First Coordinatively Saturated Carbene Complexes of Platinum(II): Synthesis, Structure, and Reactivity

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Coordinatively saturated carbene complexes of platinum(II) have been obtained by oxidative addition of [ClCH=NMe$_2$]Cl to Pt(0) precursors. The cationic products of general formula [PtCl(CHNMe$_2$)(*N*,*N*-chelate)(olefin)]Cl have been characterized through NMR spectroscopy and for [PtCl(CHNMe$_2$)(2,9-Me$_2$-1,10-phen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]Cl by X-ray diffractometry. The latter species reacts with nucleophiles affording dimethylformamide and the corresponding Pt(0) precursor [Pt(2,9-Me$_2$-1,10-phen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]. Attempts to obtain related complexes containing carbene groups Pt=CHY without a heteroatom in α-position (Y = CO$_2$Et, CO$_2$NMe$_2$, CN) have led to the isolation of complexes of formula [PtR(dmphen){η^1,η^2-CH(Y)O$_2$CCH=CHCO$_2$Me}] (R = Me, Ph), formally derived from an intramolecular nucleophilic addition to a carbene intermediate. The X-ray structure of a representative product, [PtMe(dmphen){η^1,η^2-CH(CO$_2$Et)O$_2$CCH=CHCO$_2$Me}], is reported.

Introduction

Involvement of carbene groups bound to transition ions in several useful reactions, e.g., insertion processes,[1] attracts continuous interest in carbene complexes.[2] In fact, these species are claimed to be intermediates in important catalytic processes such as olefin metathesis,[3a] metathetical polymerizations,[3b] and Fischer−Tropsch production of hydrocarbons[3c] and are useful precursors in stoichiometric syntheses.[4] Platinum(II) has afforded so far the most well-characterized carbene derivatives among the d^8 ions of the 10th column.[5] To the best of our knowledge, all the known Pt(II) complexes are coordinatively unsaturated compounds displaying the typical square-planar geometry. This work, which is related to previous studies on five-coordinate d^8 species,[6] describes the synthesis and the characterization of the first trigonal bipyramidal 18e$^-$ carbene complexes of platinum(II), of general formula [PtCl(CHNMe$_2$)(N,N)(olefin)]Cl (**1**), where N,N is a *N*,*N*-chelate. The structure of one of the complexes, i.e., [PtCl(CHNMe$_2$)(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]Cl (dmphen = 2,9-Me$_2$-1,10-phenanthroline), has been determined by X-ray diffraction and compared with that of [PtCl(H$_2$O)(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]Cl, which differs only in the presence of a pure *σ*-donor in place of the carbene. Nucleophilic additions on the carbene group have been accomplished on complexes **1**. Moreover, the synthesis of carbene derivatives related to **1** by reaction of a five-coordinate water complex with N$_2$CHY (Y = CO$_2$Et, CONMe$_2$, CN) has been attempted. The structure of the final products is of the type resulting from a nucleophilic addition to a carbene intermediate, as demonstrated by the X-ray structure of [PtMe(dmphen){η^1,η^2-CH(CO$_2$Et)O$_2$CCH=CHCO$_2$Me}].

Experimental Section

^{1}H NMR spectra were recorded on a 250 MHz Bruker model AC-250 spectrometer. CDCl$_3$, C$_2$D$_2$Cl$_4$, CD$_3$NO$_2$, and (CD$_3$)$_2$SO were used as solvents, and CHCl$_3$ (δ = 7.26), C$_2$HDCl$_4$ (δ = 5.98), CHD$_2$NO$_2$ (δ = 4.33), ^{13}CDCl$_3$ (δ = 77), ^{13}CHD$_2$NO$_2$ (δ = 62.9), and (^{13}CHD$_2$)$_2$SO (δ = 39.5) as internal standards. The following abbreviations were used for describing NMR multiplicities: no attribute, singlet; d, doublet; t, triplet; m, multiplet; app, apparent. IR spectra were recorded in Nujol mulls on a Perkin-Elmer 457 spectrophotometer using CsI windows. Solvents were dried before use. All reactions were carried out under a nitrogen atmosphere by using Schlenk techniques. The ligands 1,10-phenanthroline (phen) and 2,9-Me$_2$-1,10-phenanthroline (dmphen) were commercially available (Aldrich). 6,6′-Me$_2$-2,2′-bipyridine (dmbipy) was obtained according to literature methods.[7] The syntheses of [Pt(N,N)-

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(olefin)],[8] [PtMe(phen)(*E*-$MeO_2CCH{=}CHCO_2Me$)]BF_4,[9] [PtCl(Ph)(SMe_2)$_2$],[10] N_2CPh_2,[11] N_2CONMe_2,[12] N_2CHCN,[13] and [PtMe(dmphen)(H_2O)(olefin)]BF_4[14] are reported elsewhere. The other isomer of the latter compound, i.e., with maleate substituents pointing toward Me, was obtained by reacting the appropriate [PtMe(I)(dmphen)(*Z*-$MeO_2CCH{=}CHCO_2Me$)][14] precursor with $AgBF_4$ in dichloromethane/acetone.

