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Dynamic NMR Study of Ethene Exchange in Cationic CNN-Type Platinum(II) Complexes[#]

M. Rosaria Plutino,*,[†] Lucia Fenech,[‡] Sergio Stoccoro,[§] Silvia Rizzato,[⊥] Carlo Castellano,[⊥] and Alberto Albinati[⊥]

[†]*Istituto per lo Studio dei Materiali Nanostrutturati, ISMN−CNR, Unità di Messina-Sezione di Palermo, Messina, Italy,* [‡]*Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Salita Sperone 31, 98166 Vill. S. Agata, Messina, Italy,* [§]*Dipartimento di Chimica, Università di Sassari, via Vienna 2, 07100, Sassari, Italy, and* [⊥]*Dipartimento di Chimica Strutturale e Facoltà di Farmacia, via Venezian 21, Università di Milano, 20133, Milano, Italy*

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Cationic ethylene platinum(II) complexes of the type $[Pt(CNN)(C_2H_4)]^+$, containing a methyl fragment and different diimines (NN), or terdentate (κC-$\kappa^2 NN'$) anionic ligands, were synthesized and fully characterized both as solids and in solution [NN = 2,2′-dipyridylamine, **1**; 2,2′-dipyridylsulfide, **2**; 1,10-phenanthroline, **3**; 4,7-diphenyl-1,10-phenanthroline, **4**; 3,4,7,8-tetramethyl-1,10-phenanthroline, **5**; 2,2′-bipyridine, **6**; HC-NN = 6-*tert*-butyl-2,2′-bipyridine, **7**; 6-*neo*-pentyl-2,2′-bipyridine, **8**; 6-phenyl-2,2′-bipyridine, **9**; 6-(α-methyl)benzyl-2,2′-bipyridine, **10**; 6-(α-ethyl)benzyl-2,2′-bipyridine, **11**; 6-(α,α-dimethyl)benzyl-2,2′-bipyridine, **12**]. Crystals suitable for X-ray analysis of complexes **5** and **7** were obtained. Ethene exchange at the cyclometalated platinum(II) complexes **7**, **8**, and **10**−**12** was studied by ^{1}H NMR line-broadening experiments in chloroform-*d*, as a function of both temperature and olefin concentrations. For the other prepared complexes the process was too fast to be monitored on the NMR time scale even at the lowest temperature. The ethylene exchange rates show a linear dependence on the concentration of the free ligand, with a negligible k_1 term indicating that either a solvolytic or a dissociative pathway to the products is absent or negligible. The values of the second-order rate constants k_{exc}, as obtained by linear regression analysis of the experimental data at 298 K, are in a range of ca. 10^4-10^5 s^{-1} m^{-1}. The activation entropies are negative, ranging between −129 and −112 J K^{-1} mol^{-1}, as expected for associative processes. The activation process is largely entropy controlled: the $T\Delta S^{\ddagger}$ contribution to the free energy of activation is extremely large, amounting to more than 80% for all complexes, with a smaller enthalpy contribution. All the experimental findings evidence that the mechanism takes place via an associative attack by the entering olefin, through a well-ordered, stable pentacoordinated transition state with the two ethene molecules on the trigonal plane. The reactivity of $[Pt(CNN)(C_2H_4)]^+$ complexes is strongly dependent on the choice of coordinated 6-substituted-2,2′-bipyridines, especially when the terdentate anionic fragment is capable of generating steric crowding and congestion on the coordination plane.

Introduction

In recent years there has been an increasing interest in the chemistry of cationic Pd(II) and Pt(II) complexes bearing substituted diimine ligands and unsaturated π-ligands, which are key intermediates in many catalytic processes involving olefins.[1] Apart from the fundamental interest in their intrinsic structure and in the nature of the metal−ligand bonding, these complexes have shown good ability as catalysts in reactions involving C−C bond formation,[2] such as olefin homo- and copolymerization,[3−5] oligomerization, and dimerization.[6−9] Such processes involve platinum and palladium η^2-alkene and η^2-alkyne divalent complexes, as either

[#] Dedicated to the memory of Professor Raffaello Romeo.

*Phone: +39-090-6765734. Fax: +39-090-3974108. E-mail: rosaria.plutino@pa.ismn.cnr.it.

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precursors or active species. However, fundamental information on metal−olefin bond breaking and formation and on the factors that control olefin coordination in metal−olefin complexes is important to exploit the diverse chemistry of these complexes and can be easily achieved by studying the dynamic process of olefin exchange. In comparison to palladium(II), whose catalytic properties are well known,[10] the analogous platinum(II) complexes are usually less useful as catalysts due to their higher kinetic inertness. On the other hand, they may be exploited as model systems for attaining mechanistic insights into Pd-catalyzed reactions and other interesting information from their kinetic behavior. Despite the great activity in the field, kinetic data relative to olefin exchange in platinum(II) or palladium(II) square-planar complexes are scarce in the literature.[6,11−14]

On these bases, we have thought it interesting to investigate the thermodynamics and the mechanism of olefin exchange at square-planar platinum(II) complexes, tuning the exchange rate by an appropriate selection of ancillary ligands and temperature, as previously shown in kinetic studies on exchange[15] and substitution[16] reactions.

Scheme 1. Dynamic Behavior for Olefin Complexes in a Type 4 Mechanism

Olefin complexes typically show dynamical structures even in the solid state,[14,17,18] due to rotation, rocking, and/or librational motions.[19] Actually, to explain the dynamic behavior of the olefin ligand, the following mechanisms have been taken into account: (1) propeller-like rotation,[18,20] (2) metal−olefin bond cleavage, followed by recombination,[21,22] (3) metal−ligand bond cleavage (i.e., the ligand *trans* to the olefin moiety), followed by ligand rotation and recombination,[11,21,23,24] and/or (4) intermolecular exchange with the free olefin ligand.[9,25] In most cases the fluxional behavior of the organometallic compounds has been reported only without a complete discussion of the molecular mechanism involved. However, definitive arguments for a correct mechanistic choice might be provided by NMR line-shape analysis and by the derived kinetic parameters.

In order to focus on a pure ethene exchange (type 4 mechanism, Scheme 1), we have synthesized and fully characterized, either as solids or in solution, a number of cationic un- and cyclometalated ethylene complexes of the CNN-type, $[Pt(CNN)(C_2H_4)]^+$, containing different methyl diimine (C = Me and NN) or terdentate orthometalated diimine (κC-$\kappa^2 NN'$) anionic ligands, respectively.

The reasons for this choice are manifold, especially because we still know very little about the factors controlling the very fast exchanging rates in η^2-olefin platinum(II) complexes, in spite of the aforementioned studies and literature data. Moreover we decided to design platinum(II) complexes containing a carbon−dinitrogen skeleton by coordination of a methyl fragment and a bidentate dinitrogen moiety, or terdentate ancillary "C^N^N"-type ligands, that are remarkably robust and cannot easily be removed from the

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coordination sphere of the metal. This approach offers the opportunity of studying ethene exchange reactions in transition metal complexes, ruling out a *trans* olefin exchange mechanism (type 3 mechanism) in favor of a direct ethene intermolecular exchange (type 4 mechanism). In addition these complexes are also characterized by (i) good solubility in chlorinated solvents due to the presence of the "Brookhart" counteranion[26] $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ (i.e., the complex $[Pt(Me)(phen)(C_2H_4)]BF_4$, whose synthesis has been already reported,[27] is rather unsoluble in chloroform-*d*); (ii) an extensive planarity of the NN-ligand, as far as the dipyridyl or phenanthroline moiety is concerned; and (iii) a different steric crowding above and below the coordin ation plane due to the different number and nature of the alkyl substituents bonded to the diimine fragment, to the alkyl or aryl orthometalated anchoring pendant, and to the size of the ring, in both the non- and the cyclometalated complexes. Nevertheless, it is worth noting that cyclometalated platinum(II) species have attracted much attention due to their potential applications in many fields, such as in organic synthesis, homogeneous catalysis, and photochemistry.[28,29]

Here we report the synthesis and spectroscopic characterization of platinum(II) complexes of the type $[Pt(CNN)(C_2H_4)]^+$, together with a detailed ^{1}H NMR dynamic investigation in chloroform-*d* on the ethene exchange, as a function of both temperature and olefin concentration. The aim of this work is to see to what extent cyclometalation and/or electronic or steric factors, induced by the substituents on the ancillary ligands, may affect the ethene lability, and therefore the olefin exchange rate. To the best of our knowledge this kinetic study represents one of the few quantitative examples of a pure concerted intermolecular olefin exchange occurring with an associative mechanism in square-planar platinum(II) complexes.[9,12]

Experimental Section

General Methods and Materials. Unless otherwise stated, all synthetic procedures were carried out on the benchtop. The solvents (AR, LabScan Ltd.; SpS, Romil Ltd.) used in the synthetic procedures were distilled under nitrogen from appropriate drying and deoxygenating agents (diethyl ether from sodium/benzophenone ketyl; dichloromethane from barium oxide) according to standard literature procedures[30] and then stored in N_2-filled flasks over activated 4 Å molecular sieves. Chloroform-*d* (D, 99.96% Cambridge Isotope Laboratories) was dried standing for many days over CaH_2, distilled under nitrogen over activated magnesium sulfate and sodium carbonate, degassed by using three repeated freeze−pump−thaw cycles, and afterward stored over activated 4 Å molecular sieves and used in a glovebox. Ethene (99.95%) and all other reagents were of the highest purity grade commercially available and used without further purification. The salt $Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (hereafter, NaBArF) was prepared according to a published method.[26]

Instrumentation and Physical Measurements. ^{1}H NMR measurements were performed on a Bruker AMX R-300 spectrometer equipped with a broadband probe operating at 300.13 MHz (^{1}H). All chemical shifts were referenced to the protiated residue in $CDCl_3$ for ^{1}H NMR (7.26 ppm) and are reported in parts per million (δ/ppm), while coupling constants are given in hertz (J/Hz). The probe temperature was checked by the methanol (low temperature)[31] or ethylene glycol (high temperature)[32] method measuring the chemical shift differences between the $-OH$ and the $-CH_3/-CH_2$ resonances of a methanol/ethylene glycol standard, respectively, as a function of temperature. Samples were allowed to equilibrate for a minimum of 10 min at each temperature setting, and the probe was then gradient-shimmed prior to collection of each data set.

