

The First Class of Square-Planar Platinum(II) Complexes Containing Electron-Poor Alkenes. Rare Insertion of an Alkene into a Pt–Alkyl Bond†

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The first class of square-planar Pt(II) complexes bearing electron-poor alkenes, i.e., [PtMe(*N,N*-chelate)(η^2 -CH₂=CHCOR)]BF₄ (R = H, NMe₂, Me, OMe), is described. By using *N,N* ligands with suitable steric properties, it was possible to inhibit olefin dynamic processes in solution, thus allowing a thorough characterization of the complexes. Insertion of methyl acrylate into the Pt–Me bond provides a rare example of migratory insertion of an alkene into a Pt–alkyl bond.

Introduction

The recent discovery¹ that Pd(II) and Ni(II) complexes are able to catalyze the homogeneous polymerization of α -olefins is acknowledged as one of the most promising findings concerning the chemistry of d⁸ ions. The ability of the catalysts (**1** and **2** in Figure 1) to produce polymers with high molecular weights mainly ensues from the choice of *N,N*-chelating ligands, i.e., diimines (**a** and **b** in Figure 2) which introduce substantial steric hindrance above and below the square-planar coordination plane. This feature inhibits associative exchange processes and, hence, favors the chain growth.^{1a}

The peculiar ability of this class of *N,N* ligands of inhibiting olefin displacement reactions has also emerged from a recent study of similar platinum(II) complexes of general formula [PtMe(*N,N*-chelate)(η^2 -olefin)]BF₄ (**3**).² It was found that the kinetic stability of type **3** complexes with the hindered ligands **a** and **b** is much larger than that of the corresponding species containing the poorly hindered ligands **c** and **d**. The ability of **a** or **b** in “freezing” olefin coordination to a 16 e⁻ platinum(II) center prompted us to use these ligands for investigating a poorly studied class of platinum(II) complexes, i.e., square-planar derivatives containing electron-poor alkenes. In fact, an accurate characterization of the rare examples of such complexes described so far³ has been prevented by the occurrence of exchange processes involving the alkene.^{3c,d} Furthermore, none of them have been structurally characterized. On these grounds, we have undertaken the synthesis of type **3** complexes of electron-poor alkenes by using **a** and **b** as chelates,

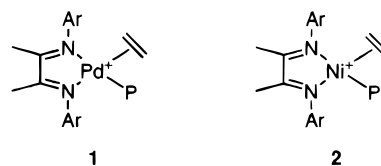
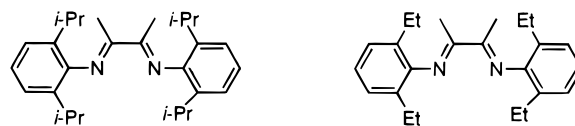
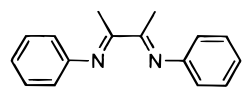


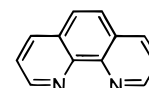
Figure 1.



diacetyl-bis(di-*i*-propylphenylimine), **a** diacetyl-bis(diethylphenylimine), **b**



diacetyl-bis(phenylimine), **c**



phen, **d**

Figure 2.

with the assumption that useful information would become available if the dynamic processes involving the alkene were hindered. This approach was successful and herein we report the results of our research.

Results and Discussion

The synthetic procedure described by Scheme 1 was adopted. By adding AgBF₄ to a dichloromethane solution of [PtMe(I)(*N,N*-chelate)] (*N,N*-chelate = diacetyl bis(di-*i*-propylphenylimine), **4a**; diacetyl bis(diethylphenylimine), **4b**) in the presence of the appropriate CH₂=CHCOR ligand, quantitative precipitation of AgI occurred within a few hours. Addition of diethyl ether to the filtered solution afforded yellow microcrystals of the wanted type **3** product.⁴ Type **3** complexes form the first homogeneous class of square-planar Pt(II) deriva-

(4) Type **3** complexes are indicated by a letter (**a**, diacetyl bis(di-*i*-propylphenylimine) or **b**, diacetyl bis(diethylphenylimine)) followed by the specification of the R group in the CH₂=CHCOR ligand.