Synthesis of [PtCl(CHNMe$_2$)(dmphen)(*Z*-MeO$_2$CCH═CHCO$_2$Me)]Cl (1a). To a magnetically stirred solution of chloromethylenedimethylammonium chloride (0.026 g, 0.20 mmol) in nitromethane (2 mL) was added solid [Pt(dmphen)(*Z*-$MeO_2CCH{=}CHCO_2Me$)] (0.11 g, 0.20 mmol) at room temperature. The reaction mixture was worked up immediately in case both isomers of the product had to be obtained. Otherwise, the solution was kept 1 h at room temperature, so as to contain only the more stable isomer (**1a′**). Careful addition of diethyl ether afforded the crystalline pale yellow product(s) in high yield (96%). Selected ^1H NMR data (δ, CD_3NO_2): **1a′**, 9.90 (1H, $^2J_{Pt-H} = 30$ Hz, Pt−C*H*), 4.60 (2H, $^2J_{Pt-H} =$ 80 Hz, ═C*H*CO$_2$Me), 3.82 (6H, OMe), 3.52 (6H, *Me$_2$*-phen), 3.17 (3H, N*Me*Me), 2.96 (3H, NMe*Me*); **1a″**, 9.80 (1H, $^2J_{Pt-H} = 10$ Hz, Pt−CH), 4.55 (2H, $^2J_{Pt-H} = 70$ Hz, ═C*H*CO$_2$Me), 3.72 (6H, OMe), 3.42 (6H, *Me$_2$*-phen), 2.90 (3H, N*Me*Me). Selected ^{13}C NMR resonances (δ, CD_3NO_2): **1a′**, 181 ($^1J_{Pt-C} = 1006$ Hz, Pt−CH), 171.3 (*C*O$_2$Me), 53.8 (N*Me*Me), 53.6 (CO$_2$*Me*), 46.2 (NMe*Me*), 42.7 ($^1J_{Pt-C} = 353$ Hz, ═*C*HCO$_2$Me), 28.6 (*Me$_2$*-phen). Anal. Calcd for $C_{23}H_{27}Cl_2N_3O_4Pt$: C, 40.90; H, 4.03; N, 6.22. Found: C, 40.78; H, 3.96; N, 6.21.

Synthesis of [PtCl(CHNMe$_2$)(dmbipy)(*Z*-MeO$_2$CCH═CHCO$_2$Me)]Cl (1b). To a magnetically stirred solution of chloromethylenedimethylammonium chloride (0.026 g, 0.20 mmol) in nitromethane (2 mL) was added solid [Pt(dmbipy)(*Z*-$MeO_2CCH{=}CHCO_2Me$)] (0.105 g, 0.20 mmol) at room temperature. Addition of diethyl ether afforded the crystalline pale yellow product(s) (isomers **1b′**/**1b″** in the ratio 3:1) (60% yield). Selected ^1H NMR data (δ, CD_3NO_2): **1b′**, 9.85 (1H, $^2J_{Pt-H} = 25$ Hz, Pt−CH); 4.46 (2H, $^2J_{Pt-H} = 80$ Hz, ═C*H*CO$_2$Me); 3.80 (6H, OMe); 3.32 (3H, N*Me*Me); 3.30 (6H, Me$_2$bipy); 2.92 (3H, NMe*Me*); **1b″**, 10.0 (1H, $^2J_{Pt-H} = 20$ Hz, Pt−CH); 3.82 (2H, $^2J_{Pt-H} = 76$ Hz, ═C*H*CO$_2$Me); 3.80 (6H, OMe); 3.33 (6H, *Me$_2$*bipy). Selected ^{13}C NMR resonances (δ, CD_3NO_2): **1b′**, 176.5 ($^1J_{Pt-C} = 1022$ Hz, Pt−CH); 166 (*C*O$_2$Me); 48.5 (N*Me*Me); 48.0 (CO$_2$*Me*); 40.5 (NMe*Me*); 37.5 ($^2J_{Pt-H} = 354$ Hz, ═*C*HCO$_2$Me); 22.8 (*Me$_2$*-bipy); **1b″**, 190 (Pt−CH). Anal. Calcd for $C_{21}H_{27}Cl_2N_3O_4Pt$: C, 38.72; H, 4.18; N, 6.45. Found: C, 38.88; H, 4.23; N, 6.61.

Synthesis of [PtCl(CHNMe$_2$)(dmphen)(*E*-RCH═CHR)]Cl (R = CO$_2$Me, 1c; R = CN, 1d). To a magnetically stirred solution of chloromethylenedimethylammonium chloride (0.026 g, 0.20 mmol) in nitromethane (2 mL) was added an equal amount of solid [Pt(dmphen)(*E*-RCH═CHR)] at room temperature. After 1 h addition of diethyl ether afforded the crystalline pale yellow product in high yield (**1c** 82%; **1d** 96%). Selected ^1H NMR data (δ, CD_3NO_2): **1c**, 9.30 (1H, $^2J_{Pt-H} = 26$ Hz, Pt−CH); 4.77 (d, 1H, ═C*H*CO$_2$Me), 4.53 (d, 1H, ═C*H*CO$_2$Me), 3.84 (3H, OMe), 3.80 (3H, OMe), 3.56 (3H, *Me*-Me-phen), 3.46 (3H, Me-*Me*-phen), 3.34 (br, 6H, NMe$_2$); **1d**, 9.60 (1H, $^2J_{Pt-H} = 20$ Hz, Pt−CH), 4.50 (m, 2H, $^2J_{Pt-H} = 70$ Hz, ═CHCN), 3.60 (3H, *Me*-Me-phen), 3.53 (3H, Me-*Me*-phen), 3.43 (3H, NMe*Me*), 3.30 (3H, N*Me*Me). Anal. Calcd for $C_{23}H_{27}Cl_2N_3O_4Pt$ (**1c**): C, 40.90; H, 4.03; N, 6.22. Found: C, 40.65; H, 4.10; N, 6.18. Calcd for $C_{21}H_{21}Cl_2N_5Pt$ (**1d**): C, 41.39; H, 3.47; N, 11.49. Found: C, 41.60; H, 3.33; N, 11.62.