Except where stated, all measurement manipulations were conducted in the absence of oxygen and water under a nitrogen or argon atmosphere, either by use of standard Schlenk methods or in a glovebox apparatus, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. NMR samples were prepared by dissolving, into a 5 mm NMR tube, about 10 mg of compound in about 0.5 mL of $CDCl_3$. Transfer of ethene was performed using gastight Hamilton syringes in an inert atmosphere. Elemental analyses were performed by Microanalytical Laboratory, Department of Chemistry, University College Dublin, Ireland.

Peak Assignment. Where necessary, the assignment of the complexes' resonances was performed by two-dimensional phase-sensitive ^{1}H 2D-NOESY experiments using a standard pulse sequence, with a mixing time of 600−800 ms, or alternatively homonuclear proton spin decoupling difference experiments were carried out. In particular as far as this second method is concerned a "control" spectrum, in which irradiation is applied in a blank region, is subtracted from one in which the center of a specific multiplet is irradiated, all the other experimental parameters being identical.

Dynamic NMR (DNMR) Studies. Variable-temperature ^{1}H NMR spectra of complexes **7**, **8**, and **10**−**12** were recorded in chloroform-*d* using a BVT200 digital temperature control unit. Samples were allowed to equilibrate for 7−10 min at the indicated probe temperature, and spectra were accumulated using 16−32 scans and 10 s recycle delays.

^{1}H NMR spectra in chloroform-*d* were recorded at a measured temperature, ranging from ca. 200 to 340 K, and full lineshape analyses were executed on the C_2H_4 portions of the resulting spectra. Since the chemical shifts of the hydrogens for the bound or free ethene are almost unaffected by temperature, the line shapes were fit at the different temperatures considering constant both chemical shifts and coupling constants. The chemical shifts observed in the slow limit exchange, i.e., in the absence of added free ethene, were used to set up the spin systems. The line widths used in the fitting procedure for each temperature were determined by comparison with the width of the solvent peak. First-order rate constants for ethene exchange (k_{obs}/s^{-1}) were obtained from line shape analysis by matching the observed ^{1}H NMR (ethene region) spectra in $CDCl_3$, both at variable ligand concentration and temperature (see Supporting Information, Table S2 and S3, respectively), with those simulated using the computer programs gNMR 4.0,[33] all spin systems for each complex being processed simultaneously. Linear and curvilinear least-squares fit and differential equations were analyzed using the SCIENTIST software package.[34]

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a. Ligand-Concentration-Dependent Experiments. ^{1}H NMR spectra were recorded at constant temperature (298 K). A weighed sample of the platinum complex was introduced in a 5 mm NMR tube containing $CDCl_3$ (0.5 mL) that was capped with a rubber septum. The initial NMR spectrum was recorded, and the subsequent spectra were taken after the addition of the olefin. Ethene was added to the solution into the sealed NMR tube by a microsyringe, and the solution was shaken to dissolve the gas. The ethene concentration was calculated by integration of the signals of the bound and the free ethene. Alternatively the integration was made only on a spectrum with the largest amount of free ethene, in which a good correspondence between the volume of added gas and the experimental olefin concentration in solution has been calculated. The ethene concentration for the diluted solutions was simply derived at each time from the precise amount of the added olefin volume. This method showed a good data reproducibility. All concentrations are expressed in moles per kilogram of solvent (m = mol kg^{-1}).

b. Variable-Temperature NMR Experiments. The ^{1}H NMR spectra were recorded over the temperature range 198−341 K, depending on the rate of the process studied at a fixed ethene concentration.

The calculated second-order exchange rate constants at each temperature, k_{exc}/s^{-1} m^{-1}, were used in the subsequent calculation of thermodynamic parameters using the linear expression of the Eyring equation

$$\ln\left(\frac{k}{T}\right) = \left(\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}\right) - \frac{\Delta H^{\ddagger}}{RT} \quad (1)$$

where $\Delta H^{\ddagger}$ is the activation enthalpy, $\Delta S^{\ddagger}$ is activation entropy, k_B, h, and R are the Boltzmann, Planck, and gas constants, respectively, and T is the absolute temperature.[35]

The activation free energy ($\Delta G^{\ddagger}$/kJ mol^{-1}) was then calculated at T = 298 K by use of the following equation:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad (2)$$

Synthetic Procedures. Alkyl-dinitrogen uncyclometalated and alkyl/aryl-dinitrogen cyclometalated complexes of the type [Pt(CNN)(C_2H_4)]X (X = BArF, CF_3SO_3, PF_6) were prepared, unless otherwise described, starting from the corresponding chloride complexes [Pt(CNN)Cl] by ethene for chloride substitution. The purity of all starting materials and reaction products was determined by ^{1}H NMR spectroscopy, and clean spectra with correct integration were obtained in all cases.

Uncyclometalated Platinum(II) Complexes. Complexes of the type [Pt(Me)(NN)(C_2H_4)]BArF [NN = 2,2′-dipyridylamine (dipy), **1**; 2,2′-dipyridylsulfide (dps), **2**; 1,10-phenanthroline (phen), **3**; 4,7-diphenyl-1,10-phenanthroline (Ph_2phen), **4**; 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen), **5**; 2,2′-bipyridine (bipy), **6**], as shown in Chart1, and [Pt(Me)(Ph_2phen)(C_2H_4)]-CF_3SO_3, **4b**, were prepared, from the corresponding chloride complexes [Pt(Cl)(Me)(NN)], **1P**−**6P**, respectively, by chloride abstraction with NaBArF or $AgCF_3SO_3$ in the presence of a continuous ethene flow. The precursor platinum(II) complexes *trans*-[Pt(Cl)(Me)(Me_2SO)$_2$][36] and [Pt(Cl)(Me)(NN)] (NN = dipy, **1P**;[37] phen, **3P**;[38] bipy, **6P**[16]) were prepared according to already published synthetic procedures.

[Pt(Cl)(Me)(dps)], 2P. *trans*-[Pt(Cl)(Me)(Me_2SO)$_2$] (0.060 g, 0.149 mmol) was reacted with 2,2′-dipyridylsulfide (0.028 g, 0.149 mmol) dissolved in 50 mL of dichloromethane under continuous stirring at room temperature. The reaction mixture was stirred until a powdery off-white solid of complex **2P** was completely formed. The excess solvent was evaporated under reduced pressure, and the pure product was obtained after several washing with Et_2O and recrystallization from a mixture of dichloromethane/ether (1:1 = v/v). Yield: 80%. Anal. Calcd for $PtC_{11}H_{11}N_2ClS$: C, 30.45; H, 2.56; N, 6.46. Found: C, 30.51; H, 2.61; N, 6.41.

^{1}H NMR ($CDCl_3$, T = 298 K): δ 9.71 (dd, $^3J_{PtH}$ = 16.0 Hz, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, $H_{6'}$), 9.20 (d, $^3J_{PtH}$ = 41.0 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, H_6), 7.90 (dd, $^3J_{HH}$ = 8.8, 7.4 Hz, 1H, H_4), 7.83 (dd, $^3J_{HH}$ = 8.8, 7.4 Hz, 1H, $H_{4'}$), 7.82 (d, $^3J_{HH}$ = 8.8 Hz, 1H, H_3), 7.71 (d, $^3J_{HH}$ = 8.8 Hz, 1H, $H_{3'}$), 7.51 (dd, $^3J_{HH}$ = 7.4, 5.5 Hz, 1H, $H_{5'}$), 7.43 (ddd, $^3J_{HH}$ = 7.4, 5.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H_5), 1.16 (s, $^2J_{PtH}$ = 77.6 Hz, 3H, Pt-CH_3).

The complexes [Pt(Cl)(Me)(Ph_2phen)], **4P**, and [Pt(Cl)(Me)-(Me_4phen)], **5P**, were obtained following the same procedure described above for the synthesis of complex **2P** (see Supporting Information for the complexes' ^{1}H NMR characterization and elemental analysis).

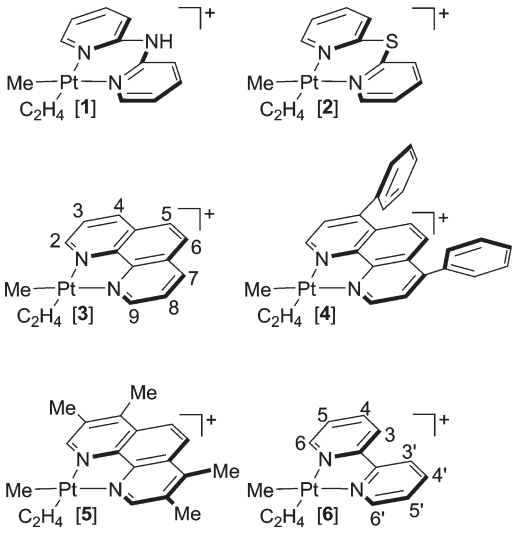
[Pt(Me)(dipy)(C_2H_4)]BArF, 1. A weighed amount of complex **1P** (0.040 g, 0.096 mmol) was dissolved in CH_2Cl_2; then a stoichiometric amount of NaBArF (0.085 g, 0.096 mmol) was added, followed by ethene bubbling into the solution. After stirring about 1 h, NaCl was filtered off, the solvent excess was evaporated under reduced pressure, and the pure product was obtained after washing with several aliquots of petroleum ether. Yield: 70%. Anal. Calcd for $PtBC_{45}H_{28}F_{24}N_3$: C, 42.47; H, 2.22; N, 3.30. Found: C, 42.19; H, 2.28; N, 3.33.

