)] (0.1 g) was dissolved in 5 mL of chloroform in a Schlenk-type flask. The vessel was evacuated and stored overnight at 40 °C. By evaporation of the solvent, 90 mg of the red four-coordinate complex [Pt(4-$MeOC_6H_4CH_2CH_2$)Cl(6-Me-py-2-CH=NPh)] was obtained. The ionic complex [Pt(4-$MeOC_6H_4CH_2CH_2$)(MeCN)(6-Me-py-2-CH=NPh)]BF_4 was prepared by $AgBF_4$ treatment, as reported above, and allowed to stand 4 days at 0 °C in chloroform solution. Formation of a type C complex was not observed within this period.

Rearrangement of [Pt(C_6D_5)(MeCN)(6-Me-py-2-CH=NPh)(C_2H_4)]BF_4 to a Type C Complex. The title complex underwent rearrangement by using the above reported procedure. The red complex obtained, [Pt(2-CH_2DCH_2Ar)Cl(6-Me-py-2-CH=NPh)], was identified by ^{1}H and ^{13}C NMR spectroscopy (see Table I). When the crude reaction product was treated with gaseous HCl (vide infra), the organic moiety was isolated and identified as labeled ethylbenzene. ^{1}H NMR data ($CDCl_3$): δ 7.20 (s, ca. 1 H), 2.65 (t, 2 H, CH_2), 1.23 (complex t, 2 H, CH_2D).

Reactions between [Pt(4-$MeOC_6H_4$)(MeCN)(6-Me-py-2-CH=NPh)]BF_4 and Propene. (A) A 0.2-mmol sample of the title complex is dissolved in 5 mL of a $CHCl_3/CH_3NO_2$ mixture (10:1 v/v) in a 25-mL Schlenk type flask. MeCN (1 mL) is added, and the solution is cooled at −20 °C. Propene is admitted to a pressure of ca. 2 atm. After 2 h the mixture is evaporated to dryness in the cold and the oily residue washed with diethyl ether to completely remove free MeCN. The five-coordinate ionic adduct is dissolved in 5 mL of chloroform and kept 2 days at −20 °C. Working up the reaction mixture as described above gives a 70% yield of a product containing the two geometrical isomers of the type C **[Pt(2-Me_2CH-5-$MeOC_6H_3$)Cl(6-Me-py-2-CH═NPh)]** complex. Anal. Calcd for $C_{23}H_{25}ClN_2OPt$: C, 47.96; H, 4.37; N, 4.86. Found: C, 47.63; H, 4.25; N, 4.72. Separation can be achieved on Florisil using methylene chloride as eluant. Relevant ^1H NMR data (δ, $CDCl_3$): I fraction (25%, Pt-bound aryl trans to the iminic nitrogen), 9.33 (s, CH═N, $^3J_{PtH}$ = 26 Hz), 6.83 (d, 3-H Ar), 6.39 (d, 4-H Ar), 5.96 (s, 6-H Ar, $^3J_{PtH}$ = 66 Hz), 3.14 (s, MeO), 2.94 (s, Mepy), 1.25 (2 superimposed d, Me_2CH); II fraction (75%, Pt-bound aryl cis to the iminic nitrogen), 9.20 (s, CH═N, $^3J_{PtH}$ = 98 Hz), 7.08 (d, 3-H Ar), 6.91 (d, 4-H Ar), 6.68 (s, 6-H Ar, $^3J_{PtH}$ = 45 Hz), 3.65 (s, MeO), 3.33 (s, Mepy), 1.97 and 1.18 (2 d, Me_2CH).

(B) A 0.2-mmol sample of the title complex is dissolved in 5 mL of a $CHCl_3/CH_3NO_2$ mixture (10:1 v/v) in a 25-mL Schlenk type flask, and the solution is cooled at −20 °C. Propene is admitted to a pressure of ca. 2 atm. After 2 days at this temperature the reaction is quenched by adding aqueous LiCl and the organic phase is separated, concentrated to a small volume, and eluted on Florisil with diethyl ether followed by a 3:1 Et_2O/CH_2Cl_2 mixture.