Synthesis of [PtCl(CHNMe$_2$)(phen)]Cl (4). To a magnetically stirred solution of chloromethylenedimethylammonium chloride (0.026 g, 0.20 mmol) in nitromethane (2 mL) was added solid [Pt(phen)(*Z*-$MeO_2CCH{=}CHCO_2Me$)] (0.11 g, 0.20 mmoL) at room temperature. The crude precipitate was washed with methylene chloride and dried, giving a yellow solid (0.083 g, 80% yield). Selected ^1H NMR resonances (δ, CD_3NO_2): 10.90 (1H, $^2J_{Pt-H} = 10$ Hz, Pt−CH); 9.45 (d, 1H, H2 or H9); 9.00 (d, 1H, H9 or H2); 4.07 (3H, NMe*Me*); 3.97 (3H, N*Me*Me). Anal. Calcd for $C_{15}H_{15}Cl_2N_3Pt$: C, 35.80; H, 3.00; N, 8.35. Found: C, 35.95; H, 3.08; N, 8.24.

Synthesis of [PtCl(Ph)(dmphen)(*Z*-MeO$_2$CCH═CHCO$_2$Me)]. To a solution of [PtCl(Ph)(SMe_2)$_2$] (0.086 g, 0.20 mmol) in chloroform (5 mL) was added dmphen (0.042 g, 0.20 mmol) and dimethylmaleate (0.14 g, 1.0 mmol). The solution was refluxed for 18 h. Diethyl ether was added to complete the precipitation of the product, which was collected, washed with ether, and dried in vacuo (70%). Selected ^1H NMR data (δ, $C_2D_2Cl_4$): 6.61 (d, 2H, $^3J_{Pt-H} = 35$ Hz, H2, H6−Ph), 4.54 (2H, $^2J_{Pt-H} = 85$ Hz, ═C*H*CO$_2$Me), 3.65 (6H, OMe), 3.42 (6H, *Me$_2$*-phen). Anal. Calcd for $C_{26}H_{25}ClN_2O_4Pt$: C, 47.31; H, 3.82; N, 4.24. Found: C, 47.50; H, 3.90; N, 4.31.

Synthesis of [PtPh(H$_2$O)(dmphen)(*Z*-MeO$_2$CCH═CHCO$_2$Me)]BF$_4$. To a suspension of [PtCl(Ph)(dmphen)(*Z*-$MeO_2CCH{=}CHCO_2Me$)] (0.066 g, 0.10 mmol) in nitromethane (5 mL) was added a solution of $AgBF_4$ (0.020 g, 0.10 mmol) in acetone (1.5 mL). After 2 h of stirring, AgCl was removed by filtration. The product was obtained in almost quantitative yield as a white powder by removing the solvents in vacuo. Selected ^1H NMR data (δ, CD_3NO_2): 6.60 (d, 2H, $^3J_{Pt-H} = 35$ Hz, H2, H6−Ph), 3.88 (6H, OMe), 3.70 (2H, $^2J_{Pt-H} = 63$ Hz, ═C*H*CO$_2$Me), 3.55 (6H, *Me$_2$*-phen). Anal. Calcd for $C_{26}H_{27}BF_4N_2O_5Pt$: C, 42.81; H, 3.73; N, 3.84. Found: C, 42.75; H, 3.83; N, 3.95.

