

[PtR(η^2 -olefin)(N-N)]⁺ Complexes Containing the Olefin and the Alkyl Ligand in a *cis* Arrangement. Preparation, Structural Characterization, and Olefin Stereochemistry

Maria Fusto, Federico Giordano, Ida Orabona, and Francesco Ruffo*

Dipartimento di Chimica, Università di Napoli "Federico II", via Mezzocannone 4, I-80134 Napoli, Italy

Achille Panunzi

Facoltà di Agraria and Dipartimento di Chimica, Università di Napoli "Federico II", via Mezzocannone 4, I-80134 Napoli, Italy

Received May 27, 1997[®]

Cationic Pt(II) complexes containing an alkyl and an olefin in *cis* positions are described. The compounds (**1**) of general formula [PtR(N-N)(olefin)]BF₄ are obtained either through oxidative addition of the trialkyloxonium salt R₃O⁺BF₄[−] to the appropriate three-coordinate precursor [Pt(N-N)(olefin)] or by substitution of an alkene for the chloride in [PtR(Cl)(N-N)] complexes. The complexes are involved in a dynamic process involving the alkene ligand. The rate of alkene exchange is strongly influenced by the steric hindrance of the N-N ligand above and below the coordination plane. This feature also controls the stereochemistry of alkene coordination. Thus, for type **1** derivatives of α -olefins containing the highly crowded diacetyl bis(di-isopropylphenylimine), only one enantiomeric couple has been detected in the temperature range 203–328 K, and its geometry has been tentatively assigned. Finally, the X-ray crystal structure of a representative complex has been determined.

Introduction

It is generally accepted¹ that the attainment of the *cis* arrangement of an unsaturated ligand and an alkyl group in the coordination sphere of a transition-metal ion precludes the subsequent insertion reaction. The *cis* geometry is generally favored by using suitable ancillary ligands, *e.g.* bidentate chelates which leave adjacent positions in the coordination polyhedron available for the coordination of the carbon ligands. The most recent findings² in line with this approach deal with olefin polymerization promoted by Ni(II) and Pd(II) complexes in the presence of suitable N-N nitrogen chelates. The active species are considered to be cationic complexes of formula [M(N-N)(Me)(olefin)]⁺, which in the case of Pd complexes could be detected in solution at 163 K through NMR spectroscopy.^{2a}

The increasing interest in these reactive systems prompted us to investigate the chemistry of stable platinum(II) species analogous to those mentioned. This aim was also suggested by the fact that only very few cationic Pt(II) complexes showing a *cis* arrangement of the olefin and of the alkyl group have been described so far,³ despite a fairly extended knowledge of the analogous *trans* species.⁴ Here we report an extension of the preliminary study.⁵

Results and Discussion

Synthesis of the Complexes. The N-N ligands and the olefins used in this work are shown in Chart 1. The choice of N-N chelates has been dictated by the aim of obtaining a wide range of steric hindrance, while the most common olefins have been used as unsaturated ligands. Table 1 lists the complexes.

Two synthetic procedures have been adopted (eqs 1 and 2 in Scheme 1). The first one⁵ is the oxidative addition of a trialkyloxonium salt to the three-coordinate platinum(0) precursor [Pt(phen)(dimethyl fumarate)] (**2a**). The resulting products [PtR(phen)(dimethyl fumarate)]BF₄ (R = Me, **1a**; R = Et, **1b**) can be either isolated in the solid state or reacted *in situ* with a suitable alkene. In the latter case, the electron-poor dimethyl fumarate is readily displaced by the incoming olefin, which affords the corresponding type **1** product. Since this route does not produce any precipitate, it is particularly useful in cases where the reactions are performed in NMR tubes.

The alternative procedure, described by eq 2, consists of the addition of AgBF₄ to a dichloromethane solution of the planar species [PtClMe(N-N)] (**3**) in the presence of the appropriate olefin. This method has been used when N-N is a diacetyl bis(diarylimine), since the corresponding type **2** precursors are not easily available.

Type **1** products are air stable and can be stored at 277 K without appreciable decomposition for several months.

Daproph, daethyph, and daph derivatives are soluble in chlorinated solvents, in which NMR investigations can be carried out at low temperatures. Slow addi-

[®] Abstract published in *Advance ACS Abstracts*, November 15, 1997.

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

(2) (a) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137–1138. (b) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415. (c) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267–268.

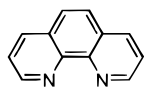
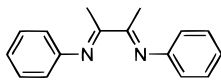
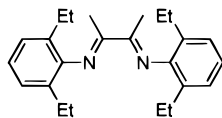
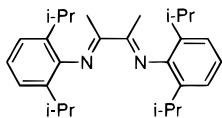
(3) (a) Clark, H. C.; Jablonsky, C. R.; von Werner, K. *J. Organomet. Chem.* **1974**, *82*, C51–C52. (b) Cucciolito, M. E.; De Felice, V.; Panunzi, A.; Vitagliano, A. *Organometallics* **1989**, *8*, 1180–1187. (c) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809–1813.

(4) Chisholm, M. H.; Clark, H. C. *Inorg. Chem.* **1973**, *12*, 991–998.

(5) Orabona, I.; Panunzi, A.; Ruffo, F. *J. Organomet. Chem.* **1996**, *525*, 295–298.

Chart 1. N-N and Olefin Ligands Used in This Work

N,N-chelates

1,10-phenanthroline
phendiacetyl bis(phenylimine)
daphdiacetyl bis(2,6-diethylphenylimine)
daethyphdiacetyl bis(2,6-isopropylphenylimine)
daproph

Olefins: dimethylfumarate, ethylene, propylene,
styrene, allyl alcohol, *trans*-2-butene

tion of toluene to their solutions in methylene chloride allows the formation of well-shaped orange-red single crystals.