NMR data (δ): I fraction (eluted by Et_2O), 4-MeO-C_6H_4-C(Me)═CH_2, 7.45 and 6.88 (2 d, 4 aromatic H), 5.30 and 5.00 (2 coupled s, ═CH_2), 3.84 (s, MeO), 2.12 (s, CMe). Anal. Calcd for II fraction, **[Pt($CH_2CH_2CH_3$)Cl(6-Me-py-2-CH═NPh)]** (ca. 40% yield after recrystallization from $CHCl_3$/petroleum ether), $C_{16}H_{19}ClN_2Pt$: C, 40.90; H, 4.08; N, 5.96. Found: C, 40.78; H, 4.15; N, 5.74. Relevant ^1H NMR data (δ, $CDCl_3$): 9.33 (s, CH═N, $^3J_{PtH}$ = 97 Hz), 3.22 (s, Mepy), 1.75 (m, CH_2Pt, $^2J_{PtH}$ = 90 Hz), 1.14 (m, $CH_2\mathit{CH_2}CH_3$), 0.56 (t, CH_3).

A third fraction containing the above described type C isomeric mixture is also isolated.

Reaction between [PtAr(MeCN)(6-Me-py-2-CH═NPh)]-BF_4 Complexes and Styrene (Ar = 4-$MeOC_6H_4$, C_6D_5). The title complexes are reacted with styrene in a 1:1 molar ratio by following the above-reported procedure. No attempts are made to identify the obtained metal complexes. The crude reaction products are treated with gaseous HCl as described below. The isolated organic moieties are identified by ^1H NMR spectroscopy (δ): 4-MeO-C_6H_4-CH(Me)Ph, 7.2 (m, 5 H, Ph), 7.12 and 6.82 (2 d, 4 aromatic H), 4.12 (q, CH), 3.77 (s, OMe), 1.62 δ (d, Me); C_6D_4H-CH(CH_2D)Ph, 7.2 (m, 6 H, aromatic H), 4.12 (t, CH), 1.67 δ (d, 2 H, CH_2D).

Double Alkylation of the Aromatic Ring. [Pt(4-Me-C_6H_4)(MeCN)(6-Me-py-2-CH═NPh)(C_2H_4)]BF_4 (0.1 mmol, 58 mg) is dissolved in 3 mL of chloroform at 0 °C and the mixture allowed to stand at this temperature for 48 h. Ethylene is then admitted at atmospheric pressure, and after another 48 h of standing, the mixture is worked up as above. The crude reaction product is treated with gaseous HCl, and the organic moiety is identified as 1,2-diethyl-4-methylbenzene (δ): 7.0 (m, 3 H, Ph), 2.65 (two superimposed q, 4 H, 2 CH_2), 2.25 (s, 3 H, Me), 1.25 δ (two superimposed t, 6 H, 2 Me).

When propene is admitted to an aged chloroform solution of [Pt(4-MeO-C_6H_4)(MeCN)(6-Me-py-2-CH═NPh)(C_2H_4)]BF_4, the HCl treatment of the crude reaction product gave 1-ethyl-2-isopropyl-4-methoxybenzene: 7.10 (d, arom 6-H), 6.82 (s, arom 3-H), 6.68 (d, arom 5-H), 3.81 (s, 3 H, OMe), 3.18 (m, 1 H, CH), 2.65 (q, 2 H, CH_2), 1.26 (d, 6 H, 2 Me), 1.23 δ (t, 3 H, Me).

Organic Moiety Identification. The Pt-bound organic moiety can be easily recovered and identified by dissolving a 0.02-g sample of the appropriate complex in 1 mL of $CDCl_3$. An equimolar amount of anhydrous gaseous HCl is bubbled into the solution that is filtered through a thin layer of Florisil to remove the nearly insoluble [$PtCl_2$(N-N)] complex. The identification is achieved by ^1H NMR spectroscopy and comparison with literature data.