Synthesis of [PtMe(dmphen){η^1,η^2-CH(Y)O$_2$CCH═CHCO$_2$Me}] (Y = CO$_2$Et, 2a; Y = CONMe$_2$, 2b; Y = CN, 2c). To a solution of [PtMe(H_2O)(dmphen)(*Z*-$MeO_2CCH{=}CHCO_2Me$)]BF_4 (0.066 g, 0.10 mmol) in methanol (0.6 mL) was added N_2CHY (0.12 mmoL) at room temperature. In the case of **2a** and **2c** the crystalline product (yield > 95%) was collected after ca. 2 h by filtration. In the case of **2b** no precipitate was formed and solvent was removed in vacuo to recover the product. The residue was washed with ether to give crude **2b** together with the precursor (ca. 35%). Selected ^1H NMR resonances (δ, CD_3NO_2): **2a**, 4.59 (1H, $^2J_{Pt-H} = 55$ Hz, C*H*CO$_2$Et), 3.77 (3H, OMe), 3.76 (d, 1H, $^2J_{Pt-H} = 80$ Hz, ═CH), 3.20 (3H, Me-*Me*-phen), 3.06 (3H, *Me*-Me-phen), 2.90 (d, 1H, $^2J_{Pt-H} = 60$ Hz, ═CH), 2.70 (m, 1H, CO$_2$C*H*HMe), 1.85 (m, 1H, CO$_2$CH*H*Me), 0.16 (app t, 3H, CO$_2$CH$_2$*Me*), −0.37 (3H, $^2J_{Pt-H} = 50$ Hz, Pt-Me); **2b**, 4.59 (1H, $^2J_{Pt-H} = 48$ Hz, C*H*CONMe$_2$), 3.80 (3H, OMe), 2.95 (3H, Me-*Me*-phen), 2.85 (3H, *Me*-Me-phen), 1.60 (1H, CONMe*Me*), 1.45 (1H, CON*Me*Me), 0.06 (3H, $^2J_{Pt-H} = 50$ Hz, Pt-Me); **2c**, 4.51 (1H, $^2J_{Pt-H} = 50$ Hz, ═CHCN), 3.80 (d, 1H, $^2J_{Pt-H} = 65$ Hz, ═CH), 3.79 (3H, OMe), 3.16 (3H, Me-*Me*-phen), 3.11 (3H, *Me*-Me-phen), 3.00 (d, 1H, $^2J_{Pt-H} = 50$ Hz, ═CH), −0.22 (3H, $^2J_{Pt-H} = 50$ Hz, Pt-Me). Selected ^{13}C NMR resonances (δ, CD_3NO_2): **2a**, 70.4 ($^1J_{Pt-C} = 397$ Hz, Pt−CH), 43.5 ($^1J_{Pt-C} = 397$ Hz, ═CH), 31.2 ($^1J_{Pt-C} = 397$ Hz, ═CH), 30.0 (Me-*Me*-phen), 29.0 (*Me*-Me-phen), −8.0 ($^1J_{Pt-C} = 437$ Hz, Pt-Me); **2c** (in (CD$_3$)$_2$SO), 52.4 ($^1J_{Pt-C} = 400$ Hz, Pt−CH), 51.5 (CO$_2$*Me*), 41.7 ($^1J_{Pt-C} = 400$ Hz, ═CH), 29.6 ($^1J_{Pt-C} = 400$ Hz, ═CH), 28.2 (*Me*-Me-phen), 27.6 (Me-*Me*-phen), −10.0 (Pt-Me). Anal. Calcd for $C_{24}H_{26}N_2O_6Pt$ (**2a**): C, 45.50; H, 4.14; N, 4.42. Found: C, 45.68; H, 4.20; N, 4.41. Calcd for $C_{22}H_{21}N_3O_4Pt$ (**2c**): C, 45.05; H, 3.61; N, 7.16. Found: C, 44.92; H, 3.76; N, 7.27.

Synthesis of [PtPh(dmphen)] {η^1,η^2-CH(Y)O$_2$CCH═CHCO$_2$Me}] (Y = CO$_2$Et, 2d; Y = CN, 2e). Compounds **2d** and **2e** were prepared by a procedure similar to that reported for

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2a by starting from [PtPh(H$_2$O)(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]BF$_4$ and isolated as crystalline precipitates from the reaction mixture in high yield (>95%). Selected ^{1}H NMR resonances (δ, CD$_3$NO$_2$): **2d**, 4.87 (1H, $^2J_{\mathrm{Pt-H}} = 53$ Hz, C*H*CO$_2$Et), 3.85 (d, 1H, $^2J_{\mathrm{Pt-H}} = 80$ Hz, =CH), 3.80 (3H, OMe), 3.40 (3H, Me-*Me*-phen), 3.38 (3H, *Me*-Me-phen), 3.12 (d, 1H, $^2J_{\mathrm{Pt-H}} = 60$ Hz, =CH), 2.80 (m, 1H, CO$_2$C*H*HMe); 1.90 (m, 1H, CO$_2$CH*H*Me), 0.07 (app t, 3H, CO$_2$CH$_2$*Me*); **2e**, 4.80 (1H, $^2J_{\mathrm{Pt-H}} = 45$ Hz, CHCN), 3.88 (d, 1H, $^2J_{\mathrm{Pt-H}} = 80$ Hz, =CH), 3.80 (3H, OMe), 3.39 (3H, Me-*Me*-phen), 3.32 (3H, Me-*Me*-phen), 3.22 (d, 1H, $^2J_{\mathrm{Pt-H}} = 61$ Hz, =CH). Anal. Calcd for $C_{29}H_{28}N_2O_6Pt$ (**2d**): C, 50.07; H, 4.06; N, 4.03. Found: C, 50.21; H, 3.99; N, 4.09. Calcd for $C_{27}H_{23}N_3O_4Pt$ (**2e**): C, 50.00; H, 3.57; N, 6.48. Found: C, 50.15; H, 3.60; N, 6.42.

Isolation of Solid [PtMe{CH(OH$_2$)CO$_2$Et}(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)][BF$_4$], 3a. To a solution of [PtMe(H$_2$O)(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]BF$_4$ (0.133 g, 0.22 mmol) in nitromethane (1 mL) was added 0.023 mL (0.22 mmol) of N$_2$CHCO$_2$Et at room temperature. An effervescence was observed, and immediately 0.5 mL of diethyl ether was added. A whitish solid precipitated, which was separated by filtration, washed with diethyl ether, and dried. The crude product (0.092 g) was impure due to the presence of significant amounts (ca. 20%) of **2a**. Selected ^{1}H NMR data (δ, CD$_3$NO$_2$): 5.60 (1H, $^2J_{\mathrm{Pt-H}} = 35$ Hz, C*H*CO$_2$Et), 4.56 (3H, OMe), 4.40 (d, 1H, =CH), 3.88 (3H, OMe), 3.26 (d, 1H, $^2J_{\mathrm{Pt-H}} = 50$ Hz, =CH), 3.24 (3H, *Me*-Me-phen), 2.99 (3H, Me-*Me*-phen), 2.90 (m, 1H, CO$_2$C*H*HMe), 2.15 (m, 1H, CO$_2$CH*H*Me), 0.21 (app t, 3H, CO$_2$CH$_2$*Me*), 0.01 (3H, $^2J_{\mathrm{Pt-H}} = 50$ Hz, Pt-Me). Selected ^{13}C NMR resonances (δ, CD$_3$NO$_2$) 89.2 ($^1J_{\mathrm{Pt-C}} = 428$ Hz, Pt−CH); 34.4 ($^1J_{\mathrm{Pt-C}} = 409$ Hz, =CH); 33.8 ($^1J_{\mathrm{Pt-C}} = 377$ Hz, =CH); 30.6 (Me-*Me*-phen); 29.4 (Me-*Me*-phen); −6.9 ($^1J_{\mathrm{Pt-C}} = 396$ Hz, Pt-Me). IR (Nujol): $\nu = 1000$ cm^{-1} (BF$_4^-$).