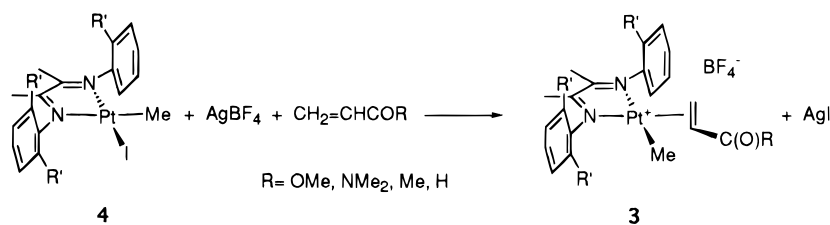
† Dedicated to the memory of Stefano Ganis.

(1) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (c) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.

(2) Fusto, M.; Giordano, F.; Orabona, I.; Panunzi, A.; Ruffo, F. *Organometallics* **1997**, *16*, 5981.

(3) (a) Paiaro, G.; Panunzi, A. *J. Am. Chem. Soc.* **1966**, *88*, 4843.

(b) Meester, A. M.; van Dam, H.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1976**, *20*, 155. (c) Scott, J. D.; Puddephatt, R. *J. Organometallics* **1986**, *5*, 1253. (d) Orabona, I.; Panunzi, A.; Ruffo, F. *J. Organomet. Chem.* **1996**, *525*, 295–298.

Scheme 1^a

^a One R' group on an aryl ring has been omitted for clarity.

Table 1. Selected ¹H NMR Data^a for Type 3 Complexes

| entry | formula | Pt-Me ^b | H(olefin) ^b |
|-------------------------------|--|--------------------|---|
| 3a (OMe) | [PtMe{diacetyl bis(di- <i>i</i> -propylphenylimine)}(η ² -CH ₂ =CHCO ₂ Me)]BF ₄ | 0.20 (70, 3H) | 4.22 (m, 2H) 3.76 (m, 1H) |
| 3a (Me) | [PtMe{diacetyl bis{di- <i>i</i> -propylphenylimine)}(η ² -CH ₂ =CHCOMe)]BF ₄ | 0.12 (71, 3H) | 4.72 (80, dd, 1H) 4.00 (56, d, 1H) 3.37 (65, d, 1H) |
| 3a (NMe ₂) | [PtMe{diacetyl bis{di- <i>i</i> -propylphenylimine)}(η ² -CH ₂ =CHCONMe ₂)]BF ₄ | 0.18 (71, 3H) | 4.97 (84, dd, 1H) 4.24 (53, d, 1H) |
| 3a (H) | [PtMe{diacetyl bis{di- <i>i</i> -propylphenylimine)}(η ² -CH ₂ =CHCHO)]BF ₄ | 0.45 (69, 3H) | ^c 4.42 (61, d, 1H) 4.21 (63, d, 1H) |
| 3b (OMe) | [PtMe{diacetyl bis{diethylphenylimine)}(η ² -CH ₂ =CHCO ₂ Me)]BF ₄ | 0.15 (70, 3H) | 3.97 (70, m, 1H) 4.28 (59, d, 1H) 3.96 (dd, 1H) 3.55 (71, d, 1H) |

^a At 200, 270, 400 MHz and 298 K. In CDCl₃ (CHCl₃ (δ = 7.26 ppm) as internal standard). Abbreviations: no attribute, singlet; d, doublet; dd, double doublet; m, multiplet. ^b ¹J_{Pt-H} (Hz) in parentheses (when measurable). ^c Hidden by more intense resonances.