^{1}H NMR ($CDCl_3$, T = 298 K): δ 8.25 (d, $^3J_{PtH}$ = 40.3 Hz, $^3J_{HH}$ = 5.9 Hz, 1H, H_6), 7.81 (dd, $^3J_{av}$ = 7.4 Hz, 1H, H_4), 7.76 (d, $^3J_{PtH}$ = 17.1 Hz, $^3J_{HH}$ = 5.9 Hz, 1H, $H_{6'}$), 7.69 (s, br, 8H, $H_{o'\text{-}BArF}$), 7.68 (obscured by $H_{o'\text{-}BArF}$, 1H, $H_{4'}$), 7.49 (s, br, 4H, $H_{p'\text{-}BArF}$), 7.36 (s, br, 1H, NH), 7.18 (dd, $^3J_{HH}$ = 7.4, 5.9 Hz, 1H, H_5), 7.09 (dd, $^3J_{HH}$ = 7.4, 5.9 Hz, 1H, $H_{5'}$), 7.01 (d, $^3J_{HH}$ = 8.1 Hz, 1H, H_3), 6.96 (d, $^3J_{HH}$ = 8.1 Hz, 1H, $H_{3'}$), 4.01 (s, br, 4H, C_2H_4), 0.57 (s, $^2J_{PtH}$ = 69.1 Hz, 3H, Pt-CH_3).

The other complexes **2**−**6** were obtained by following the same procedure previously reported for compound **1** (see Supporting Information for the complexes' ^{1}H NMR characterization and elemental analysis).

[Pt(Me)(Ph_2phen)(C_2H_4)]CF_3SO_3, 4b, was obtained with a procedure similar to that of the parent complex **4** by reaction of **4P** (0.030 g, 0.052 mmol) and $AgCF_3SO_3$ (0.013 g, 0.052 mmol) in dichloromethane under continuous stirring and a constant

Chart 1. Structural Formulas for the Complexes **1**−**6**, with the Numbering Scheme



(35) Activation parameters, $\Delta H^{\ddagger}$/kJ mol^{-1} and $\Delta S^{\ddagger}$/J K^{-1} mol^{-1}, were calculated from the slope and the intercept of the best line obtained by a least-squares analysis performed with the SCIENTIST software.

(36) Eaborn, C.; Kundu, K.; Pidock, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 933–938.

(37) Romeo, R.; Nastasi, N.; Scolaro, L. M.; Plutino, M. R.; Albinati, S.; Macchioni, A. *Inorg. Chem.* **1998**, *37*, 5460–5466.

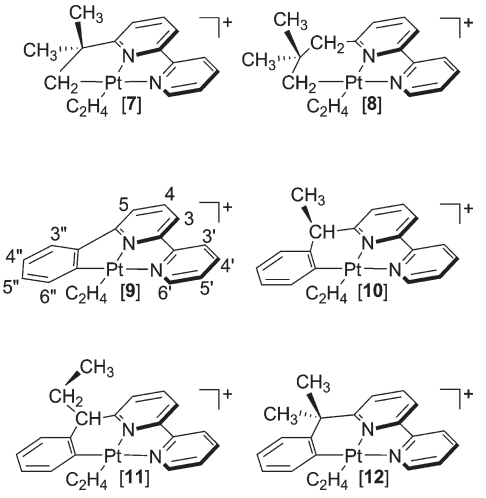
(38) Romeo, R.; Monsú Scolaro, L. *Inorg. Synth.* **1998**, *32*, 153–158.

ethene atmosphere. After the complete formation of **4b** and the removal of AgCl, the filtrated solution was concentrated under reduced pressure on a rotary evaporator; then petroleum ether (10 mL, 1:1 = v/v) was added to obtain **4b** as a pure product with a 60% yield. Anal. Calcd for $PtC_{28}H_{23}F_3N_2O_3S$: C, 46.73; H, 3.22; N, 3.89. Found: C, 46.81; H, 3.26; N, 3.85.

^{1}H NMR ($CDCl_3$, T = 298 K): δ 9.24 (d, $^3J_{PtH}$ = 51.6 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, H_2), 9.05 (d, $^3J_{PtH}$ = 14.2 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, H_9), 8.23 (d, $^3J_{HH}$ = 5.5 Hz, 1H, H_8), 8.14 (AB system, $^3J_{HH}$ = 9.4 Hz, 1H, H_5), 8.08 (AB system, $^3J_{HH}$ = 9.4 Hz, 1H, H_6), 8.06 (d, $^3J_{HH}$ = 5.5 Hz, 1H, H_3), 7.66−7.51 (m, 10H, *Ph*), 4.58 (s, br, $^2J_{PtH}$ = 68.2 Hz, 4H, C_2H_4), 0.93 (s, $^2J_{PtH}$ = 69.8 Hz, 3H, Pt-CH_3).

Cyclometalated Platinum(II) Complexes. Similarly to the noncyclometalated species, complexes of the type [Pt(CNN)-(C_2H_4)]BArF [HC-NN = 6-*tert*-butyl-2,2′-bipyridine (bipy^t), **7**; 6-*neo*-pentyl-2,2′-bipyridine (bipy^n), **8**; 6-phenyl-2,2′-bipyridine (bipy$^\phi$), **9**; 6-(α-methyl)benzyl-2,2′-bipyridine (bipy$^{\alpha Me}$), **10**; 6-(α-ethyl)benzyl-2,2′-bipyridine (bipy$^{\alpha Et}$), **11**; 6-(α,α-dimethyl)benzyl-2,2′-bipyridine (bipy^c), **12**], as shown in Chart 2 and

Chart 2. Structural Formulas for the Complexes **7**−**12**, Together with the Adopted Numbering Scheme



[Pt(CNN)(C_2H_4)]CF_3SO_3 [HC-NN = 6-*tert*-butyl-2,2′-bipyridine (bipy^t), **7b**; 6-(α-ethyl)benzyl-2,2′-bipyridine (bipy$^{\alpha Et}$), **11b**] were prepared from the analogous chloride complexes [Pt(CNN)Cl] [HC-NN = bipy^t, **7P**;[39] bipy^n, **8P**;[29] bipy$^\phi$, **9P**;[40] bipy$^{\alpha Me}$, **10P**;[41] bipy$^{\alpha Et}$, **11P**;[16] bipy^c, **12P**[42]] by reaction with ethene and a stoichiometric amount of NaBArF or $AgCF_3SO_3$ to remove the bound chloride ligand.

[Pt(bipy^t-H)(C_2H_4)]BArF, 7. A 0.047 g amount of complex **7P** (0.106 mmol) was dissolved in CH_2Cl_2, and a stoichiometric amount of NaBArF (0.094 g, 0.106 mmol) was added under stirring, while ethene was bubbled through the solution. After NaCl precipitated completely from the reaction mixture, the solution was filtered and reduced in volume under low pressure. Then an equal volume of petroleum ether was added until complete precipitation of a pale yellow solid product. Yield: 60%. Anal. Calcd for $PtBC_{48}H_{31}F_{24}N_2$: C, 44.43; H, 2.41; N, 2.16. Found: C, 44.18; H, 2.41; N, 2.17.

^{1}H NMR ($CDCl_3$, T = 298 K): δ 8.08 (d, $^3J_{HH}$ = 5.3 Hz, 1H, $H_{6'}$), 8.02 (dd, $^3J_{av}$ = 8.0 Hz, 1H, H_4), 7.98 (ddd, $^3J_{av}$ = 8.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, $H_{4'}$), 7.86 (d, $^3J_{HH}$ = 8.0 Hz, 1H, $H_{3'}$), 7.70 (d, 1H, obscured by $H_{o'\text{-}BArF}$, H_3), 7.68 (s, br, 8H, $H_{o'\text{-}BArF}$), 7.56 (ddd, $^3J_{HH}$ = 8.0, 5.3 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, $H_{5'}$), 7.51 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H_5), 7.47 (s, br, 4H, $H_{p'\text{-}BArF}$), 4.32 (s, $^2J_{PtH}$ = 63.4 Hz, 4H, C_2H_4), 2.20 (s, $^2J_{PtH}$ = 69.4 Hz, 2H, CCH_2Pt), 1.41 (s, 6H, CCH_3).

[Pt(bipy^t-H)(C_2H_4)]CF_3SO_3, 7b, was obtained by a similar route to **7**, reacting complex **7P** (0.025 g, 0.056 mmol) with the stoichiometric amount of $AgCF_3SO_3$ (0.014 g, 0.056 mmol) in dichloromethane as solvent and flushing ethene through the solution. Yield: 55%. Anal. Calcd for $PtC_{17}H_{19}F_3N_2O_3S$: C, 34.99; H, 3.28; N, 4.80. Found: C, 34.95; H, 3.30; N, 4.78.

^{1}H NMR ($CDCl_3$, T = 298 K) δ: 8.70 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H_{3'}$), 8.59 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 10.2 Hz, 1H, H_3), 8.37 (dd, $^3J_{av}$ = 7.7 Hz, 1H, H_4), 8.35 (d, $^3J_{HH}$ = 5.5 Hz, 1H, $H_{6'}$), 8.31 (ddd, $^3J_{HH}$ = 8.2, 7.7 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, $H_{4'}$), 7.77 (ddd, $^3J_{HH}$ = 7.7, 5.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, $H_{5'}$), 7.57 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.1 Hz, $^4J_{PtH}$ = 10.1 Hz, 1H, H_5), 4.46 (s, $^2J_{PtH}$ = 62.1 Hz, 4H, C_2H_4), 2.20 (s, $^2J_{PtH}$ = 69.8 Hz, 2H, CCH_2Pt), 1.46 (s, 6H, CCH_3).

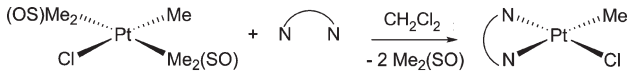
[Pt(bipy^t-H)(C_2H_4)]PF_6, 7c, was prepared and characterized *in situ* by anion exchange reaction of **7** with an excess of (^{n}Bu$_4$N)PF_6 in 0.5 mL of chloroform-*d* directly into the NMR tube (C_{Pt} = 5.5 m*m*, [(^{n}Bu$_4$N)PF_6] = 54.3 m*m*).