NMR Tube Reactions of [PtR(H$_2$O)(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]BF$_4$ with N$_2$CHY (Y = CONMe$_2$ and R = Me, 3b; Y = CO$_2$Et and R = Ph, 3d). To an NMR tube containing a solution of [PtR(H$_2$O)(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]BF$_4$ (0.03 mmol) in deuterionitromethane (0.5 mL) was added N$_2$CHY (0.036 mmol) at room temperature. The spectrum monitored after 5 min showed that all the precursor had reacted to give the type **3** intermediates. Selected ^{1}H NMR resonances (δ): **3b**, 6.00 (1H, $^2J_{\mathrm{Pt-H}} = 30$ Hz, C*H*CONMe$_2$), 4.50 (3H, OMe), 4.40 (d, $^2J_{\mathrm{Pt-H}} = 70$ Hz, =CH), 3.88 (3H, OMe), 3.30 (3H, Me-*Me*-phen), 3.21 (d, =CH), 3.01 (3H, *Me*-Me-phen), 1.39 (3H, CON*Me*Me), 1.30 (3H, CONMe*Me*); **3d**, 5.93 (1H, $^2J_{\mathrm{Pt-H}} = 38$ Hz, C*H*CO$_2$Et), 4.69 (3H, OMe), 4.51 (d, $^2J_{\mathrm{Pt-H}} = 75$ Hz, =CH), 3.98 (3H, OMe), 3.50 (3H, Me-*Me*-phen), 3.48 (d, $^2J_{\mathrm{Pt-H}} = 50$ Hz, =CH), 3.33 (3H, *Me*-Me-phen), 3.06 (m, 1H, CO$_2$C*H*HMe), 2.23 (m, 1H, CO$_2$CH*H*Me), 0.13 (app t, 3H, CO$_2$CH$_2$*Me*). When the above-reported procedures were attempted by reacting the [PtMe(dmphen) (H$_2$O)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]BF$_4$ isomer in which maleate substituents face Me, mixtures of several unidentified compounds were obtained.

NMR Tube Reactions of [PtMe(phen)(*E*-MeO$_2$CCH=CHCO$_2$Me)]BF$_4$ with N$_2$CXY (X = H, Y = CO$_2$Et; X = Y = Ph). To an NMR tube containing a solution of [PtMe(phen)-(*E*-MeO$_2$CCH=CHCO$_2$Me)]BF$_4$ (0.03 mmol) in deuterionitromethane (0.5 mL) was added N$_2$CXY (0.036 mmol) at room temperature. The ^{1}H NMR spectrum monitored after 5 min showed that all the precursor had reacted to give CH$_2$=CPh$_2$ (X = Y = Ph) or CH$_2$=CHCO$_2$Et (X = H, Y = CHCO$_2$Et) and a mixture of platinum compounds, whose analysis was not attempted.

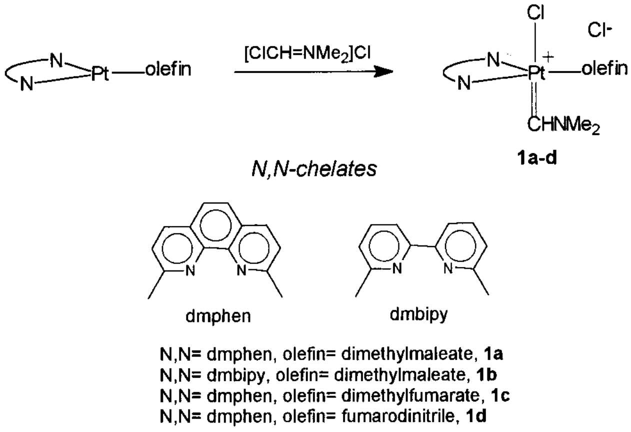
Nucleophilic Addition to 1a. In a typical experiment, **1a** (0.03 g, 0.05 mmol) was suspended in deuteriomethanol (0.75 mL) in a nitrogen atmosphere. To this stirred suspension was added the appropriate nucleophile (MeONa, NaBH$_4$, LiOH, or KCH(CO$_2$Me)$_2$, 0.15 mmol), dissolved in a minimum amount of the same solvent. After 16 h a yellow precipitate was removed by filtration. This was identified as [Pt(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]. By monitoring the ^{1}H NMR spectrum of the solution, dimethylformamide was detected in all cases, accompanied by methanol in case of methoxide addition and by dimethyl malonate in the case of malonate addition.