Table 2. Selected ¹³C NMR Data^a for Free Olefins and Type 3 Complexes

| entry | formula | Pt-Me ^b | CH= ^b | Δδ ^c | CH ₂ = ^b | Δδ ^d |
|-------------------------------|--|--------------------|------------------|-----------------|--------------------------------|-----------------|
| | CH ₂ =CHCO ₂ Me | | 128.2 | | 130.4 | |
| | CH ₂ =CHCOMe | | 137.2 | | 128.7 | |
| | CH ₂ =CHCONMe ₂ | | 127.6 | | 127.1 | |
| | CH ₂ =CHCHO | | 138.1 | | 137.5 | |
| 3a (OMe) | [PtMe{diacetyl bis{di- <i>i</i> -propylphenylimine)}(η ² -CH ₂ =CHCO ₂ Me)]BF ₄ | -0.2 | 74.9 (189) | 53.3 | 69.6 (170) | 60.8 |
| 3a (Me) | [PtMe{diacetyl bis{di- <i>i</i> -propylphenylimine)}(η ² -CH ₂ =CHCOMe)]BF ₄ | 0.5 (658) | 83.0 (209) | 54.2 | 66.8 (171) | 61.9 |
| 3a (NMe ₂) | [PtMe{diacetyl bis{di- <i>i</i> -propylphenylimine)}(η ² -CH ₂ =CHCONMe ₂)]BF ₄ | -1.4 (666) | 79.4 (213) | 48.2 | 69.0 (172) | 58.1 |
| 3a (H) | [PtMe{diacetyl bis{di- <i>i</i> -propylphenylimine)}(η ² -CH ₂ =CHCHO)]BF ₄ | -3.7 (644) | 82.2 (202) | 55.9 | 71.6 (194) | 65.9 |
| 3b (OMe) | [PtMe{diacetyl bis{diethylphenylimine)}(η ² -CH ₂ =CHCO ₂ Me)]BF ₄ | -0.5 (645) | 75.9 (216) | 52.3 | 69.6 (174) | 60.8 |

^a At 50.3 or 62.9 MHz and 298 K. In CDCl₃ (¹³CDCl₃ (δ = 77.0 ppm) as internal standard). ^b ¹J_{Pt-C} (Hz) in parentheses (when measurable). ^c Difference between δ(CH) of the free olefin and δ(CH) of the coordinated olefin. ^d Difference between δ(CH₂) of the free olefin and δ(CH₂) of the coordinated olefin.

tives containing alkenes with electron-withdrawing functions (i.e., an aldehyde, a ketone, an ester, and an amide). They have been characterized through elemental analysis, NMR spectroscopy (Tables 1 and 2), and, in one case, X-ray crystallography (see below).

According to our expectations, the olefins did not show fast exchange processes on the NMR time scale, as suggested by the presence of coupling to ¹⁹⁵Pt in both the carbon and proton spectra. Furthermore, the presence of a unique spectral pattern suggests selective formation of only one enantiomeric pair,⁵ most probably **3'** (Figure 3) according to the previous discussion made for similar complexes of propene and styrene.² It is clear that both results stem from the steric properties

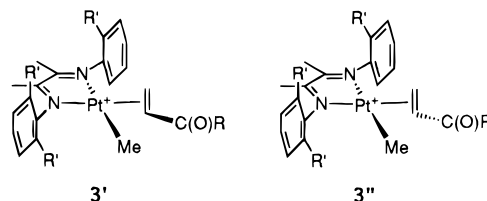


Figure 3. Type **3'** and **3''** isomers. One R' group on an aryl ring has been omitted for clarity.

of **a** and **b**. Indeed, when **c** was used as the chelate, the spectrum of the isolated product mainly consisted of broad signals, revealing both the presence of more than one species and their fast interconversion in solution.

The absence of fast dynamic processes allowed a thorough characterization of type **3** complexes, and important parameters such as olefin carbon chemical shifts and the corresponding couplings to ¹⁹⁵Pt could be

(5) Although both isomers have been detected at 200 K for the Pd(II) derivative [PdMe{diacetyl bis{di-*i*-propylphenylimine)}(η²-CH₂=CHCO₂Me)]⁺,^{1b,c} only one pattern of NMR signals was detected in the range of temperature 203–298 K in the spectrum of the analogue Pt(II) complex **3a**(OMe).

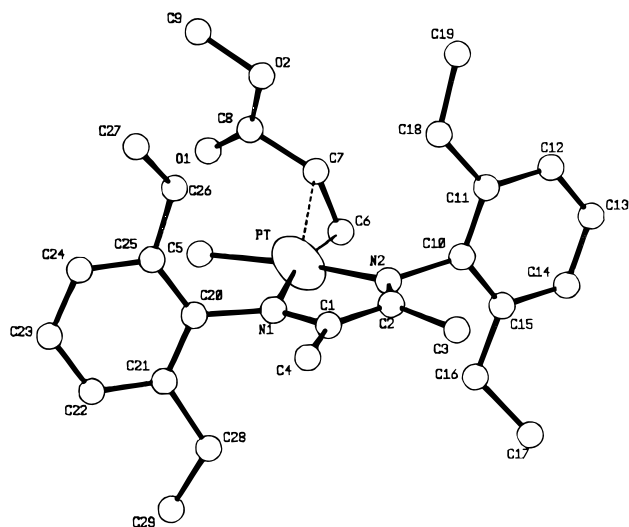


Figure 4. ORTEP drawing of **3b(OMe)**. Except for Pt, all the atoms have been treated with equal isotropic thermal parameters.