Complexes of phen are white microcrystalline solids poorly soluble in chlorocarbons but fairly soluble in nitromethane. This has limited the study of their solution behavior (see below), since the melting point of deuterionitromethane is *ca.* 243 K.

The characterization of type **1** complexes has been carried out through elemental analyses, NMR spectroscopy, and, in one case, through the determination of the X-ray crystal structure (**1o**; see below).

NMR Spectroscopy and Olefin Dynamic Behavior.⁶ **A. General Features.** ¹H and ¹³C NMR spectra (Tables 1 and 2) show the nonequivalence of the halves of the complexes.⁷ The differences in $J_{\text{Pt-H}}$ or $J_{\text{Pt-C}}$ of corresponding nuclei in the halves of the N-N ligands are in agreement with the higher *trans* influence of alkyl groups relative to olefins.⁸ As an example, the $^3J_{\text{Pt-H}}$ coupling constant of the phen proton which is close to the N atom *trans* to the alkene is *ca.* 50 Hz. The value drops to *ca.* 15 Hz when the corresponding nucleus opposite to Me or Et is considered.

In phen complexes, as also observed for closely related methyl/alkyne [PtMe(phen)(alkyne)]⁺ derivatives,⁹ ¹H NMR peaks pertaining to Pt-Me groups appear at *ca.* 1 ppm. The olefin protons resonate within 1 ppm upfield with respect to the free ligand. The corresponding signals in diacetyl bis(diarylimine) derivatives undergo a larger high-field shift, possibly owing to the shielding due to the aryl groups, which lie almost perpendicular to the coordination plane and thus face the olefin protons (see X-ray structure of **1o**).

In ¹³C spectra, no significant difference ensues between phen and diacetyl bis(diarylimine) complexes. In

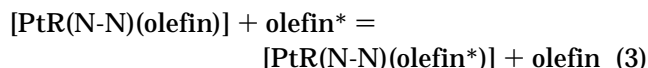
all cases, Pt-¹³CH₃ resonances lie in the range -10 to 0 ppm. The olefin carbons resonate in the range typical for square-planar Pt(II)-olefin complexes; *i.e.*, $\Delta\delta$ values between free and coordinated olefins are within 30-55 ppm.¹⁰

B. Olefin Exchange. In the presence of chelates which do not introduce substantial steric hindrance below and above the coordination plane (*i.e.* phen or daph), the protons of ethylene, styrene, and allyl alcohol do not couple to ¹⁹⁵Pt at room temperature. More precisely, ethylene appears as a slightly broadened singlet, as also observed^{3c} for the related complex [PtMe-(4,4'-*t*-Bu-2,2'-bipy)(ethylene)]⁺. Styrene and allyl alcohol give rise to the typical α -olefin pattern (*e.g.* an AMX multiplet for styrene).

On the other hand, propylene and *trans*-2-butene protons do couple to ¹⁹⁵Pt at room temperature in the spectra of the phen or daph derivatives. However, in the presence of 0.1 equiv of free propylene, the olefin protons of **1e**, **1f**, and **1q** lose their satellites and give rise to averaged signals accounting for the free and the coordinated molecule.

Thanks to the fair solubility of the daph derivatives **1p**, **1r** in dichloromethane, their spectra could be recorded in the range 328-203 K. At the lower temperature, broadening of the ethylene resonance in **1p** is observed. The behavior of **1r** is similar but deserves further comment (see below).

The above NMR findings¹¹ clearly show that type **1** complexes of phen and daph are involved in a fast dynamic process, most probably exchange between coordinated and free olefin¹² (eq 3).



The observations that excess alkene enhances the rate of exchange and that the halves of the N-N ligands are not equivalent suggest that the process may occur *via* an associative mechanism involving a five-coordinate bis(olefin) intermediate (**III** in Scheme 2). In this case, by considering that the N atom labeled with a prime is always *trans* to Me, it is clear that the overall process occurs without exchanging the halves of the N-N chelate.

The hypothesis concerning an associative mechanism is supported by the results obtained by using N-N ligands with steric crowding below and above the coordination plane. These ligands are known^{2b} to inhibit the associative exchange of a ligand on a four-coordinate d⁸ ion, according to the expectation that the square-pyramidal initial adducts (in our case **II** and **IV**) would suffer severe steric constraints. This approach was effectively used in the inhibition of associative processes in polymerizations promoted by Pd(II).^{2b} In fact, in daproph type **1** derivatives, the protons of ethylene, styrene, and allyl alcohol of **1k-n** couple to ¹⁹⁵Pt in the NMR spectra at room temperature. Noticeably, even at 328 K and in the presence of an excess

(6) Since the olefin dynamic behavior has been investigated through NMR spectroscopy, henceforth a process which is *slow* (or *fast*) on the NMR time scale will be simply indicated as *slow* (or *fast*).

(7) In the NMR spectra of the dimethyl fumarate derivatives **1a,1b** both phen and the olefin are symmetric.⁵ A possible explanation of the high symmetry displayed by the complexes may be given by admitting that the electronic properties of the electron-poor alkene allow the occurrence of a fast dissociative/associative equilibrium.

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

(9) Cucciolito, M. E.; De Felice, V.; Orabona, I.; Ruffo, F. *J. Chem. Soc., Dalton Trans.* **1997**, 1351-1355.