Crystallography. Crystal data and details of the data collection for [PtCl(CHNMe$_2$)(2,9-Me$_2$-1,10-phen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]Cl·H$_2$O, **1a·H$_2$O**, [PtMe(dmphen){η^1,η^2-CH(CO$_2$Et)O$_2$CCH=CHCO$_2$Me}], **2a**, and [PtCl(H$_2$O)(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]Cl·H$_2$O are given in Table 1. The diffraction experiments were carried out at low temperature for all compounds on a fully automated Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The unit cell parameters were determined by a least-squares fitting procedure using 25 reflections. Data were corrected for Lorentz and polarization effects, and for two species, namely, **1a·H$_2$O** and **2a** a decay correction (25% and 8%, respectively) was applied. An empirical absorption correction was applied to all compounds by using the azimuthal scan method.[15] The positions of the metal atoms were found by direct methods using the SHELXS 86 program[16] and all the non-hydrogen atoms located from difference Fourier maps. Most hydrogen atoms were experimentally located in the final stages of refinement but were placed in calculated positions and refined riding the pertinent carbon atoms. The carbene hydrogen H(15) in **1a** was freely refined. Isotropic thermal parameters for the H atoms were assigned 1.2 and 1.5 times U_{eq} of the carrier atoms for sp^2 and sp^3 carbons, respectively. The final refinement on F^2 proceeded by full-matrix least-squares calculations (SHELXL 93)[17] using anisotropic thermal parameters for all the non-hydrogen atoms.

Results and Discussion

Syntheses. The procedure that so far has proved to be effective[18] in the preparation of type **1** compounds involves the oxidative addition of chloromethylenedimethylammonium chloride[20] to a suitable nucleophilic Pt(0) species of the type [Pt(N,N)(olefin)] (Scheme 1):

Scheme 1



The syntheses have been carried out in carefully dried nitromethane, since the iminium salt is poorly soluble

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[15] North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect A* **1968**, *24*, 351.

[16] Sheldrick, G. M. *SHELXS 86*, Program for crystal structure solution; University of Gottingen, 1986.

[17] Sheldrick, G. M. *SHELXL 93*, Program for crystal structure refinement; University of Gottingen, 1993.

[18] During this work one other method was attempted, i.e., addition of electrophiles to five-coordinate complexes of the type [PtCl(COR)-(N,N)(olefin)].[19] In our hands a few preliminary attempts gave unidentified mixtures of products.

[19] De Felice, V.; Giovannitti, B.; Panunzi, A.; Ruffo, F.; Tesauro, D. *Gazz. Chim. Ital.* **1993**, *123*, 65.

[20] See for instance: Hartshorn, A. J.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1978**, 348.

Table 1. Crystal Data and Experimental Details for $[PtCl(CHNMe_2)(dmphen)(Z\text{-}MeO_2CCH{=}CHCO_2Me)]Cl\cdot H_2O$, 1a·$H_2O$, $[PtMe(dmphen)\{\eta^1,\eta^2\text{-}CH(CO_2Et)O_2CCH{=}CHCO_2Me\}]$, 2a, and $[PtCl(H_2O)(dmphen)(Z\text{-}MeO_2CCH{=}CHCO_2Me)]Cl\cdot H_2O$

	1a·H_2O	**2a**	
formula	$C_{23}H_{27}Cl_2N_3O_4Pt\cdot H_2O$	$C_{24}H_{26}N_2O_6Pt$	$C_{20}H_{22}Cl_2N_2O_5Pt\cdot H_2O$
M	693.48	633.56	654.40
temperature, K	200(2)	200(2)	220(2)
wavelength, Å	0.71069	0.71069	0.71069
crystal symmetry	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$ (No. 14)	Pbn2_1 (No. 33)	P 1 bar (No. 2)
a, Å	16.257(9)	11.492(7)	8.157(6)
b, Å	9.766(4)	13.779(8)	9.987(3)
c, Å	17.632(7)	14.253(9)	14.049(8)
α, deg	90	90	98.93(3)
β, deg	114.41(5)	90	101.47(6)
γ, deg	90	90	93.65(4)
cell volume, Å^3	2549(2)	2257(2)	1103(1)
Z	4	4	2
D_c, Mg m^{-3}	1.807	1.865	1.971
μ(Mo Kα), mm^{-1}	5.753	6.261	6.644
$F(000)$	1360	1240	636
crystal size, mm	0.15 × 0.17 × 0.20	0.12 × 0.20 × 0.38	0.05 × 0.075 × 0.15
θ limits, deg	2−28	2−30	2−27
scan mode	ω	ω	ω
reflns collected	6101($\pm h$, $+k$, $+l$)	7737($\pm h$, $+k$, $+l$)	4790($\pm h$, $\pm k$, $+l$)
no. of unique observed reflns [$F_o > 4\sigma(F_o)$]	6094	3218	4782
goodness of fit on F^2	1.040	1.068	1.003
$R_1(F)^a$, $wR_2(F^2)^b$	0.0370, 0.0899	0.0312, 0.0643	0.0379, 0.0903
weighting scheme a, b	0.0515, 6.9685	0.0341, 2.9443	0.0618, 2.5249^b
largest diff peak and hole, e·Å^{-3}	1.54 and −1.49	1.20 and −0.74	2.35 and −2.33