measured for electron-poor alkenes in a square-planar environment. A large coordination shift ($\Delta\delta$) of the olefin protons with respect to those of the free ligands (ca. 2 ppm) was observed. An important contribution to the shift ensues from the shielding due to the aryl rings of the chelates, which are orthogonal to the coordination plane of Pt. The carbon NMR spectra deserve some comment. Though not clearly established whether olefin-to-metal π -back-donation is strongly reflected by ^{13}C trends,⁶ $\Delta\delta$'s values of alkene carbons have been previously used as a measure of the extent of π -back-donation in five-coordinate complexes of formula $[\text{PtCl}(\text{Me})(N,N\text{-chelate})(\eta^2\text{-olefin})]$.⁷ $\Delta\delta$'s values for type **3** complexes of electron-poor olefins are smaller than those measured on the just mentioned five-coordinate species (ca. 57 vs. ca. 90 ppm⁸), where a substantial contribution of π -back-donation is acknowledged. However, on the average they are ca. 7 ppm larger than that measured on the related ethylene complex $[\text{PtMe}\{\text{diacetyl bis}(\text{di-}i\text{-propylphenylimine})\}(\eta^2\text{-ethylene})]\text{BF}_4$.² Likely, this shift at higher field can be ascribed to a significant contribution of π -back-donation prompted by the electron-withdrawing substituents.

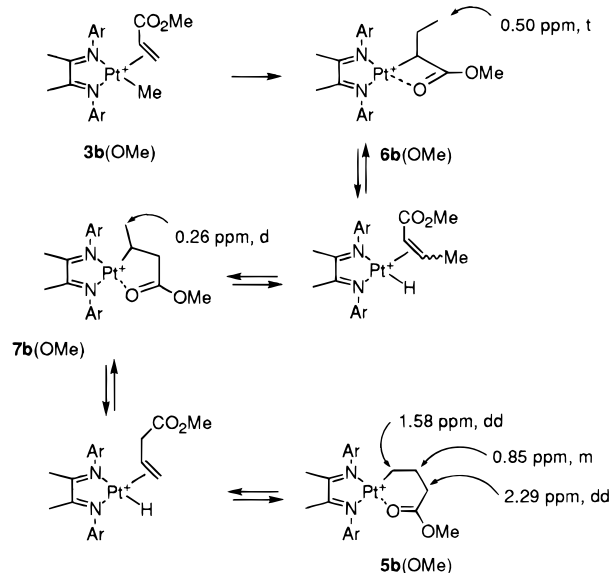
Hoping to gain further information on the nature of the Pt–olefin bond, the X-ray crystal structure of a representative complex, i.e., $[\text{PtMe}\{\text{diacetyl bis}(\text{diethylphenylimine})\}(\eta^2\text{-CH}_2=\text{CHCO}_2\text{Me})]\text{BF}_4$ [**3b(OMe)**], was determined (Figure 4). Unfortunately, as found for similar cationic diacetyl bis(diarylimine) derivatives,^{2,9} the structure is characterized by a relevant statistical disorder due to rotations or wide librations of all of the four ethyl groups and to the usually imprecise localization of the BF_4^- ions. Some reliable and significant geometrical parameters of the complex are reported in Table 3.

Although no particular meaning can be ascribed to the molecular parameters due to their very large