^{1}H NMR ($CDCl_3$, T = 298 K) δ: 8.37 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, $H_{3'}$), 8.34 (d, $^3J_{HH}$ = 5.3 Hz, 1H, $H_{6'}$), 8.31 (dd, $^3J_{av}$ = 8.0 Hz, 1H, H_4), 8.25 (ddd, $^3J_{av}$ = 8.0 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, $H_{4'}$), 8.24 (d, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H_3), 7.80 (ddd, $^3J_{HH}$ = 7.8, 5.3 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, $H_{5'}$), 7.60 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.1 Hz, $^4J_{PtH}$ = 10.1 Hz, 1H, H_5), 4.44 (s, $^2J_{PtH}$ = 63.6 Hz, 4H, C_2H_4), 2.21 (s, $^2J_{PtH}$ = 69.2 Hz, 2H, CCH_2Pt), 1.45 (s, 6H, CCH_3).

Complexes **8**−**12** were obtained following the same procedure described for **7** by using the complexes **8P**−**12P** as starting materials. The triflate derivative **11b** was prepared as well as compound **7b** (see Supporting Information for the detailed ^{1}H NMR and elemental analysis complexes' characterization).

X-ray Data Collection and Structure Determination for [5]BArF and [7]BArF. It proved impossible to grow crystals of good quality of **5** and **7**. Moreover, as shown by the structural determinations, both compounds contain disordered counterions; thus the accuracy of the structural determinations is limited. However, the mean features of the coordination are unambiguously determined. Data collections, structural details and Table S1 with all the experimental crystallographic data are given as Supporting Information.

Scheme 2. Synthetic Pathway to Methyl Chloride Platinum(II) Complexes **1P**−**6P**



N-N = dipy, **1P**; dps, **2P**; phen, **3P**; Ph_2phen, **4P**; Me_4phen, **5P**; bipy, **6P**.

Results and Discussion

Synthetic Procedures. The neutral chloride platinum(II) complexes [Pt(Cl)(Me)(NN)] (NN = dipy, **1P**; dps, **2P**; phen, **3P**; Ph_2phen, **4P**; Me_4phen, **5P**, bipy, **6P**) have been prepared following a general method[38] reported in the literature, using the complex *trans*-[Pt(Cl)(Me)-($Me_2SO)_2$] as a useful synthon to introduce the organometallic fragments {PtMe} and {PtClMe}. Thus, the addition of an equimolecular amount of the diimine ligand NN to a dichloromethane solution of *trans*-[Pt-(Cl)(Me)($Me_2SO)_2$] led to the rapid substitution of both sulfoxide ligands, yielding compounds **1P**−**6P** in a pure

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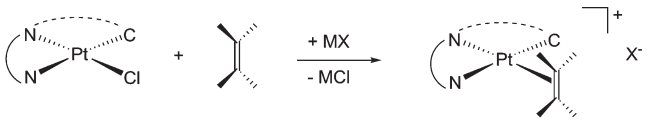
(40) Constable, E. C.; Henney, R. P. G.; Leese, T. A.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1990**, 443–449.
(41) Cinellu, M. A.; Gladiali, S.; Minghetti, G. *J. Organomet. Chem.* **1989**, *363*, 401–408.
(42) Sanna, G.; Minghetti, G.; Zucca, A.; Pilo, M. I.; Seeber, R.; Laschi, F. *Inorg. Chim. Acta* **2000**, *305*, 189–205.

Scheme 3. Synthetic Pathway to Uncyclometalated (**1**−**6**) and Cyclometalated (**7**−**12**) Platinum(II) Ethene Complexes[a]



X=TFPB, C= Me, N-N = dipy, **1**; dps, **2**; phen, **3**; Ph_2phen, **4**; Me_4phen, **5**; bipy, **6**;
X=TFPB, N-N-CH = bipy^t, **7**; bipy^n, **8**; bipy$^\phi$, **9**; bipy$^{\alpha Me}$, **10**; bipy$^{\alpha Et}$, **11**; bipy^c, **12**;
X=CF_3SO_3, C= Me, N-N = Ph_2phen, **4b**;
X=CF_3SO_3, N-N-CH = bipy^t, **7b**; bipy$^{\alpha Et}$, **11b**;

[a] Chloride abstraction was performed by using the salt MX = NaBArF or $AgCF_3SO_3$.

crystalline form and in almost quantitative yield, according to Scheme 2.

The synthesis and the spectroscopic properties of the platinum(II) species [Pt(Me)(N−N)(Cl)] (NN = dipy, **1P**;[37] phen, **3P**;[38] bipy, **6P**[16]) and of the cyclometalated platinum(II) [Pt(CNN)Cl] complexes [containing 6-alkyl-2,2′-bipyridine (**7**, **8**),[29,39] 6-phenyl-2,2′-bipyridine (**9**),[40] and substituted 6-benzyl-2,2′-bipyridine (**10**−**12**)][16,41,42] have been described in detail elsewhere except for complexes **2P**, **4P**, and **5P** (containing dinitrogen ligands such as dps, Ph_2phen, and Me_4phen, respectively), whose synthesis and spectroscopic characterization are reported in the Experimental Section or given as Supporting Information.

The cationic ethene platinum(II) complexes of general formula $[Pt(CNN)(C_2H_4)]^+$, **1**−**12**, have been prepared as previously shown for other similar cationic diimine methyl platinum(II) complexes [Pt(CNN)X] (X = sulfoxides or phosphanes),[37,43] in dichloromethane solution, starting from the corresponding chloride complexes [Pt(CNN)(Cl)], by use of an appropriate chloride-removing reagent, under a constant olefin atmosphere.

The addition of an equivalent amount of NaBArF salt to a dichloromethane solution of the neutral chloride-containing platinum(II) compounds (CNN) **1P**−**12P** led to the easy replacement of chloride from the coordination sphere of the complexes, yielding NaCl and a very labile and reactive cationic solvento species that, in the presence of bubbling ethene, afforded the desired corresponding compounds **1**−**12**.

The trifluoromethanesulfonate complex salts **4b**, **7b**, and **11b** were obtained following the same procedure described above using silver triflate, $AgCF_3SO_3$, as the reagent for chloride abstraction (see Scheme 3).

All the obtained complexes (cyclometalated and not), **1**−**6** and **7**−**12** (in Charts 1 and 2, respectively), are air stable and can be stored at 277 K without appreciable decomposition for several months; they are very soluble in chlorinated solvents, especially the derivatives with the Brookhart counteranion ($BArF^-$), on which all the NMR investigations have been carried out (see Experimental Section).

As far as compound $[Pt(bipy^t\text{-}H)(C_2H_4)]PF_6$, **7c**, is concerned, the synthesis has been performed *in situ* in a NMR tube by moving the equilibrium shown in eq 3 toward the products with an excess of $(^nBu_4N)PF_6$.

$$\underset{\mathbf{7}}{[Pt(bipy^t\text{-}H)(C_2H_4)]BArF} + (^nBu_4N)PF_6 \overset{K_{eq}}{\rightleftharpoons} \underset{\mathbf{7c}}{[Pt(bipy^t\text{-}H)(C_2H_4)]PF_6} + (^nBu_4N)BArF \quad (3)$$

An increase of the counteranion concentration shifts the resonances of the aromatic protons to higher frequencies (see Supporting Information, Figure S1, upper plot), while the aliphatic ones (not shown in the figure for the sake of clarity) are just slightly affected. The most shifted protons appear to be H_3 and $H_{3'}$, suggesting that compound **7c** exists in chloroform-*d* solution in the form of a tight ion pair. As already observed for similar platinum(II) or palladium(II) complexes containing aromatic dinitrogen ligands,[3,8,37,44] the counteranion lies above or below the coordination plane close to the H_3 and $H_{3'}$ protons (see Supporting Information, lower plot of Figure S1). Indeed the shift of their resonances to higher frequencies is pronounced due to the progressive weakening of the ring current effect due to the replacement of the tetra-arylborate anion $BArF^-$ by an excess of the PF_6^- one (according to eq 3).

$$K_{eq} = \frac{[\mathbf{7c}][(^nBu_4N)BArF]}{[\mathbf{7}][(^nBu_4N)PF_6]} = \frac{x^2}{(A-x)(B-x)} \quad (4)$$

$$\delta_{av} = \delta_{\mathbf{7}}\chi_{\mathbf{7}} + \delta_{\mathbf{7c}}\chi_{\mathbf{7c}} \quad (5)$$

$$\delta_{av} = \frac{A\delta_{\mathbf{7}} + x(\delta_{\mathbf{7c}} - \delta_{\mathbf{7}})}{A} \quad (5')$$

Chemical shifts ($\delta_{av}(^1H)$/ppm) measured for all the aromatic signals (H_{3-5}, $H_{3'-6'}$) versus the concentration of the added hexafluorophosphate salt ($[(^nBu_4N)PF_6]/m$) were globally fitted to eqs 4 and 5′ with a nonlinear least-squares routine of the SCIENTIST program,[34] yielding the fits shown in Figure S1, which interpolate the experimental data with a calculated value of the equilibrium constant of $K_{eq} = 0.93 \pm 0.09$. In eqs 4−5′, A denotes the total starting concentration of **7**, B is the concentration of added $(^nBu_4N)PF_6$, x is the equilibrium concentration of the products **7c** and $(^nBu_4N)BArF$, and δ_{av} is the average observed chemical shift at the equilibrium between **7** and **7c**, with molar fractions $\chi_{\mathbf{7}}$ and $\chi_{\mathbf{7c}}$, respectively. The equilibrium concentrations of all the species involved in eq 3 were calculated for every single addition of $(^nBu_4N)PF_6$.

Solid-State Structures of 5 and 7. Figure 1 shows ORTEP views of cations **5** and **7**, respectively, while a discussion of the structures is given in the Supporting Information, together with selected bond lengths (Å) and angles (deg) in Figures S2 and S3.

The immediate coordination sphere of both platinum(II) complexes consists of the two N donor atoms of

(43) (a) Romeo, R.; Fenech, L.; Carnabuci, S.; Plutino, M. R.; Romeo, A. *Inorg. Chem.* **2002**, *41*, 2839–2847. (b) Romeo, R.; Carnabuci, S.; Fenech, L.; Plutino, M. R.; Albinati, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 4494–4498.

(44) Macchioni, A.; Magistrato, A.; Orabona, I.; Ruffo, F.; Rothlisberger, U.; Zuccaccia, C. *New J. Chem.* **2003**, *27*, 455–458.