[a] $R_1 = \sum||F_o| - |F_c|/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

in other common solvents and is quite sensitive to hydrolysis. On the other hand, the isolated carbenes are air stable. They are slightly soluble in methanol and chloroform, but fairly soluble in nitromethane. The type of the coordinated olefins was suggested by previous findings[6] on the favorable influence of electron-withdrawing substituents on the stability of complexes similar to **1**. The selection of the N,N ligands was dictated by sterical requirements, as it is known[6] that the stabilization of the five-coordinate geometry in complexes related to **1** requires in-plane steric hindrance of the *N*,*N*-chelate. In fact, if phen is substituted for dmphen in the precursor of **1a**, upon reaction with the iminium salt, the olefin is lost and the carbene complex formed is a typical square-planar 16e$^-$ species (eq 1):

$$[Pt(phen)(Z\text{-}MeO_2CCH{=}CHCO_2Me)] + [(CHCl{=}NMe_2)]Cl = [PtCl(CHNMe_2)(phen)]Cl\ (\mathbf{4}) + Z\text{-}MeO_2CCH{=}CHCO_2Me \quad (1)$$

The reactions affording complexes **1** have been monitored by ^1H NMR in CD_3NO_2 and are complete in the time required for the acquisition of the spectrum. Dimethylmaleate can afford two geometrical isomers generated by the orientation of the CO_2Me groups relative to the axial ligands. Actually both of them have been observed shortly after the addition, in 2:1 (**1a′**:**1a″**) and 3:1 (**1b′**:**1b″**) ratio, respectively. In the former case aging of the solution affords only one isomer (**1a′**), while in the case of **1b**, containing a less rigid chelate, the equilibrium mixture attained by isomerization still contains a large amount of the less favored compound **1b″** (ca. 30%). As for the configuration assignment to the isomers, the X-ray structure of **1a** shows that the carbomethoxy groups face the carbene ligand (see later). By comparing the ^1H NMR spectrum of **1a′** and **1a″**, and also from previous results[21] on compounds similar to **1**, a lower field shift and a higher ^{195}Pt coupling constant can be reasonably assigned to olefin protons facing the halide ligand. Thus, it is reasonable that also in the thermodynamically preferred isomer **1b′** the carbomethoxy groups are on the carbene side.

Other noteworthy features of the NMR spectra of the carbene complexes are as follows: (a) The low-field shifts and the J_{Pt-H} constants (20−30 Hz) of the signals pertaining to the carbene hydrogens are within the typical range for related octahedral Pt(IV) carbene derivatives.[22] (b) The two halves of the *N*,*N*-chelate appear chemically equivalent. This could result either from a “free” rotation about the Pt−carbene bond or from a frozen conformation of the carbene group maintaining C_s symmetry. The first hypothesis seems more reasonable also considering the unsymmetrical carbene conformation found in the solid state (see later). Low-temperature NMR spectra (213 K) do not disclose further splitting of the signals. (c) Separate signals for the two NMe groups give evidence of hindered rotation around the $C_{carbene}$−N bond. No coalescence of the two signals is observed in high-temperature spectra (350−390 K in deuterionitrobenzene). Distinct ^{13}C signals are also observed for the two NMe carbons. These spectroscopic features are explained by the double-bond character of the C−N interaction discussed further on.

Taking into account the good stability of type **1** compounds, the synthesis of non heteroatom-stabilized

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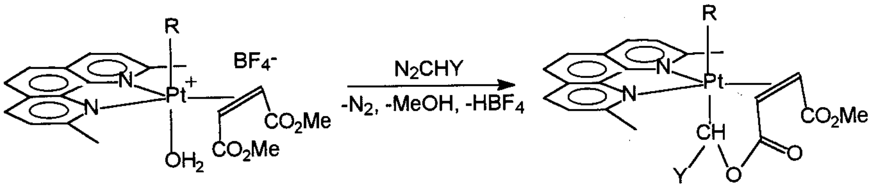
(21) Bartolucci, S.; Carpinelli, P.; De Felice, V.; Giovannitti, B.; De Renzi, A. *Inorg. Chim. Acta* **1992**, *197*, 51.

(22) Rendina, L. M.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 1030.

Scheme 2



R= Me, Y= CO_2Et, **2a**
R= Me, Y= $CONMe_2$, **2b**
R= Me, Y= CN, **2c**
R= Ph, Y= CO_2Et, **2d**
R= Ph, Y= CN, **2e**

2a-e

carbenes[23] has also been attempted. To achieve this purpose, some diazoaceto derivatives N_2CHY (Y = CO_2Et, $CONMe_2$, or CN) have been reacted with the five-coordinate complexes $[PtR(H_2O)(dmphen)(Z\text{-}MeO_2CCH{=}CHCO_2Me)]BF_4$, bearing the labile H_2O ligand in axial position. A clean reaction occurs only with the isomer in which carbomethoxy groups face water. The final products are not carbene derivatives, and type **2** species are obtained instead (Scheme 2).

The presence in apical position of a ligand stronger than water (methyl cyanide or pyridine) prevents the formation of any reaction product. Type **2** products have been characterized by ^1H NMR spectroscopy, and the X-ray structure of **2a** has been determined (see later).

A type **2** compound could derive from the intramolecular attack of one carbomethoxy oxygen on an axially bound CHY carbene group with involvement of a water molecule. To gain further information on the mode of formation of **2**, the reaction yielding **2a** has been monitored in an NMR tube. The addition of diazoacetate affords immediate release of nitrogen, and the spectrum of the fresh solution shows that another five-coordinate compound (**3a**) is initially formed, which then decomposes to **2a** and methanol. Attempts to isolate pure **3a** have been unsuccessful, and only solid mixtures of **3a** and at least 20% of **2a** could be recovered upon careful workup of the reaction mixture.