Table 3. Selected Geometrical Parameters for **3b(OMe)**

| Bond Lengths (Å) | | | |
|-------------------------|---------|-------------------------|---------|
| Pt–N(1) | 2.16(3) | Pt–N(2) | 1.92(3) |
| Pt–C(5) | 2.04(4) | Pt–C(6) | 2.10(3) |
| Pt–C(7) | 2.18(4) | N(1)–C(1) | 1.29(4) |
| N(1)–C(20) | 1.52(5) | N(2)–C(2) | 1.28(4) |
| N(2)–C(10) | 1.50(4) | C(1)–C(2) | 1.40(6) |
| C(1)–C(4) | 1.52(4) | C(2)–C(3) | 1.59(4) |
| C(6)–C(7) | 1.36(5) | B–F(1) | 1.07(4) |
| B–F(2) | 1.15(4) | B–F(3) | 1.19(4) |
| B–F(4) | 1.18(4) | | |
| Bond Angles (deg) | | | |
| N(2)–Pt–C(5) | 174(2) | N(1)–Pt–C(5) | 102(1) |
| N(1)–Pt–N(2) | 74(1) | N(1)–C(1)–C(2) | 113(2) |
| N(2)–C(2)–C(1) | 117(2) | C(6)–C(7)–C(8) | 136(3) |
| Torsion Angles (deg) | | | |
| N(2)–Pt–C(7)–C(6) | 80 | N(2)–Pt–C(6)–C(7) | –107 |
| C(1)–N(1)–C(20)–C(25) | 93 | C(2)–N(2)–C(10)–C(11) | –92 |
| N(1)–C(1)–C(2)–N(2) | –7 | C(6)–C(7)–C(8)–O(2) | 179 |
| C(12)–C(11)–C(18)–C(19) | 10 | C(14)–C(15)–C(16)–C(17) | 28 |
| C(22)–C(21)–C(28)–C(29) | 26 | C(24)–C(25)–C(26)–C(27) | 32 |

Scheme 2. NMR Chemical Shifts of the Insertion Products Starting from **3b(OMe)**^a



^a The abbreviations used for describing NMR multiplicities are: d, doublet; dd, double doublet; m, multiplet; t, triplet.

standard deviations, the overall molecular features are not invalidated. As expected, the methyl acrylate substituent is oriented as in **3'**. The aromatic rings of the ligand lie orthogonal to the coordination plane of Pt, such as to relieve, at best, any interaction with the methyl acrylate substituent. Furthermore, a relevant difference of the bond lengths Pt–N(1) (2.16(3) Å) and Pt–N(2) (1.91(3) Å) confirms the stronger trans influence of alkyl groups with respect to olefins.²

The solution behavior of some type **3** complexes was also preliminarily investigated. When a chloroform solution of **3b(OMe)** was heated at 333 K, formation of the corresponding cyclometalated insertion product **5b(OMe)** quantitatively occurred within a few hours (Scheme 2).¹⁰ The complex could be crystallized by slow addition of pentane to the reaction mixture. Coordination of the carbonyl group was suggested by the shift of

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

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

(8) $\Delta\delta$ values increase ca. 9 ppm on going from ethylene to methyl acrylate in trigonal-bipyramidal complexes.⁷

(9) Giordano, F. Private communication.

(10) The corresponding Pd(II) complex $[\text{PdMe}\{\text{diacetyl bis}(\text{di-}i\text{-propylphenylimine})\}(\eta^2\text{-CH}_2=\text{CHCO}_2\text{Me})]^+$ displayed a similar behavior.^{1b,c}

its band in the IR spectrum from 1720 cm^{-1} in **3b**(OMe) to ca. 1600 cm^{-1} in **5b**(OMe).¹¹ By monitoring the reaction through NMR spectroscopy, it was also possible to detect signals diagnostic of the intermediate σ -alkyl compounds **6b**(OMe) and **7b**(OMe). We suggest that in the case of **6b**(OMe) and **7b**(OMe), one carbonyl group also coordinates to Pt, in analogy with the corresponding Pd complexes.^{1b,c} Similar results were obtained by starting from **3a**(OMe).

We underline the importance of the above-reported results. Actually, insertion of electron-rich monoalkenes into Pt–alkyl bonds are not known.^{12,13} Moreover, theoretical calculations¹⁴ do predict a large activation barrier for this process. As far as we know, the sole reported insertion of a monoalkene into a Pt(II)–R bond involves an electron-poor olefin, i.e., the highly activated tetrafluoroethylene.¹⁵ Detailed studies on the properties and reactivity of type **3** compounds are now in progress.

Experimental Section

NMR spectra were recorded on a 200-MHz (Varian model Gemini), 250-MHz (Bruker model AC-250), or 400-MHz spectrometer (Bruker model DRX-400). The solvent was CDCl_3 ($\delta = 7.26$ ppm) or CDCl_3 ($\delta = 77.0$) as internal standards). The following abbreviations were used for describing NMR multiplicities: no attribute, singlet; dd, double doublet; m, multiplet. The complexes [PtCl(Me){diacetyl bis-(di-*i*-propylphenylimine)}] and [PtCl(Me){diacetyl bis(diethylphenylimine)}] were prepared according to literature methods.² Dichloromethane was distilled from CaH_2 immediately before use.