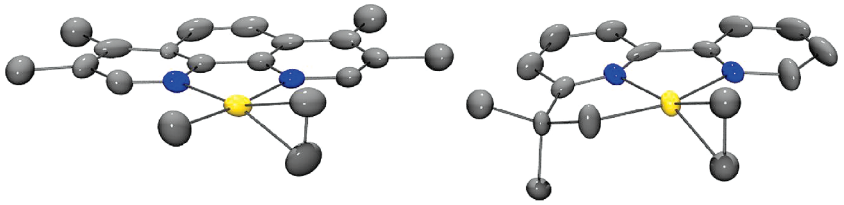


Figure 1. ORTEP view for the platinum(II) cationic complexes **5** and **7**.

Table 1. Relevant ^{1}H NMR Data for the Uncyclometalated Platinum(II) Complexes of the Type [Pt(Me)(NN)(C_2H_4)]X (X = BArF, CF_3SO_3)[a]

		δ		
n	complex	NN ligand	C_2H_4-Pt	Me-Pt
1	[Pt(Me)(dipy)(C_2H_4)]BArF	8.25 (40.3, H_6), 7.76 (17.1, $H_{6'}$)	4.01[b]	0.57 (69.1)
2	[Pt(Me)(dps)(C_2H_4)]BArF	8.40 (50.4, H_6), 8.18 (22.0, $H_{6'}$)	4.07[c]	0.68 (70.4)
3	[Pt(Me)(phen)(C_2H_4)]BArF	9.13 (50.4, H_2), 8.36 (16.7, H_9)	4.33 (63.0)	0.90 (69.0)
4	[Pt(Me)(Ph_2phen)(C_2H_4)]BArF	9.16 (50.6, H_2), 7.90 (15.4, H_9)	4.32 (68.7)	0.92 (70.4)
4b	[Pt(Me)(Ph_2phen)(C_2H_4)]CF_3SO_3	9.24 (51.6, H_2), 9.05 (14.2, H_9)	4.58 (68.2)	0.93 (69.8)
5	[Pt(Me)(Me_4phen)(C_2H_4)]BArF	8.83 (51.5, H_2), 8.06 (14.8, H_9)	4.27 (66.9)	0.86 (69.9)
6	[Pt(Me)(bipy)(C_2H_4)]BArF	8.81 (50.0, H_6), 7.95 (14.0, $H_{6'}$)	4.20 (64.7)	0.78 (70.2)

[a] Chemical shifts in parts per million, coupling constants in hertz; J_{PtH} in parentheses, $CDCl_3$ as solvent, T = 298 K. The assignment follows the numeration pattern shown in Chart 1. [b] Broad singlet. [c] Broad AA′BB′ system.

Table 2. Relevant ^{1}H NMR Data for the Cyclometalated Platinum(II) Complexes of the Type [Pt(CNN)(C_2H_4)]X (X = BArF, CF_3SO_3, PF_6)[a]

		δ					
		CNN ligand					
n	complex	$H_{6'}$	$H_{6''}$	C*H*	CH_2	CH_3	C_2H_4-Pt
7	[Pt(bipy′-H)(C_2H_4)]BArF	8.08			2.20 (69.4)	1.41	4.32 (63.4)
7b	[Pt(bipy′-H)(C_2H_4)]CF_3SO_3	8.37			2.20 (69.8)	1.46	4.46 (62.1)
7c	[Pt(bipy′-H)(C_2H_4)]PF_6	8.37			2.21 (69.2)	1.45	4.44 (63.6)
8	[Pt(bipy″-H)(C_2H_4)]BArF	7.93			1.68 (70.3)	1.06	4.08 (69.9)
9	[Pt(bipy$^{\phi}$ -H)(C_2H_4)]BArF	7.94 (14.0)	6.57 (43.0)				4.66 (60.2)
10	[Pt(bipy$^{\alpha Me}$-H)(C_2H_4)]BArF	8.10 (17.2)	6.84 (47.0)	4.48		1.75	4.72, 4.64 (65.0)[b]
11	[Pt(bipy$^{\alpha Et}$-H)(C_2H_4)]BArF	8.08 (18.8)	6.83 (44.0)	4.10	2.12	0.76	4.71, 4.61 (67.2)[b]
11b	[Pt(bipy$^{\alpha Et}$-H)(C_2H_4)]CF_3SO_3	8.41 (16.4)	6.86 (43.8)	4.08	2.12	0.76	4.80, 4.75 (65.0)[b]
12	[Pt(bipy^{c}-H)(C_2H_4)]BArF	8.09 (18.0)	6.79 (47.0)			2.05	4.64 (65.6)

[a] Chemical shifts in parts per million, coupling constants in hertz; J_{PtH} in parentheses, $CDCl_3$ as solvent, T = 298 K. The assignment follows the numeration pattern shown in Chart 2. [b] AA′BB′ system.

the substituted di-imine ligand, the methyl group, and the η^2-coordinated ethylene molecule. The coordination in **5** (see Figure 1) is square planar and comparable to that found in similar square-planar complexes,[45] while that in **7** is distorted square planar, with the two rings of the dipyridyl ligand slightly twisted (dihedral angle between rings of 3.1(4)°).

Solution Structure and NMR Characterization. The ^{1}H NMR spectra of the cationic complexes **1**−**12** were assigned on the basis of 1D selective irradiation or 2D NOESY experiments. Selected ^{1}H NMR resonances at 298 K for all the synthesized un- and cyclometalated compounds are reported in Tables 1 and 2, respectively.

^{1}H NMR spectra of compounds [Pt(Cl)(Me)(NN)] (**1P**−**6P**) as well as those of the cationic complexes [Pt(Me)(NN)(C_2H_4)]$^+$ (**1**−**6**) show, as expected, the nonequivalence of the two halves of the complexes, especially for the signals belonging to the di-imine fragment. The differences in the ^{195}Pt coupling constants, $^3J_{Pt-H}$/Hz, of the corresponding nuclei in the two halves of the dinitrogen NN ligands are in agreement with the higher *trans* influence exerted by the alkyl group in comparison with the chloride or the ethylene moiety.[46] As an example, the $^3J_{PtH}$ coupling constant of the H_2 proton for the 4,7-diphenyl-1,10-phenanthroline ligand in complex **4P** is 62.5 Hz, while this value drops to 17.3 Hz for the H_9 proton that is *trans* to the methyl ligand. Similarly, the ethene derivatives exhibit coupling constants, $^3J_{PtH}$, of ca. 40−50 Hz for the protons in *ortho* position to the nitrogen donor atom *trans* to the ethylene and of ca. 15−20 Hz for those *trans* to the methyl group.

Proton resonances of the Pt-Me groups, as reported for related methyl/alkene and methyl/alkyne derivatives,[27,47] appear just below δ 1 ppm, with typical ^{195}Pt satellites of ca. 70 Hz.

The most interesting feature in the ^{1}H NMR spectra of all the cationic complexes [Pt(CNN)(C_2H_4)]$^+$ (**1**−**12**) is

(45) Plutino, M. R.; Scolaro, L. M.; Albinati, A.; Romeo, R. *J. Am. Chem. Soc.* **2004**, *126*, 6470–6484.

(46) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Saunders: London, 1985; pp 704−705.

(47) Cucciolito, M. E.; De Felice, V.; Orabona, I.; Ruffo, F. *J. Chem. Soc., Dalton Trans.* **1997**, 351–355.

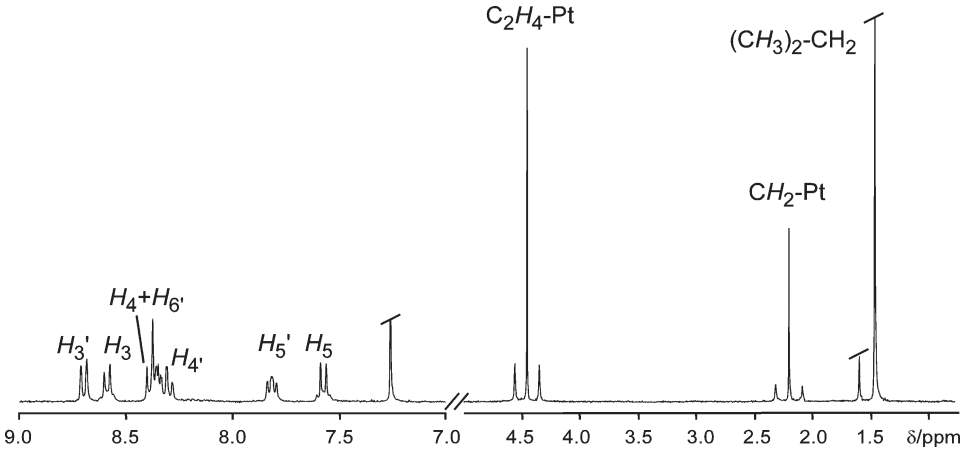


Figure 2. ^{1}H NMR spectrum of complex **7b** recorded at 300.13 MHz in chloroform-*d* at 298 K.

relative to the ethylene protons. In all these compounds the corresponding signal is shifted upfield with respect to free ethene (δ 4.01−4.80 ppm), indicating that olefin is coordinated to platinum through the C=C double bond [that is, for Pt(II) ethylene compounds typical signals occur at δ 5.4 (free); 4.8−4.3 (four-coordinate complexes); 3.7−1.7 (trigonal-bipyramidal complexes)].[48]

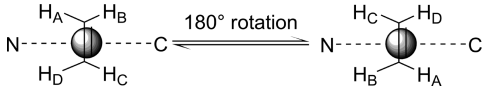
At room temperature, the ^{1}H NMR spectra of all these complexes display an averaged peak for the four protons (a singlet for complexes **7**, **8**, and **12**; an AA′BB′ system for complexes **10** and **11**,**11b**), which is not consistent with an olefin in a static asymmetric square-planar arrangement.