(10) Cooper, D. G.; Powell, J. *Inorg. Chem.* **1976**, *15*, 1959-1968.

(11) The conclusions which will be henceforth presented are mainly derived from ¹H NMR spectra. ¹³C NMR spectra are fully consistent with them.

(12) Traces of free olefin may be generated after dissolution of the complexes, either by dissociation or by an associative process involving the solvent.

Table 1. Selected ¹H NMR Data^a for Type 1 Complexes

compd no.	formula	Pt-CH _x ^b	H(olefin) ^b	other signals ^c
1a ^{d,e}	[PtMe(phen)(dimethyl fumarate)]BF ₄	1.10 (75, 3H)	5.33 (br, 2H)	9.47 (d, 2H)
1b ^f	[PtEt(phen)(dimethyl fumarate)]BF ₄	1.60 (br, 2H)	5.00 (br, 2H)	9.40 (d, 1H) 8.69 (d, 1H)
1c ^{d,e}	[PtMe(phen)(ethylene)]BF ₄	0.93 (71, 3H)	4.54 (br, 4H)	9.20 (50, d, 1H) 8.67 (14, d, 1H)
1d ^d	[PtEt(phen)(ethylene)]BF ₄	1.35 (74, q, 2H)	4.45 (br, 4H)	9.20 (50, d, 1H) 1.09 (29, t, 3H)
1e ^{d,e}	[PtMe(phen)(propylene)]BF ₄	0.93 (73, 3H)	5.41 (m, 1H) 4.45 (m, 1H) 4.26 (m, 1H)	9.17 (58, d, 1H)
1f ^d	[PtEt(phen)(propylene)]BF ₄	1.45 (73, q, 2H)	5.40 (m, 1H) 4.3 (m, 2H)	9.30 (48, d, 1H) 1.10 (30, t, 3H)
1g ^{d,e}	[PtMe(phen)(styrene)]BF ₄	0.77 (73, 3H)	6.62 (dd, 1H) 4.88 (dd, 1H) 4.53 (m, 1H)	9.16 (53, d, 1H) 8.66 (15, d, 1H)
1h ^d	[PtEt(phen)(styrene)]BF ₄	1.35 (69, q, 2H)	6.52 (dd, 1H) 4.92 (d, 1H) 4.54 (d, 1H)	0.83 (t, 3H)
1i ^d	[PtMe(phen)(allyl alcohol)]BF ₄	0.95 (73, 3H)	5.39 (m, 1H) 4.45 (m, 2H)	9.20 (45, d, 1H)
1j	[PtMe(phen)(<i>trans</i> -2-butene)]BF ₄	1.11 (74, 3H)	5.15 (67, br, 2H)	9.25 (48, d, 1H) 1.97 (46, br, 6H)
1k ^f	[PtMe(daproph)(ethylene)]BF ₄	0.18 (70, 3H)	3.72 (68, 4H)	2.51 (3H) 2.28 (3H)
1l ^f	[PtMe(daproph)(propylene)]BF ₄	0.25 (70, 3H)	4.30 (80, m, 1H) 3.75 (m, 2H)	2.48 (3H) 2.27 (3H) 1.61 (60, d, 3H)
1m ^f	[PtMe(daproph)(styrene)]BF ₄	-0.26 (72, 3H)	5.73 (87, dd, 1H) 4.05 (58, d, 1H) 3.33 (70, d, 1H)	2.49 (3H) 2.33 (3H)
1n ^f	[PtMe(daproph)(allyl alcohol)]BF ₄	0.27 (71, 3H)	4.36 (73, m, 1H) 3.70 (m, 2H)	2.45 (3H) 2.23 (3H)
1o ^f	[PtMe(daethyph)(ethylene)]BF ₄	0.13 (70, 3H)	3.68 (68, 4H)	2.50 (3H) 2.20 (3H)
1p ^f	[PtMe(daph)(ethylene)]BF ₄	0.20 (70, 3H)	3.71 (br, 4H)	2.39 (3H) 2.12 (3H)
1q ^f	[PtMe(daph)(propylene)]BF ₄	0.25 (71, 3H)	4.57 (77, dd, 1H) 3.80 (72, d, 1H) 3.57 (64, d, 1H)	2.35 (3H) 2.12 (3H)
1r ^f	[PtMe(daph)(styrene)]BF ₄	-0.04 (70, 3H)	5.50 (br, 1H) 4.15 (br, 1H) 3.75 (br, 1H)	2.37 (3H) 2.12 (3H)
1s ^f	[PtMe(daph)(<i>trans</i> -2-butene)]BF ₄	0.36 (72, 3H)	4.52 (66, m, 1H) 4.00 (70, m, 1H)	2.62 (d, 3H) 2.50 (30, d, 3H) 2.37 (3H) 2.10 (3H)

^a At 200 or 270 MHz and 298 K. Abbreviations: no attribute, singlet; br, broad; d, doublet; m, multiplet; q, quartet; t, triplet. ^b ²J_{Pt-H} (Hz) in parentheses. ^c ³J_{Pt-H} (Hz) in parentheses. ^d Data from ref 5. ^e In CD₃NO₂ (CHD₂NO₂ (δ 4.33 ppm) as internal standard). ^f In CDCl₃ (CHCl₃ (δ 7.26 ppm) as internal standard).

alkene, no exchange is observed for the α-olefin derivatives **1l–n**.

On the other hand, in the case where the unsaturated ligand is the less bulky ethylene (**1k**), the olefin resonance is sharp and is coupled up to 328 K, while broadening of the signal occurs if some ethylene is added to the solution at 298 K.