Syntheses of [PtI(Me)(*N,N*-chelate)] Precursors, *N,N*-Chelate = Diacetyl Bis(di-*i*-propylphenylimine) (4a**) or Diacetyl Bis(diethylphenylimine) (**4b**).** To a solution of the appropriate complex [PtCl(Me)(*N,N*-chelate)] (1.0 mmol) in 10 mL of dichloromethane was added under nitrogen AgBF_4 (0.20 g, 1.0 mmol) dissolved in 10 mL of acetonitrile. After 24 h of stirring at room temperature, AgCl was removed by filtration on Celite and the solvents were removed under vacuum. The residue was dissolved in 10 mL of chloroform, and the resulting solution was shaken with 10 mL of a KI-saturated water solution. The organic phase was separated, and the water phase was extracted with chloroform (3 \times 5 mL). The combined organic phases were dried over sodium sulfate. After filtration, removal of the solvent under vacuum afforded the product as a red-purple solid. Yield 90–95%. ¹H NMR Pt–Me resonance (δ): **3a** 1.10 (² $J_{\text{Pt-H}} = 77$ Hz); **3b** 0.98 (² $J_{\text{Pt-H}} = 76$ Hz).

Syntheses of [PtMe(*N,N*-chelate)(η^2 -olefin)] BF_4 Complexes (3**).** To a suspension of AgBF_4 (0.20 g, 1.0 mmol) in 10 mL of dichloromethane was added an excess of the ap-

Table 4. Summary of the Crystal Data and Intensity Collection for **3b(OMe)**

| | |
|--|--|
| formula | $\text{C}_{29}\text{H}_{41}\text{BF}_4\text{N}_2\text{O}_2\text{Pt}$ |
| mw | 731.55 |
| space group | $P2_1/c$ |
| <i>a</i> /Å | 12.030(2) |
| <i>b</i> /Å | 14.755(2) |
| <i>c</i> /Å | 18.631(2) |
| α /deg | 90 |
| β /deg | 106.1(1) |
| γ /deg | 90 |
| <i>V</i> /Å ³ | 3177.35 |
| <i>Z</i> | 4 |
| cryst dimens/mm | $0.3 \times 0.3 \times 0.1$ |
| <i>F</i> (000) | 1456 |
| <i>D_x</i> /g cm ⁻³ | 1.53 |
| μ /cm ⁻¹ | 42.74 |
| <i>T</i> /K | 298 |
| radiation (λ /Å) | graphite-monochromated Mo K α ($\lambda = 0.7107$) |
| take-off angle/deg | 3 |
| scan speed/deg min ⁻¹ | 2.0 in the 2 θ mode |
| 2 θ range/deg | $3.0 \leq 2\theta \leq 45$ |
| no. of unique reflns [$F_0 \geq 2\sigma(F_0)$] | 1924 |
| <i>R</i> (on F_0) ^a | 0.104 |
| highest map residual/e Å ⁻³ | 0.7 |

$$^a R = \sum |F_c| - |F_0| / \sum |F_0|.$$

propriate olefin (4–6 equiv) under nitrogen. To the resulting mixture was added a solution of [Pt(I)Me(*N,N*-chelate)] (1.0 mmol) in 5 mL of dichloromethane. After 5 h of stirring (12 h in the case of $\text{CH}_2=\text{CHCONMe}_2$), AgI was removed by filtration on Celite and the volume of the resulting solution was reduced to 5 mL under vacuum. Yellow crystals of product were obtained by careful addition of diethyl ether. The crystals were washed with diethyl ether (2 \times 5 mL) and dried under vacuum. Yield: 70–80%.