Thus, the chemical equivalence of the four ethene protons indicates a fast dynamic process of the coordinated C_2H_4 molecule around the Pt−ethene bond. This motion averages one or both pairs of signals for the protons $H_{A,C}$ and $H_{B,D}$, as shown in Scheme 4, where the 180° rotation of the ligand is observed along the Pt−ethene bond. On the other hand, the ethylene AA′BB′ pattern observed in complexes **10** and **11** could be ascribed to a sterically retarded rotation, combined with a lower symmetry given by the orthometalated ancillary ligands bipy$^{\alpha Me}$-H and bipy$^{\alpha Et}$-H, respectively.

For all these complexes, with the exception of complexes **1** and **2**, the signals for the ethylene protons showed ^{195}Pt satellites of ca. 60−70 Hz. On the other hand, as far as complexes **1** and **2** are concerned, ^{195}Pt satellites are undetectable and the olefin peak is clearly broad. In any case, the olefin protons resonate in a range considered typical for square-planar platinum(II) complexes. At low temperature, where the rotation is almost frozen, the ^{1}H NMR spectra of all the compounds (except **9**) displayed a static structure for the ethene, showing an AA′BB′ or AA′XX′ system for complexes **7**, **8**, and **12** and an ABCD system for complexes **10** and **11**, respectively.

Figure 2 shows the spectrum of [Pt(bipy^t-H)-(C_2H_4)]CF_3SO_3, **7b**. In the aliphatic region the sharp signal at δ 4.46 ppm with $^2J_{PtH}$ = 62.1 Hz is clearly attributable to the four protons of the bound ethylene.[48] The *tert*-butyl fragment in the bipy^t-H ligand gives two

Scheme 4. Ethene Rotation around the Pt−C_2H_4 Bond[a]



[a] The sketches are shown with a view in front of the platinum(II)−alkene bond, where the metal center lies behind the olefin moiety.

expected singlets, one at δ 2.20 ppm with $^2J_{PtH}$ = 69.8 Hz, for the methylene group bound to the platinum(II), and the other at δ 1.46 ppm, assigned to the two methylic protons. The aromatic region exhibits seven different resonances for the asymmetric bipy ligand. The related compound **7**, containing the $BArF^-$ counteranion, evidences clearly detectable upfield shifts of the aromatic protons (see Figure S4 in the Supporting Information), while the aliphatic signals are almost unaffected. As already described in the previous section, this phenomenon is attributable to the ring current effect exerted by the four 3,5-$(CF_3)_2C_6H_3$ aromatic pendants of the anion on the central protons, H_3 and $H_{3'}$, of the bipyridine moiety.

The aromatic region of the ^{1}H NMR spectra of the complex [Pt(bipy^t)(C_2H_4)]BArF (**7**) is also affected by temperature variation or changing the solvent and/or the counteranion. Addition of different amounts of CD_3OD or benzene-d_6 to a sample of compound **7** in chloroform-*d* solution led to significant shifts of all the aromatic protons. In particular, downfield shifts of the bipyridine proton signals are observed upon CD_3OD addition, while upfield shifts are detected with benzene-d_6. These phenomena usually are related to ion-pair formation and to the relative strength of opposite charges' interactions. Accordingly, addition of an increasing amount of (^{n}Bu$_4$N)PF_6 salt in solution produced similar chemical shift changes (see Supporting Information, Figure S1). In all these experiments, the most shifted protons were always H_3 and $H_{3'}$. These findings suggest that compound **7** exists as a tight ion pair in $CDCl_3$ and that the counterion lies on the side and in proximity to the bipyridine fragment close to H_3 and $H_{3'}$.

The compound [Pt(Me)(bipy)(C_2H_4)]BArF, **6**, possessing a similar CNN skeleton in the series of uncyclometalated species, shows the expected pattern for the aromatic proton signals, together with two singlets in the aliphatic region relative to the ethene protons (δ 4.20,

(48) Albano, V. G.; Natile, G.; Panunzi, A. *Coord. Chem. Rev.* **1994**, *133*, 67–114.

$^2J_{PtH}$ = 64.7 Hz) and to the methyl fragment (δ 0.78, $^2J_{PtH}$ = 70.2 Hz; see ^{1}H NMR spectrum of **6** at T = 298 K in chloroform-*d*, Figure S5).

Dynamic Processes in 1−12. In order to determine the ethene exchange rate constants, line-shape analyses were performed for all the investigated complexes at different ethene concentrations and/or temperature. For almost all the complexes the ethylene proton resonances, at room temperature, appeared with ^{195}Pt satellites ($^3J_{PtH}$ = 60.2−70.4 Hz). On adding free ethene, the olefinic proton signals lose their satellites, showing a typical concentration-dependent broadening, which is accounted for by a relatively fast exchange between free and coordinated ethene. Only in the case of the uncyclometalated species [Pt(Me)(dipy)(C_2H_4)]BArF (**1**) and [Pt(Me)(dps)(C_2H_4)]-BArF (**2**) can a dominant chemical shift anisotropy relaxation mechanism explain the unresolved spin−spin coupling to ^{195}Pt; ethylene protons appear as a slightly broadened singlet, as already reported in the literature for the related [PtMe(daph)(ethylene)]$^+$ or [PtMe(4,4′-Bu^t-2,2′-bipy)(ethylene)]$^+$ complexes.[27,49] The broad olefinic signal exhibited at room temperature indicates that these complexes, even in the absence of added external ethene, might be involved in a fast dynamic process, most probably an exchange between coordinated and free ethene that may be produced after dissolution of the complexes, either by ligand dissociation or by an associative process involving the solvent.[50] Any attempt to study the ethene exchange on these two species, as well as for the other uncyclometalated compounds **3**−**6** and for the highly planar cyclometalated complex [Pt(bipy$^\phi$)(C_2H_4)]BArF (**9**), failed even when we used a very low ethene concentration at the lowest investigated temperature (T = 203 K). This fact led us to conclude that, in these cases, ethene exchange reaction was too fast to be monitored on the NMR time scale, maybe due to a less congested platinum(II) environment brought about by the CNN-type spectator ligands.

Therefore, the intermolecular exchange between coordinated and free ethylene was studied by the DNMR technique for the cyclometalated complexes **7**, **8** and **10**−**12**, which react at room temperature with free ethylene with rates suitable for the proton NMR technique. The process takes place according to Scheme 5, with no evidence throughout of olefin insertion into the Pt−C bond or of five-coordinated species formation.

The exchange rates were determined by line-broadening ^{1}H NMR experiments at room temperature, as a function of the concentration of ethylene added in solution, while the temperature dependence of the ethene exchange rates was obtained by full line-shape analysis of spectra taken at different temperatures.

Kinetics of Ethene Exchange. i. Ligand Concentration Dependence. Figure 3 shows typical ^{1}H NMR spectra as a function of ethene concentration, recorded at 298 K on a chloroform-*d* solution of complex **8**. At comparable ethene and complex concentrations, the spectra show broad averaged signals relative to the free and the coordinated ligand. Comparison between experimental and calculated peak shapes afforded the values of the rate constants for each olefin concentration.

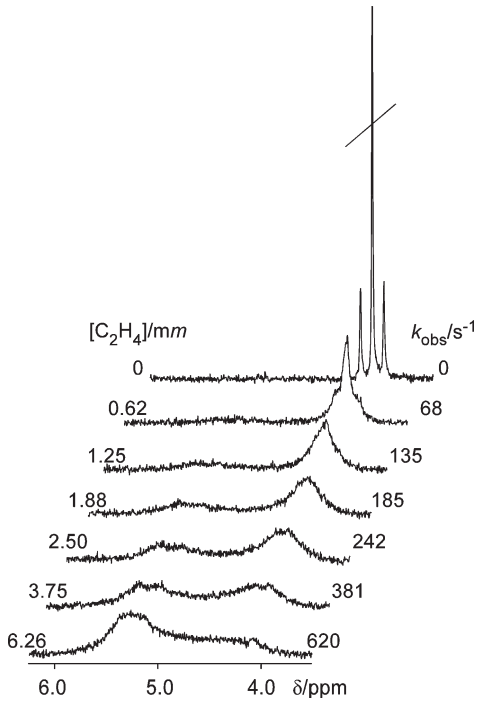
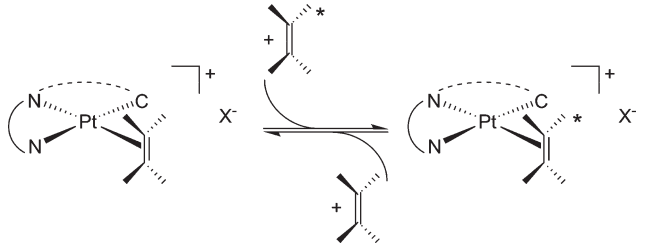


Figure 3. Aliphatic portion of the ^{1}H NMR spectra of **8** showing the line-broadening effect on the signal of the coordinated olefin as a function of ethene concentration (chloroform-*d*; 300.13 MHz; experimental conditions: T = 298 K; C_{Pt} = 3.55 m*m*; ligand concentrations, [C_2H_4]/m*m*, and best-fit first-order rate constants, k_{obs}/s^{-1}, for the ethene exchange are reported on the left and the right side of the spectra, respectively).

Scheme 5. Ethene Exchange on Cationic Platinum(II) Complexes of the Type [Pt(CNN)(C_2H_4)]$^+$



For all the investigated systems, these pseudo-first-order rate constants (k_{obs}/s^{-1}) when plotted against the ethylene concentrations give straight lines with no intercept value (Figure 4). The second-order rate law (eq 6) assumed for this exchange reaction is as follows:

$$k_{obs} = k_{exc}[C_2H_4] \quad (6)$$

Pseudo-first-order rate constants for complexes **7**, **8**, and **10**−**12** as a function of ethene concentrations, together with the corresponding second-order rate constants ($k_{exc}/s^{-1}\ m^{-1}$), obtained from linear regression analysis of the rate law, are given as Supporting Information in Table S2.

ii. Variable-Temperature Experiments. The intermolecular ethylene exchange process on complexes **7**, **8**, and **10**−**12** was investigated in the temperature range 198−341 K in $CDCl_3$.

(49) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809–1813.
(50) Kaplan, P. D.; Schmidt, P.; Brause, A.; Orchin, M. *J. Am. Chem. Soc.* **1969**, *91*, 85−88, and references therein.