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Registry No. A (N-N = **2**, R^1 = H, R^2 = OMe), 143632-86-4; A (N-N = **2**, R^1 = OMe, R^2 = H), 143632-88-6; A (N-N = **2**, R^1 = H, R^2 = Me), 143632-90-0; A (N-N = **2**, R^1 = Me, R^2 = H), 143632-92-2; A (N-N = **2**, R^1 = R^2 = H), 143632-94-4; A (N-N = **3**, R^1 = H, R^2 = OMe), 143632-96-6; A (N-N = **3**, R^1 = OMe, R^2 = H), 143632-98-8; A (N-N = **3**, R^1 = H, R^2 = Me), 143633-00-5; A (N-N = **3**, R^1 = Me, R^2 = H), 143840-90-8; A (N-N = **4**, R^1 = H, R^2 = OMe), 143633-02-7; B (N-N = **1**, olefin = a, R^1 = H, R^2 = OMe), 143633-04-9; B (N-N = **1**, olefin = b, R^1 = H, R^2 = OMe), 143633-06-1; B (N-N = **1**, olefin = c, R^1 = H, R^2 = OMe), 143633-08-3; B (N-N = **2**, olefin = a, R^1 = H, R^2 = OMe), 143633-10-7; B (N-N = **2**, olefin = a, R^1 = OMe, R^2 = H), 143633-12-9; B (N-N = **2**, olefin = a, R^1 = H, R^2 = Me), 143667-92-9; B (N-N = **2**, olefin = a, R^1 = Me, R^2 = H), 143667-94-1; B (N-N = **2**, olefin = a, R^1 = R^2 = H), 143633-14-1; C (N-N = **2**, R = R^1 = H, R^2 = OMe), 143633-15-2; C (N-N = **2**, R = R^2 = H, R^1 = OMe), 143633-16-3; C (N-N = **2**, R = R^1 = H, R^2 = Me), 143633-17-4; C (N-N = **2**, R = R^2 = H, R^1 = Me), 143633-18-5; C (N-N = **2**, R = H, R^1 = R^2 = D), 143633-19-6; C (N-N = **2**, R = Me, R^1 = H, R^2 = OMe; isomer 1), 143633-33-4; C (N-N = **2**, R = Me, R^1 = H, R^2 = OMe; isomer 2), 143728-56-7; C (N-N = **3**, R = R^1 = H, R^2 = OMe), 143667-95-2; C (N-N = **3**, R = R^1 = H, R^2 = Me), 143667-96-3; D (N-N = **2**, R^1 = H, R^2 = OMe), 143633-20-9; D (N-N = **2**, R^1 = OMe, R^2 = H), 143667-97-4; D (N-N = **2**, R^1 = H, R^2 = Me), 143633-21-0; D (N-N = **2**, R^1 = Me, R^2 = H), 143633-22-1; E (N-N = **2**, R^1 = H, R^2 = OMe), 143633-25-4; E (N-N = **3**, R^1 = H, R^2 = OMe), 143633-26-5; E (N-N = **3**, R^1 = OMe, R^2 = H), 143633-27-6; E (N-N = **3**, R^1 = H, R^2 = Me), 143633-28-7; E (N-N = **3**, R^1 = Me, R^2 = H), 143633-29-8; E (N-N = **4**, R^1 = H, R^2 = OMe), 143633-30-1; [Pt(C_6D_5)(MeCN)(6-Me-py-2-CH═NPh)(C_2H_4)]BF_4, 143633-32-3; [Pt($CH_2CH_2CH_3$)Cl(6-Me-py-2-CH═NPh)], 143633-34-5; [Pt(4-MeO-C_6H_4)Cl(**2**)], 143633-35-6; [Pt(3-MeO-C_6H_4)Cl(**2**)], 143633-36-7; [Pt(4-Me-C_6H_4)Cl(**2**)], 143633-37-8; [Pt(3-Me-C_6H_4)Cl(**2**)], 143633-38-9; [Pt(C_6H_5)Cl(**2**)], 143633-39-0; [Pt(4-MeO-C_6H_4)Cl(**3**)], 119744-08-0; [Pt(3-MeO-C_6H_4)Cl(**3**)], 143633-40-3; [Pt(4-Me-C_6H_4)Cl(**3**)], 143633-41-4; [Pt(3-Me-C_6H_4)Cl(**3**)], 143633-42-5; [Pt(4-MeO-C_6H_4)Cl(**4**)], 143633-43-6; [Pt(4-MeO-C_6H_4)Cl(**1**)(a)], 119743-84-9; [Pt(4-MeO-C_6H_4)Cl(**1**)(b)], 143633-44-7; [Pt(4-MeO-C_6H_4)Cl(**1**)(c)], 143633-45-8; [Pt(4-MeO-C_6H_4)Cl(**2**)(a)], 143633-46-9; [Pt(3-MeO-C_6H_4)Cl(**2**)(a)], 143633-47-0; [Pt(4-Me-C_6H_4)Cl(**2**)(a)], 143633-48-1; [Pt(3-MeC_6H_4)Cl(**2**)(a)], 143633-49-2; [Pt(C_6H_5)Cl(**2**)(a)], 143633-50-5; [Pt(4-MeO-$C_6H_4CH_2CH_2$)-(MeCN)(6-Me-py-2-CH═NPh)]BF_4, 143667-99-6; C_6D_4H-CH-(CH_2D)Ph, 143633-24-3; 4-MeO-C_6H_4-CH(Me)Ph, 2605-18-7; ethylene, 74-85-1; propylene, 115-07-1; styrene, 100-42-5; 1,2-diethyl-4-methylbenzene, 13732-80-4; 1-ethyl-2-isopropyl-4-methoxybenzene, 143633-23-2.

Supplementary Material Available: Tables of elemental analyses and ^1H NMR parameters (5 pages). Ordering information is given on any current masthead page.

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