Reactions of [PtMe(*N,N*-chelate)(η^2 - $\text{CH}_2=\text{CHCO}_2\text{Me}$)]- BF_4 [3a**(OMe), **3b**(OMe)].** A solution of the appropriate type **3** complex (0.10 mmol) in 1 mL of chloroform was heated at 333 K for 12 h. *n*-Pentane was added to the dark solution, which was stored 24 h at 253 K. Red crystals of the corresponding type **5** product were collected, washed with *n*-pentane, and dried under vacuum. Yield: 60–65%. Selected ¹H NMR resonances (δ): **5a**(OMe) 3.10 (3H, OMe), 2.32 (2H, dd, Pt– $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$), 2.19 and 2.11 (6H, N=C(*Me*)–C'–(*Me*)=N), 1.65 (2H, dd, Pt– $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$), 0.89 (2H, m, Pt– $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$); **5b**(OMe) 3.12 (3H, OMe), 2.29 (2H, dd, Pt– $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$), 2.12 and 1.95 (6H, N=C(*Me*)–C'–(*Me*)=N), 1.58 (2H, dd, Pt– $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$), 0.85 (2H, m, Pt– $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$). Selected ¹³C NMR resonances (δ): **5a**(OMe) 55.0 (OMe), 35.6 (³ $J_{\text{Pt-C}} = 33$ Hz, Pt– $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$), 28.4 and 28.0 (Ar– CHMe_2 and Ar– CHMe_2), 24.1, 23.9, 23.5, 23.2 (Ar– CHMeMe' and Ar– $\text{C}'\text{HMeMe}'$), 21.7 (Pt– $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$), 21.5 and 19.7 (N=C(*Me*)–C'–(*Me*)=N), 9.2 (¹ $J_{\text{Pt-C}} = 748$ Hz, Pt– $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$); **5b**(OMe) 55.0 (OMe), 35.5 (³ $J_{\text{Pt-C}} = 36$ Hz, Pt– $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$), 24.0 and 23.2 (Ar– CH_2Me and Ar– $\text{C}'\text{H}_2\text{Me}$), 21.5 (² $J_{\text{Pt-C}} = 38$ Hz, Pt– $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$), 20.5 and 19.3 (N=C(*Me*)–C'–(*Me*)=N), 14.2 and 13.0 (Ar– CH_2Me and Ar– $\text{CH}_2\text{Me}'$), 8.9 (¹ $J_{\text{Pt-C}} = 745$ Hz, Pt– $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})$).

Crystal Structure Determination of **3b(OMe).** Crystals suitable for diffractometric analysis were obtained from a chloroform/pentane solution. Crystal data, intensity data, and procession details are presented in Table 4. The data were obtained with a Philips PW-100 four-circle automated diffractometer with a graphite monochromator. Intensity data were collected at 298 K using the θ – 2θ scan method. Two reference reflections, monitored periodically, showed no significant variation in intensity. Data were corrected for Lorentz and polarization effects but not for absorption. The position of Pt was determined from a three-dimensional Patterson function. The difficulty to localize the atoms of the ethyl and acrylate groups and those of the BF_4^- ions was at once apparent, which

(11) Coordination of the carbonyl group to Pt generally causes a lowering of its stretching frequency, see, for example: De Felice, V.; De Renzi, A.; Ruffo, F.; Tesauro, D. *Inorg. Chim. Acta* **1994**, *219*, 169 and references therein. In the case of **5b**(OMe), the band was shifted in the region pertaining to the aromatic C–C stretchings and, hence, its frequency could not be accurately determined.

(12) Actually, insertion of an electron-rich alkene into a Pt–C bond has been described for an alkene hanging from a σ -bonded alkyl chain, see: Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076.

(13) On the other hand, insertion of electron-rich olefins into Pt–aryl bonds is a well-known process, see, for example: De Felice, V.; De Renzi, A.; Tesauro, D.; Vitagliano, A. *Organometallics* **1992**, *11*, 3669.

(14) Strömberg, S.; Svensson, M.; Zetterberg, K. *Organometallics* **1997**, *16*, 3165.

(15) Clark, H. C.; Puddephatt, R. *J. Inorg. Chem.* **1970**, *9*, 2670.

implied a noticeable degree of structural disorder due to high libration of these groups. Most of the coordinates of the corresponding atoms were chosen among the constellation of maxima around their expected position with the highest electron density. They have not been refined, and their isotropic thermal factors were also blocked. The hydrogen atoms were not included in the calculations. A detailed description of the involved disorder could not be established with certainty from structure refinements and difference Fourier synthesis. These facts explain the relatively high value of the final *R* index and the large standard deviations of the structural parameters. Blocked cascade least-squares refinements converged to *R* = 0.105. The final positional parameters of the non-hydrogen atoms are listed in Table S2.

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Supporting Information Available: Text giving elemental analysis and tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles **3b**(OMe) (4 pages). Ordering information is given on any current masthead page.

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