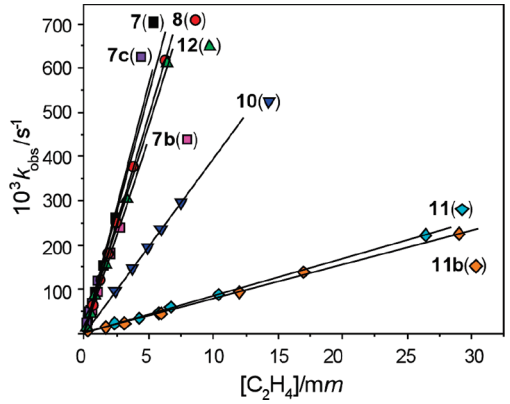


Figure 4. Dependence of the observed pseudo-first-order rate constants (k_{obs}/s^{-1}) for ethene exchange on complexes **7**, **8**, and **10**−**12** as a function of different amounts of free ethylene (experimental conditions: C_{Pt} = 3−5 m*m*, $[C_2H_4]$ = 0−30 m*m* in chloroform-*d* at 298 K).

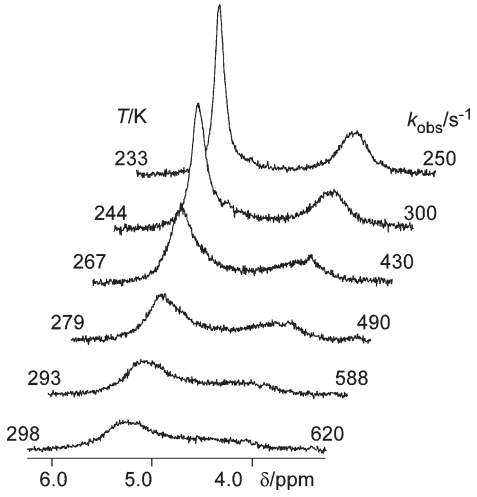


Figure 5. Variable-temperature ^{1}H NMR spectra of complex **8** showing the free and coordinated ethylene protons peaks (chloroform-*d*; 300.13 MHz; experimental conditions: C_{Pt} = 3.55 m*m*; $[C_2H_4]$ = 6.26 m*m*; temperature, *T*/K, and rate constants, k_{obs}/s^{-1}, for the ethene exchange are reported on the left and the right side of the spectra, respectively).

At a sufficiently low temperature a significant amount of ethene (about 2:1 with respect to the complex concentration) was added in solution and the ^{1}H NMR spectrum was recorded. Separated broad signals for free and coordinated ethene were observed (Figure 5), which averaged on raising the temperature, according to the corresponding increase of the exchange rate constants.

The activation parameters for the exchange of ethene were obtained from Eyring plots (Figure 6) over the temperature range 198−341 K.

Rate constants of the exchange reaction as determined by full line shape analysis and the activation parameters for the process derived from Eyring plots are collected and given as Supporting Information in Table S3.

iii. The Mechanism. Square-planar un- and cyclometalated platinum(II) complexes of the type $[Pt(CNN)(C_2H_4)]^+$ (**1**−**6** and **7**−**12**, respectively) were particularly designed to have the following characteristics: (i) they must be soluble and thermally stable in organic solvents; (ii) in the cationic complex ion all but one coordination sites must be blocked by robust ligands in order to prevent side reactions or possible ring-opening or -closures; (iii)

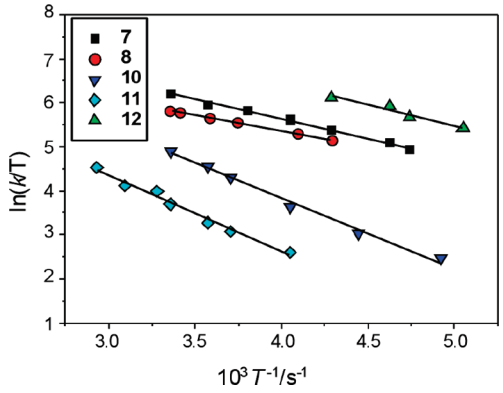


Figure 6. Eyring plots obtained for ethene exchange on cyclometalated platinum(II) complexes **7**, **8**, and **10**−**12** from ^{1}H DNMR data measured in chloroform-*d*.

only one of the coordinated ligands, namely, the olefin group in this case, must undergo substitution. Accordingly, the ethene exchange in these cyclometalated complexes (where HC-NN = bipy^t, **7**; bipy^n, **8**; bipy$^{\alpha Me}$, **10**; bipy$^{\alpha Et}$, **11**; bipy^c, **12**) takes place in a single step according to Scheme 5.The fused [5,5]- and [5,6]-ring systems are robust, and there is no evidence of ring-opening or of other concurrent processes. The systematic kinetics of these reactions studied at different olefin concentrations by DNMR techniques prove the dependence of the pseudo-first-order rate constants described by straight lines (Figure 4). The contribution of the reagent-independent term k_1 is negligible (k_1 usually refers to a solvolytic path, and k_2, i.e., k_{exc}, is the second-order rate constant for the bimolecular attack of the olefin on the substrate, as shown in Supporting Information Scheme S1). The absence of a k_1 term indicates that, as expected, a poor nucleophilic solvent such as chloroform cannot provide a solvolytic pathway to the products, but also proves the absence of a possible parallel dissociative pathway.

The values of k_{exc}, with their standard deviations, from the linear regression analysis of the dependence of k_{obs} on $[C_2H_4]$, at 298 K, are listed in Table 3, together with the obtained corresponding activation parameters. The values of the activation entropies, obtained by Eyring analysis of variable-temperature kinetic data, are negative, as expected for associative processes. Significantly, the $T\Delta S^{\ddagger}$ contribution to the free energy of activation is extremely large, amounting to more than 80% for all complexes, while the enthalpy terms are correspondingly small. Analogous situations with formation of a well-ordered, stable transition state have been previously reported in other substitution or exchange reactions involving leaving groups *trans* to an olefin.[51−53,12,54]

All the results illustrated above strongly suggest that a nondissociative alkene exchange is operative,[12] a process already discussed for square-planar platinum(II) complexes[27] and also found in the case of the isostructural

(51) Steyn, G. J. J.; Roodt, A.; Poletaeva, I.; Varshavsky, Y. S. *J. Organomet. Chem.* **1997**, *536*/*537*, 197–205.
(52) Holloway, C. E.; Fogelman, J. *Can. J. Chem.* **1970**, *48*, 3802–3806.
(53) Guillot-Edelheit, G.; Chottard, J.-C. *J. Chem. Soc., Dalton Trans.* **1984**, 169–173.
(54) (a) Fanizzi, F. P.; Intini, f. P.; Maresca, L.; Natile, G.; Gasparini, F. *J. Chem. Soc., Dalton Trans.* **1990**, 1019–1022. (b) Hahn, C.; Morvillo, P.; Herdtweck, E.; Vitagliano, A., *Organometallics* **2002**, 2002, 1807−1818.

Table 3. Second-Order Rate Constants and Activation Parameters for Ethene Exchange in Some Square-Planar Platinum(II) Complexes

complex	$10^{-3}k_{exc}{}^{298a}$	$\Delta H^{\ddagger b}$	$\Delta S^{\ddagger c}$	$\Delta G^{\ddagger d}$	ref
[Pt(bipy^{t}-H)(C_2H_4)]BArF (**7**)	109 ± 2	7.3 ± 0.2	−121.5 ± 0.9	43.5	this work
[Pt(bipy^{t}-H)(C_2H_4)]CF_3SO_3 (**7b**)	88.7 ± 0.7			44.7[e]	this work
[Pt(bipy^{t}-H)(C_2H_4)]PF_6 (**7c**)	113 ± 1			44.1[e]	this work
[Pt(bipy^{n}-H)(C_2H_4)]BArF (**8**)	99 ± 1	5.9 ± 0.1	−129.4 ± 0.4	44.5	this work
[Pt(bipy$^{\phi}$-H)(C_2H_4)]BArF (**9**)				≪40	this work
[Pt(bipy$^{\alpha Me}$-H)(C_2H_4)] BArF (**10**)	39.3 ± 0.1	13.4 ± 0.5	−112 ± 2	46.8	this work
[Pt(bipy$^{\alpha Et}$-H)(C_2H_4)] BArF (**11**)	8.4 ± 0.1	14.5 ± 0.8	−118 ± 3	49.5	this work
[Pt(bipy$^{\alpha Et}$-H)(C_2H_4)]CF_3SO_3 (**11b**)	7.8 ± 0.1			50.8[e]	this work
[Pt(bipy^{c}-H)(C_2H_4)]BArF (**12**)	94 ± 1	8 ± 1	−112 ± 5	41.4	this work
$[PtCl_3(C_2H_4)]^-$[f]	2.1 ± 0.1	19.1 ± 0.3	−117 ± 1	53.8	12
trans-[$PtCl_2(C_2H_4)$MeOH][f]	500 ± 20	10.2 ± 0.4	−102 ± 2	40.6	12
trans-[$PtCl_2(C_2H_4)$(imidazole)][g]	0.148 ± 0.01	29.3 ± 0.6	−105 ± 2	60.6	51
[Pt$Cl(C_2H_4)$(acac)]	2.6 ± 0.2	8.8 ± 0.7	−150 ± 20	53.5	52
trans-[$PtCl_2$(ol)(py)]	4.3 ± 0.4	45 ± 8	−140 ± 20	46.2	53
[Pt(Et)(N−N)(C_2H_4)]BArF[h]	3.7			52.8	9

[a] At 298 K, s^{-1} m^{-1}, in chloroform-*d* unless otherwise stated. [b] kJ mol^{-1}. [c] J K^{-1} mol^{-1}. [d] At 298 K, kJ mol^{-1}. [e] Calculated from the single value of k_{exc} at 298 K. [f] In methanol-d_4. [g] In acetone-d_6. [h] In CD_2Cl_2 at 300 K. N−N = [(2,6-$Me_2C_6H_3$)N=C(An)-C(An)=N(2,6-$Me_2C_6H_3$)] (An = 1,8-naphthalenediyl).