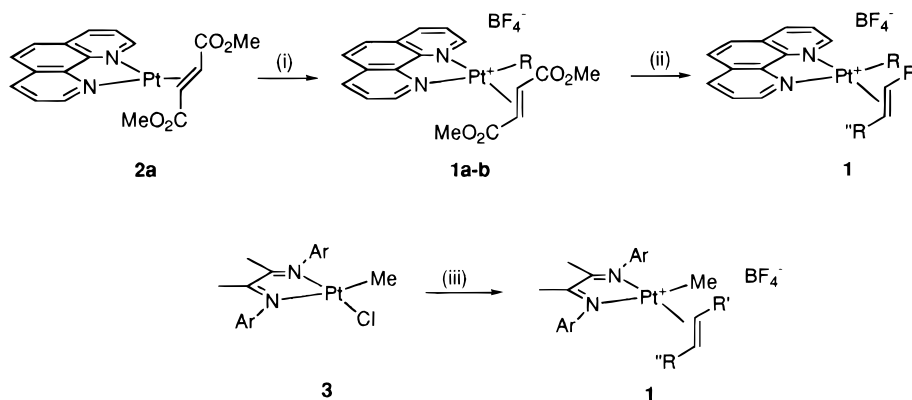
C. Olefin Rotation and Coordination Selectivity. As for olefin rotation around the Pt–alkene bond, the spectra provide information only when the olefin exchange is slow, *i.e.* coupling to ¹⁹⁵Pt is detectable. In this situation, one may be able to observe more than one isomer for a given complex, depending on the symmetry of the alkene.

Ethylene can afford only one species. In the case of the complexes **1k,o** the presence of a sharp singlet

(flanked by satellites) clearly indicates that at room temperature ethylene is rotating rapidly. Only below 213 K does broadening of the signals occur in the NMR spectra recorded in CD₂Cl₂, which reflects slower rotation on the NMR time scale.

α-Olefins may give rise to two enantiomeric pairs (respectively, 1' and 1'' in Figure 1 in the case of daph or daproph). They differ in the orientation of the alkene substituent, which can be oriented toward the Pt–Me bond or the opposite side. A 180° rotation of the olefin (Figure 1) converts each isomer of one enantiomeric pair into an isomer belonging to the other pair.

The spectra of the α olefin complexes of daproph **1l–n** consist of a unique spectral pattern between 203 and 308 K, with no significant variations of the chemical shifts along the whole range of temperatures (in Figure

Scheme 1^a

^a Legend: (i) +R₃OBF₄, -R₂O; (ii) +R'CH=CHR'', -(dimethyl fumarate); (iii) +AgBF₄, +R'CH=CHR'', -AgCl.

Table 2. Selected ¹³C NMR Data^a for Type 1 Complexes

compd no.	formula	Pt-CH _x ^b	C(olefin) ^b	other signals ^c
1c^{d,e}	[PtMe(phen)(ethylene)]BF ₄	-6.7 (673, 1C)	71.3 (br, 2C)	
1d^d	[PtEt(phen)(ethylene)]BF ₄	11.4 (613, 1C)	71.2 (br, 2C)	18.9 (89, 1C)
1e^{d,e}	[PtMe(phen)(propylene)]BF ₄	-5.2 (702, 1C)	96.0 (br, 1C) 67.2 (br, 1C)	
1f^d	[PtEt(phen)(propylene)]BF ₄	8.5 (681, 1C)	94.5 (br, 1C) 67.5 (br, 1C)	20.7 (1C) 16.1 (39, 1C)
1g^{d,e}	[PtMe(phen)(styrene)]BF ₄	-2.6 (705, 1C)	95.8 (br, 1C) 1C ^f	
1h^d	[PtEt(phen)(styrene)]BF ₄	11.1 (627, 1C)	95.8 (br, 1C) 65.4 (br, 1C)	15.9 (35, 1C)
1i^d	[PtMe(phen)(allyl alcohol)]BF ₄	-5.5 (636, 1C)	97.0 (br, 1C) 66.1 (br, 1C)	63.5 (1C) 15.9 (35, 1C)
1j	[PtMe(phen)(<i>trans</i> -2-butene)]BF ₄	-3.8 (739, 1C)	90.5 (180, 1C) 88.1 (217, 1C)	20.0 (2C)
1k^g	[PtMe(daproph)(ethylene)]BF ₄	-4.7 (1C)	73.8 (192, 2C)	
1l^g	[PtMe(daproph)(propylene)]BF ₄	-3.0 (706, 1C)	98.0 (185, 1C) 70.5 (171, 1C)	
1m^g	[PtMe(daproph)(styrene)]BF ₄	0.5 (716, 1C)	96.4 (176, 1C) 61.3 (193, 1C)	
1n^g	[PtMe(daproph)(allyl alcohol)]BF ₄	-4.2 (687, 1C)	97.9 (205, 1C) 68.3 (173, 1C)	62.1 (1C)
1o^g	[PtMe(daethyph)(ethylene)]BF ₄	-5.1 (660, 1C)	74.0 (190, 2C)	
1p^g	[PtMe(daph)(ethylene)]BF ₄	-4.8 (660, 1C)	72.2 (br, 2C)	
1q^g	[PtMe(daph)(propylene)]BF ₄	-3.2 (699, 1C)	96.6 (188, 1C) 68.8 (121, 1C)	20.2 (1C)
1r^g	[PtMe(daph)(styrene)]BF ₄	-0.2 (1C)	95.9 (br, 1C) 62.6 (br, 1C)	
1s^g	[PtMe(daph)(<i>trans</i> -2-butene)]BF ₄	-2.6 (714, 1C)	91.0 (171, 1C) 90.4 (189, 1C)	19.7 (1C) 19.1 (1C)

^a At 50.3 MHz and 298 K. Abbreviations: no attribute, singlet; br, broad. ^b ¹J_{Pt-C} (Hz) in parentheses. ^c ²J_{Pt-C} (Hz) in parentheses.

^d Data from ref 5. ^e In CD₃NO₂ (¹³CHD₂NO₂ (δ 62.81 ppm) as internal standard). ^f Overlapped by the solvent signal. ^g In CDCl₃ (¹³CDCl₃ (δ 77.0 ppm) as internal standard).

2a we report the olefin region in the spectrum of **1l** recorded at 203 K in CD₂Cl₂). This may reflect either a fast interconversion **1'** ↔ **1''** or the presence of only one enantiomeric pair, "frozen" by a strongly hindered rotation.

We propose the latter hypothesis is the more reasonable and further suggest that only type **1'** isomers form. We note the following. (i) α-Olefins should suffer more constraints than ethylene when coordinated to the metal center. Thus, if ethylene rotation slows down at 203 K in **1k**, the same should hold true for substituted alkenes. (ii) An inspection of molecular models reveals that very unfavorable contacts would arise between the substituent

of the α-olefin and one *o*-substituent of one phenyl ring in type **1''** isomers. These constraints do not operate in **1'**. (iii) Attempts to obtain the complex [PtMe(daproph)(*trans*-2-butene)]⁺ failed. This, plausibly, is due to the fact that in this case the aforementioned unfavorable contacts cannot be avoided. (iv) When the steric hindrance of the ligand is substantially reduced by using daph, the *trans*-2-butene complex [PtMe(daph)(*trans*-2-butene)]⁺ (**1s**) can be isolated in high yield. (v) The Pt-Me resonance in the styrene complex **1m** is unusually high field (δ -0.26 ppm). This might be due to the shielding of the aromatic olefin substituent, which in a type **1'** isomer lies next to Me.

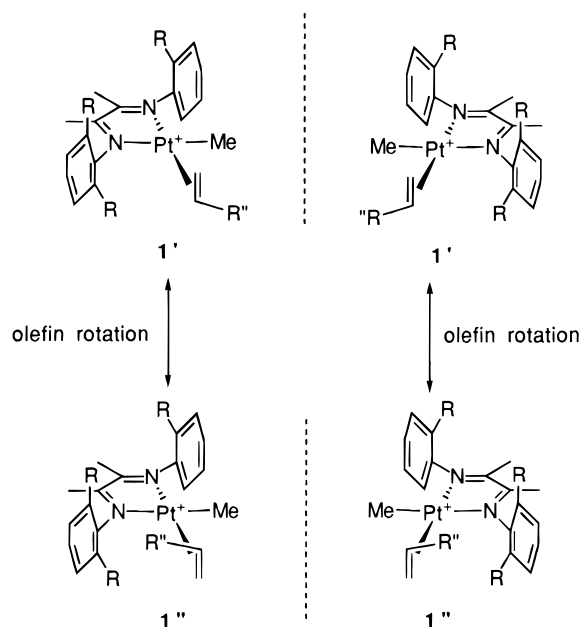
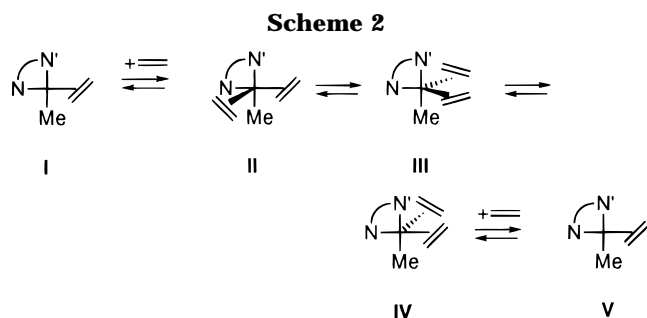


Figure 1. Type 1' and 1'' isomers (for the sake of clarity, one R substituent on one Ph group has been omitted).



On the other hand, the spectrum of the propylene derivative of daph species **1q** changes with temperature (Figure 2). At 298 K only one sharp (and coupled) spectral pattern is present. Below 233 K broadening of the signals occurs, and at 203 K the two expected enantiomeric pairs 1' and 1'' become clearly detectable in a 3:1 ratio. These data indicate that at room temperature a fast interconversion 1' \leftrightarrow 1'' occurs, which is inhibited on cooling. Since at 203 K the olefin chemical shifts of the most abundant pair are very close to those of the daproph analogue **1l** (Figure 2), it could be assumed that the former one has a type 1' structure.

Similarly, the styrene daph complex **1r** at 203 K exists as two pairs of enantiomers in the approximate ratio 4:1. Two broad resonances at -0.32 and 0.38 ppm are attributed respectively to the Pt-Me groups of the type 1' and the type 1'' couple, on the grounds of the argument already presented (point v).