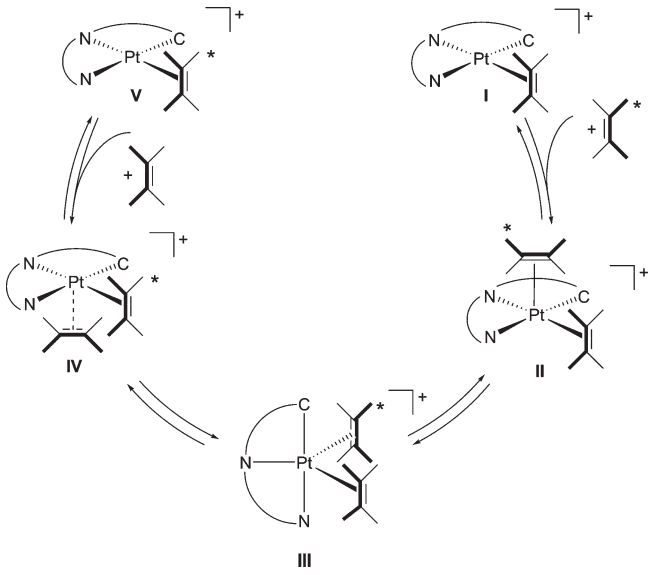
rhodium(I) ethylene complex, by freezing the five-coordinated species as the intermediate at low temperature.[55]

Scheme 6 illustrates the suggested associative mechanism, similarly to that proposed for dynamic processes in alkene complexes.[23,27] It involves a five-coordinated bis(ethylene) intermediate that accounts for the dynamic NMR behavior through a twisting of the trigonal faces of the square-planar pyramid, thus resulting in the interconversion of two square-planar pyramid intermediates (**II** and **IV**) via a five-coordinated bis(ethylene) trigonal-bipyramid intermediate (**III**).

Interestingly, as far as compounds **8**, **10**, and **11** are concerned, a good correlation is found between the rates of ethene exchange (k_{exc}) and the rates of chloride for triphenylphosphane associative substitution on the analogous chloride compounds.[16] A comparison of the bimolecular rate constants indicates that the second process is at least 3 orders of magnitude slower than olefin exchange (in that case kinetics were followed by UV-Vis stopped-flow technique) and the changes in rate constants are less sensitive than k_{exc} to structural variations in the substrates. It is worthwhile to remark that the former compound [Pt(bipy$^{\phi}$-H)(Cl)], **9P**, in the case of the phosphane substitution process showed the fastest kinetic rate, i.e., almost 2 orders of magnitude greater than **2P**. This result must be compared to that obtained in the present study on olefin exchange processes, thus further confirming our deduction of a quite low activation free energy for **9**, $\Delta G^{\ddagger} \ll 40$ kJ mol^{-1} vs the related value of 43.5 kJ mol^{-1} calculated for [Pt(bipy^{t}-H)(C_2H_4)]BArF, **7**. Indeed, complex **9** evidences the fastest observable exchange rate constant within the series of the studied cyclometalated platinum(II) complexes. Interestingly, its extreme lability could also be explained in terms of ground-state destabilization, as the quite low value of the ^{195}Pt coupling constant for the bound ethene in this species ($^2J_{PtH}$ = 60 Hz) strongly suggests a longer and weaker platinum(II)−(η^2-olefin) bond.

Table 3 collects rate constants and free activation energies for ethene exchange reactions in square-planar platinum(II) complexes already reported in the literature, together with those from the present study. An inspection of this table reveals that the most closely related kinetic parameters are those of the cyclometalated complexes (**7**, **8**, **10**-**12**) together with that of complex [Pt(Et)(N−N)(C_2H_4)]BArF,[9] recently reported by Shiotsuki et al. Undoubtedly for all of them ethene exchange takes place with the associative mechanism reported above.

Scheme 6. Associative Mechanism for the Ethene Exchange on Square-Planar Cyclometalated Platinum(II) Species **7**−**12** in Chloroform-*d* Solutions



Further comments on the data included in Table 3 relative to platinum(II) complexes with very different arrangement of ancillary ligands could be tricky, as we do not have any information whether they refer to a concerted olefin exchange (see Scheme 6) or to an associative mechanism involving consecutive displacement of ligands. This latter mechanism was shown to be operative in the ethene exchange on $[PtCl_3(C_2H_4)]^-$ and in the corresponding methanol solvolysis product, *trans*-[$PtCl_2$-(C_2H_4)(MeOH)].[56] Here the much higher reactivity of the

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solvento species (k_{exc} = 500 × 10^3 M^{-1} s^{-1}) with respect to the chloride species (k_{exc} = 2.1 × 10^3 M^{-1} s^{-1}) is justified only by the much greater lability of MeOH with respect to Cl^-, while it is clearly in disagreement with the poor *trans*-activating ability of MeOH with respect to the chloride anion. The mechanism for olefin exchange in *trans*-[$PtCl_2(C_2H_4)$(MeOH)] and [$PtCl_3(C_2H_4)]^-$ [12] thus, as already reported in other nucleophilic processes in olefinic complexes,[50,57] most probably involves rate-determining associative attack by the entering olefin at the labile site *trans* to the coordinated olefin. This site is occupied by either a chloride or a solvent molecule through the formation of the bis-ethylene platinum(II) complex *trans*-[$PtCl_2(C_2H_4)_2$], whose presence in solution was confirmed later.[58]

In the case of the cyclometalated complexes bipy^t (**7**), bipy^n (**8**), and bipy^c (**12**), the values of the rate constants and of the free energy of activation are compared for the reactions listed in Table 3. The differences of reactivity among the three members of the series are negligible (k_{exc} ca. 10^5 s^{-1} m^{-1}), suggesting that the energy barrier involved in the formation of the five-coordinate transition state appears to be marginally affected by changes in the nature and in the structural properties of the coordinated CNN ligands.

As previously suggested by literature data, the exchange process can be strongly retarded or frozen by steric hindrance induced by bulky substituents on the adjacent ligands.[27,59] In the series of studied cyclometalated complexes, we may conclude that when the ligands' steric hindrance comes into action, as for bipy$^{\alpha Me}$ and bipy$^{\alpha Et}$, the lability of ethene is decreased at least 1 order of magnitude (k_{exc} = 39.3 vs 8.4 × 10^5 s^{-1} m^{-1} for **10** and **11**, respectively). In these complexes the steric congestion of the CNN-terdentate ancillary orthometalated ligands, combined with the reduced symmetry brought about on the square-planar coordination plane, seems to inhibit even ethene rotation, and at room temperature both compounds show an AA′BB′ system for the four ethylene protons.

Conclusions

In this study, we have described the synthesis and the reactivity of a large class of cationic platinum(II) complexes [$Pt(CNN)(C_2H_4)]^+$, containing a η^2-ethene moiety, different diimines (N−N), and a methyl fragment or terdentate (κC-$\kappa^2 NN'$) anionic cyclometalating ligands.

The two kinds of platinum(II) complexes, [$Pt(Me)(NN)(C_2H_4)]^+$ (**1**−**6**) and [$Pt(CNN)(C_2H_4)]^+$ (**7**−**12**), exhibit a fair difference in the coordinated alkene lability. A detailed kinetic study of the dynamic behavior of ethene was performed by line-broadening NMR techniques as a function of ligand and temperature dependence in complexes **7**, **8**, and **10**−**12**, where the process was not too fast on the NMR time scale to be investigated. The ethene lability may be correlated to differences in the bulkiness of the spectator ligands around the platinum(II) center (i.e., the carbon dinitrogen CNN skeleton). In the case of the uncyclometalated complexes **1**−**6** and of the cyclometalated species **9**, all showing lower steric hindrance above and below the coordination plane and a lower congestion around the platinum(II) center, a fast exchange between coordinated and free olefin takes place in solution (even at the lower accessible temperature). The ethylene exchange in **7**, **8**, and **10**−**12** complexes is first order in ethylene concentration and is characterized by large negative activation entropy. As in the reaction of chloride for phosphanes substitution in uncharged parent chloride complexes **7P**−**12P**,[16] the kinetic data for olefin exchange are compatible with an associative mechanism involving the interconversion of two short-lived labile square-pyramid intermediates via a five-coordinated bis(η^2-ethylene) trigonal-bipyramid intermediate, in which both ethene moieties lie in the trigonal coordination plane. All the experimental findings indicate that, in such cationic platinum(II) [$Pt(CNN)(C_2H_4)]^+$ complexes, ethene exchange is particularly sensitive to the choice of the coordinated 6-substituted-2,2′-bipyridines, depending on the nature of the bonded organic moiety or anchoring pendant (alkyl or aryl), on the size of the ring, or on the number of alkyl substituents on it. Considering the data as a whole, a crucial role seems to be played by the capability of the anionic CNN-type fragments to introduce steric hindrance above and below the square-planar coordination plane and the involved trigonal- and square-pyramidal intermediates increasing the reaction energetics, as in **10** and **11**, where the ethene lability is strongly reduced.

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Supporting Information Available: Experimental Section includes the ^{1}H NMR characterization and elemental analysis for the precursor complexes **4P** and **5P**, the non-cyclometalated species **2**−**6**, and the cyclometalated compounds **8**−**12** and **11b**; X-ray data collection and structure determination for **5** and **7**, together with their structural studies; a paragraph on the error analysis. Tables include the experimental data for the X-ray diffraction study of compounds **5** and **7**; the ethene and temperature dependence, respectively, of the observed exchange rate constants (k_{obs}/s^{-1}) together with derived second-order rate constants (k_{exc}/s^{-1} m^{-1}) and the activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$) for the ethene exchange reaction on [$Pt(CNN)(C_2H_4)$]BArF complexes in $CDCl_3$. Figures include the chemical shift changes for the aromatic protons of complex **7** as a function of the added counteranion, (^{n}Bu$_4$N)PF_6 (upper side) and ball-and-stick representation of the tight ion-pair complex 7c, together with numbering (lower side); ORTEP view of the platinum(II) cationic complexes **5** and **7**, with selected bond lengths (Å) and angles (deg) given in the figure captions; ^{1}H NMR spectra of complexes **6** and **7**. Crystallographic data for structures **5** and **7** are available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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