The comparison between the behaviors of the corresponding daph and daproph complexes (*e.g.* **1l** vs **1q**) points out the effectiveness of the steric features of the latter ligand in promoting the selective coordination of α -olefins to a square-planar metal center. We remember that stereoselectivity in olefin coordination can also be successfully controlled by electronic factors, *e.g.* intramolecular attractive interactions.¹³

Finally, *trans*-2-butene can only afford one couple of enantiomers, obviously not distinguishable through NMR spectroscopy. For this olefin a comparatively low rotation rate is observed. This is reasonably due to

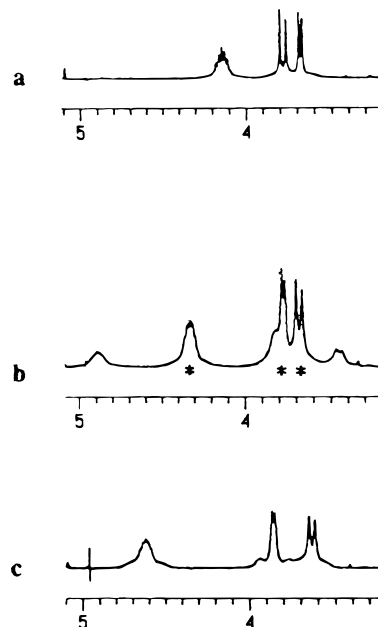


Figure 2. Olefin region in the 400 MHz ¹H NMR spectra of (a) **1l** at 203 K and of **1q** at (b) 203 K and (c) 298 K. Asterisks indicate the peaks pertaining to the most abundant isomer (1') of **1q** (see text).

steric reasons, as already discussed elsewhere for other square-planar Pt(II) complexes.¹⁴ More precisely, NMR spectra indicate that rotation of *trans*-2-butene in **1s** is hindered at room temperature, since the olefin protons are not equivalent and give rise to two multiplets. The signals slightly broaden at 328 K. The olefin is more dynamic in the phen derivative **1j**, in which spectrum broadening of the signals is detectable even at room temperature.

X-ray Crystal Structure of [PtMe(daethyph)-(ethylene)]BF₄ (1o**).** Complex **1o** has been chosen for X-ray studies because it represents a very close model of the active species in Pd(II)-catalyzed homogeneous polymerization.² However, the lack of X-ray investigations on similar complexes does not allow a thorough discussion about its structural features (see below). Indeed, compounds similar to **1o**, *i.e.* [PtMe(*o*-phenylenebis(dimethylarsine))(ethylene)]PF₆^{3a} and [PtMe(4,4'-*t*-Bu-2,2'-bipy)(ethylene)][B(Me)(C₆F₅)₃],^{3c} have only been investigated spectroscopically, while those characterized through X-ray studies¹⁵ do not display sufficient analogies with type 1 species.

A perspective view of the cation is shown in Figure 3, and the most relevant bond distances and angles are presented in Table 3.

Pt is in a square-planar coordination environment with the ethylene ligand nearly perpendicular to the coordination plane defined by Pt, N(1), N(2), and C(3). In fact, the C(1)–C(2) axis is tilted by 87(1)° on the coordination plane and its center is displaced 0.07(2) Å out of it.

(13) (a) Erickson, L. E.; Hayes, P.; Hooper, J. J.; Morris, K. F.; Newbrough, S. A.; Van Os, M.; Slangan, P. *Inorg. Chem.* **1997**, *36*, 284–290 and references therein. (b) Lazzaroni, R.; Uccello-Barretta, G.; Bertozzi, S.; Salvadori, P. *J. Organomet. Chem.* **1985**, *297*, 117–129 and references therein.

(14) Holloway, C. E.; Hulley, G.; Johnson, B. F. G.; Lewis, J. J. *Chem. Soc. A* **1969**, 53–57.

(15) Hartley, F. R. In *Comprehensive Coordination Chemistry*; Pergamon Press: New York, 1982; 642–650.

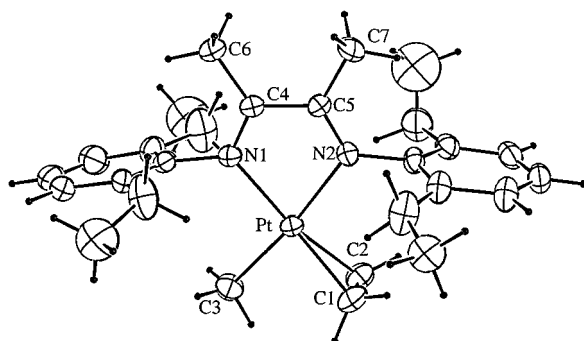


Figure 3. Ortep view of the **1o** cation. For the sake of clarity, only some of the atoms are labeled.

Table 3. Selected Bond Lengths (Å) and Valence Angles (deg) with Their Esd's in Parentheses

Pt–N(1)	2.075(9)	Pt–N(2)	2.117(9)
Pt–C(1)	2.11(2)	Pt–C(2)	2.14(2)
Pt–C(3)	2.07(1)	N(1)–C(4)	1.27(1)
N(2)–C(5)	1.28(1)	C(1)–C(2)	1.27(3)
C(4)–C(5)	1.46(2)		
N(1)–Pt–N(2)	76.3(4)	N(1)–Pt–C(1)	163.7(7)
N(1)–Pt–C(2)	160.3(7)	N(1)–Pt–C(3)	97.0(5)
N(2)–Pt–C(1)	99.3(7)	N(2)–Pt–C(2)	97.8(6)
N(2)–Pt–C(3)	173.2(5)	C(1)–Pt–C(2)	34.8(7)
C(1)–Pt–C(3)	87.0(8)	C(2)–Pt–C(3)	88.7(7)
Pt–N(1)–C(4)	116.5(8)	Pt–N(2)–C(5)	114.8(8)
Pt–C(1)–C(2)	74(1)	Pt–C(2)–C(1)	71(1)
N(1)–C(4)–C(5)	116(1)	N(2)–C(5)–C(4)	116(1)

The length (1.27(1) Å) of the olefinic bond C(1)–C(2) is surprisingly short and would require confirmation from an X-ray analysis where the disorder and absorption effects were absent and minimized, respectively. Also, the phenyl groups at N(1) and N(2) are perpendicular to the equatorial plane within a few degrees. The ethyl groups linked to them were found to be disordered, as were the BF_4^- ions. According to the NMR results, the length of the Pt–N(2) bond (2.117(9) Å), which is opposite to the methyl group, is significantly larger than that of the Pt–N(1) bond (2.075(9) Å), which faces the ethene group, most probably as a consequence of the aforementioned higher *trans* influence of alkyl groups relative to olefins.

Concluding Remarks

This paper describes two effective methods for the synthesis of cationic platinum(II) complexes containing the *cis*-{PtR(olefin)} moiety. The complexes are stable to heat and air and do not undergo insertion of the olefin into the Pt–R bond. They are involved in a dynamic exchange process involving the alkene ligand, which has been investigated through NMR spectroscopy. It has been found that nitrogen chelates which afford crowding above and below the coordination plane strongly hinders the exchange. The same steric feature prompts the selective coordination of α -olefins, leading to the formation of a single pair of enantiomers.

Studies on the reactivity of type **1** complexes are now in progress.

Experimental Section

NMR spectra were recorded on a 200 MHz (Varian Model Gemini), a 250 MHz (Bruker Model AC-250), or a 400 MHz spectrometer (Bruker Model DRX-400). The solvents were

$\text{C}_2\text{D}_2\text{Cl}_4$, CDCl_3 , CD_3NO_2 , and CD_2Cl_2 (C_2DHCl_4 (δ 5.98 ppm), CHCl_3 (δ 7.26 ppm), CD_2HNO_2 (δ 4.33 ppm), or CDHCl_2 (δ 5.32 ppm) as internal standard). Low-temperature spectra of daph and daph derivatives were recorded in CD_2Cl_2 . $[\text{PtClMe}(\text{SMe}_2)_2]$,¹⁶ $[\text{Pt}(\text{phen})(\text{dimethylfumarate})]$,¹⁷ **1a**,⁵ **1c**,⁵ **1e**,⁵ **1g**,⁵ diacetyl bis(diarylimines)¹⁸ and Et_3OBF_4 ¹⁹ were prepared according to literature methods. Me_3OBF_4 (Aldrich) is commercially available and was used without further purification. Nitromethane was stored over A4 molecular sieves. Dichloromethane was distilled from CaH_2 immediately before use. Elemental analyses of the products were satisfactory and are reported in the Supporting Information for representative compounds.

Syntheses of Type 3 Complexes [PtCl(Me)(N–N)] (N–N = daph (3a), daethyph (3b), daproph (3c). To a suspension of $[\text{PtClMe}(\text{SMe}_2)_2]$ (0.37 g, 1.0 mmol) in 10 mL of diethyl ether is added the appropriate N–N ligand (1.2 mmol). After 48 h of stirring at room temperature the orange-red precipitate is collected, washed with diethyl ether (3×3 mL), and dried under vacuum (70–75% yield). ^1H NMR Pt–Me resonance (δ): **3a** (in $\text{C}_2\text{D}_2\text{Cl}_4$) 0.91 ($^2J_{\text{Pt-H}} = 79$ Hz); **3b** (in CDCl_3) 0.89 ($^2J_{\text{Pt-H}} = 79$ Hz); **3c** (in CDCl_3) 0.98 ($^2J_{\text{Pt-H}} = 80$ Hz).

Synthesis of [PtEt(phen)(dimethyl fumarate)] BF_4 (1b). A solution of Et_3OBF_4 (0.19 g, 1.0 mmol) in 5 mL of dry dichloromethane is added to $[\text{Pt}(\text{phen})(\text{dimethyl fumarate})]$ (0.52 g, 1.0 mmol). Diethyl ether (4 mL) is added to the resulting red solution, affording a brown oil, which slowly transforms into a solid. This is washed with diethyl ether (2×4 mL) and dried under vacuum (80% yield).

Syntheses of [PtMe(phen)(olefin)] BF_4 (1i,j). A solution of Me_3OBF_4 (0.15 g, 1.0 mmol) in 2 mL of dry nitromethane is added to $[\text{Pt}(\text{phen})(\text{dimethyl fumarate})]$ (0.52 g, 1.0 mmol). To the resulting solution containing **1a** is added an excess of the appropriate olefin. The product is crystallized by careful addition of toluene, washed with toluene (1×2 mL) and pentane (2×5 mL), and dried under vacuum (65–70% yield).

Synthesis of [PtEt(phen)(ethylene)] BF_4 (1d). To a solution of **1b** in dry dichloromethane prepared as described above with 0.52 g (1.0 mmol) of $[\text{Pt}(\text{phen})(\text{dimethyl fumarate})]$ as starting material is added an excess of ethylene. Crystallization of the product starts at once. After 10 min the complex is collected, washed with dichloromethane, and dried under vacuum (80% yield).

Syntheses of [PtEt(phen)(olefin)] BF_4 (olefin = Propylene (1f), Styrene (1h). To a solution of **1b** in dry dichloromethane prepared as described above, with 0.52 g (1.0 mmol) of $[\text{Pt}(\text{phen})(\text{dimethyl fumarate})]$ as starting material, is added an excess of olefin. The product is crystallized by careful addition of toluene, washed with toluene (1×2 mL) and pentane (2×5 mL), and dried under vacuum (65–70% yield).

Syntheses of [PtMe(N–N)(olefin)] BF_4 (1k–s). To a suspension of AgBF_4 (0.195 g, 1.0 mmol) in 10 mL of dichloromethane is added an excess of the appropriate olefin. To the resulting mixture is added a solution of $[\text{PtClMe}(\text{N–N})]$ (1.0 mmol) in 5 mL of dry dichloromethane at 273 K. After 48 h of stirring at room temperature AgCl is removed by filtration on Celite and the volume of the resulting solution is reduced to 5 mL under vacuum. Toluene (15 mL) is stratified on the solution and the mixture kept at 277 K for 24 h. The resulting crystals are washed with toluene (1×5 mL) and pentane (2×5 mL) and dried under vacuum (80–90% yield). In the case of the complexes **1m,1r** crystallization is best achieved by substituting diethyl ether for toluene.

Crystal Structure Determination of [PtMe(daethyph)(ethylene)] BF_4 (1o). The compound was recrystallized from

(16) Scott, D.; Puddephatt, R. J. *Organometallics* **1986**, 1643–1648.

(17) De Felice, V.; De Renzi, A.; Ruffo, F.; Tesauero, D. *Inorg. Chim. Acta* **1993**, 219, 169–178.

(18) tom Dieck, H.; Svoboda, M.; Greiser, T. Z. *Naturforsch.* **1981**, 36B, 823–832.

(19) Meerwin, H. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, pp 1080–1082.

methylene chloride/toluene. X-ray data were collected at room temperature on an Enraf-Nonius CAD4-F automatic diffractometer using Cu K α graphite-monochromated radiation operating in the ω/θ scan mode. The unit cell parameters were obtained by a least-squares fitting of the setting values of 25 strong reflections in the θ range $24 \leq \theta \leq 27^\circ$. Three monitoring reflections, measured every 500 reflections, showed insignificant intensity fluctuations. In addition to the usual corrections for Lorentz and polarization factors, a semiempirical correction for absorption²⁰ was applied (maximum and minimum values of the correction factor were 0.78 and 1.00).

The systematic absences of the diffraction pattern and the value of measured density are consistent with two space groups: *C2/c* (No. 15 in International Tables) with one molecule and *Cc* (No. 9) with two molecules in the asymmetric unit, respectively. The structure was solved by the heavy-atom method by using the space group *C2/c*. Throughout the refinement procedure clear evidence of disorder effects affecting the ethyl groups and the BF₄⁻ anion were detected. In particular, for BF₄⁻ the difference Fourier map showed, unexpectedly, not one but two independent volumes of electron density apt to describe the ion in a disordered arrangement. With a best fitting of BF₄⁻ in these volumes and assigning occupancy factors equal to 0.5, the structure was refined to completeness with a final *R* index of 0.057.

In an attempt to get a better description of the BF₄⁻ anion, the refinement procedure was repeated by using the space group *Cc*, which is the less restrained basis for describing the crystal structure. Although the results were substantially unchanged for the complex molecules, the use of the *Cc* space group was preferred because it allows a better treatment of the disordered anions. The skeletons of the two cations related by a pseudo symmetry center at $x = 0$, $y = 0$, and $z = 0$ were constrained in the least-squares procedure. The minimized quantity was $\sum w(\Delta F)^2$ with $w^{-1} = \sigma^2(F_o) + (0.02F_o)^2 + 1.0$, where σ is derived from counting statistics. Details of the structure analysis are listed in Table 4.

The non-hydrogen atoms of the cation skeleton were refined anisotropically and those of the disordered ethyl groups isotropically. A standard BF₄⁻ group with isotropic thermal parameters equal for all atoms was fitted as well as possible in the appropriate regions of the electron density map and included in structure factor calculations. H-atoms, placed in

Table 4. Summary of Crystallographic Data

cryst size/mm	0.05 × 0.10 × 0.20
formula	PtN ₂ C ₂₇ H ₃₉ ·BF ₄
fw	673.5
cryst syst	monoclinic
space group	<i>Cc</i>
<i>a</i> /Å	35.834(9)
<i>b</i> /Å	9.856(1)
<i>c</i> /Å	18.207(5)
β /deg	116.89(2)
<i>V</i> /Å ³	5735(2)
<i>Z</i>	4 (2 mols. in asymm. unit)
<i>F</i> (000)	2672
<i>D</i> _{meas} /g cm ⁻³	1.56
<i>D</i> _{calc} /g cm ⁻³	1.56
λ (Cu K α)/Å	1.540 56
θ_{\max} /deg	72
μ /cm ⁻¹	96.1
no. of indep rflns	5640
no. of rflns above 3 $\sigma(I)$	3609
no. of refined params	259
goodness of fit	0.929
<i>R</i>	0.051
<i>R</i> _w	0.060

calculated positions, were assigned the isotropic equivalent thermal parameters of the carrier atoms and included in the final refinement as riding atoms. The H-atoms of ethyl groups were neglected. The final Fourier difference map showed no peaks greater than 0.98 e Å⁻³. The largest shift to esd ratio in the final cycle was 0.1.

Full lists of bond distances and angles, atom parameters, and anisotropic thermal parameters of the non-hydrogen atoms have been deposited as Supporting Information.

Acknowledgment. We thank the Consiglio Nazionale delle Ricerche and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial support and the Centro Interdipartimentale di Metodologie Chimico-Fisiche, Università di Napoli "Federico II", for NMR, X-ray, and computing facilities.

Supporting Information Available: Tables giving anisotropic thermal parameters, bond distances and angles, and atomic coordinates for **1o** and a table of elemental analyses for representative complexes (5 pages). Ordering information is given on any current masthead page.

OM970428F

(20) North, A. C. T.; Phillips, D. C.; Mathewes, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.