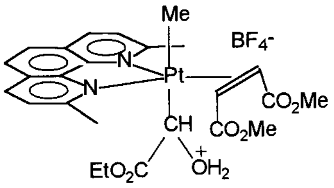
The more significant features of the signals pertaining to **3a** in the ^1H NMR spectrum are the following: (a) a one-proton signal appears at δ 5.60 coupled to ^{195}Pt ($J_{Pt-H} = 35$ Hz); (b) the two halves of the chelate are magnetically nonequivalent; (c) two different signals (δ 4.40, 3.26; $J_{Pt-H} = 35$ Hz) pertain to the olefin protons; (d) two different signals are observed for the methoxy protons; (e) a signal at δ 0.01 is typical of axially bound methyl. Further information on **3a** includes the following: (i) The mixture of solid **3a** and **2a**, dissolved in nitromethane, is conducting. Considering that **2a** is nonionic, the data are consistent with **3a** being a 1:1 electrolyte (85.3 S mol^{-1} cm^2). (ii) The IR spectrum of the mixture shows a broad band around 1000 cm^{-1}, typical of BF_4^-. (iii) The elemental analyses of the mixture disclose a fluorine content consistent with the presence of BF_4^- in **3a** (in 1:1 ratio).

On the grounds of all the above data, **3a** could be considered a carbene complex only in the case where asymmetry of the N,N and olefin ^1H NMR patterns could be ascribed to a high rotation barrier around the Pt−C bond, and a strong shielding could be responsible for the quite peculiar low-field shift (δ 5.60) of the putative carbene proton. More reasonably, it can be conceived that a water molecule has attacked this unrevealed carbene, and **3a** is in fact a protonated form of this addition product, i.e. an oxo-cation stabilized by intramolecular interactions, as indicated in Figure 1. Further support for this assignment stems from the ^{13}C NMR spectra. The shifts for the Pt-bound carbon atom in deuteronitromethane solution are 70.4 and 89.2 ppm for **2a** and **3a**, respectively. It should be noted that in the same solvent the carbon shifts pertaining to Me_2O and $Me_3O^+BF_4^-$ are 67.1 and 86.7 ppm, respectively.

Substantially similar results have been obtained by reacting the phenyl complex with diazoacetate or the methyl precursor with dimethyldiazoacetamide. No type **3** intermediate is detected by NMR spectroscopy on reaction of both aqua complexes with diazoacetonitrile, before the formation of **2c** and **2e**, respectively.

It is to be noted that when the synthesis of the carbene complex is attempted by reacting N_2CHCO_2Et with $[PtMe(phen)(E\text{-}MeO_2CCH{=}CHCO_2Me)]BF_4$ (i.e., avoiding stabilization of tbp geometry by the chelate ligand), ethyl acrylate is obtained. A similar reaction affording $Ph_2C{=}CH_2$ is observed when the carbene precursor is N_2CPh_2. Also on the grounds of previous findings[25] it seems reasonable that a reactive 16e$^-$ intermediate undergoes carbene insertion in the Pt−Me bond, finally affording the unsaturated product by β-elimination.

Solution Behavior and Reactivity of Carbenes. None of the type **1** carbene complexes described here show any tendency to intramolecular insertion of the carbene group in the Pt−Cl bond, in contrast to square-planar derivatives.[25] This is in keeping with the trans arrangement of the methyl and carbene ligands in the



3a

Figure 1. Proposed structure of **3a**.

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[23] Very few examples of similar carbenes are known, as in the case of coordinatively saturated Ru(II).[24] In the platinum group this type of carbene has been invoked as an intermediate[25] in insertion processes, but as far as we know, it has never been isolated.

[24] Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E.; Wright, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 4570.

[25] Bergamini, P.; Costa, E.; Orpen, A. G.; Pringle, P. G.; Smith, H. B. *Organometallics* **1995**, *14*, 3178.

Scheme 3

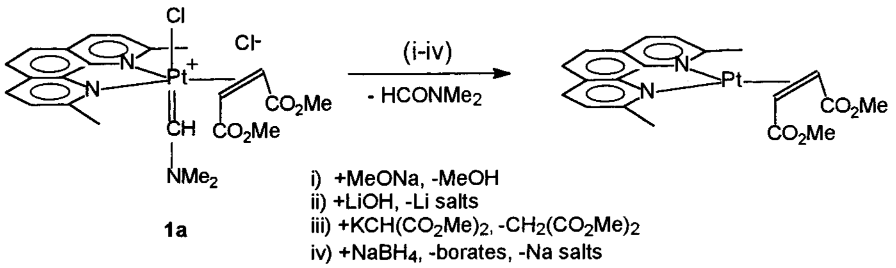

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [PtCl(CHNMe$_2$)(2,9-Me$_2$-1,10-phen)-(*Z*-MeO$_2$CCH=CHCO$_2$Me)]Cl·H$_2$O, 1a·H$_2$O

Pt−C(15)	2.006(6)	C(18)−C(19)	1.428(9)
Pt−C(18)	2.073(6)	C(18)−C(20)	1.502(9)
Pt−C(19)	2.066(6)	C(19)−C(21)	1.501(9)
Pt−N(2)	2.161(5)	C(20)−O(20)	1.206(8)
Pt−N(3)	2.210(4)	C(21)−O(21)	1.185(8)
Pt−Cl(1)	2.389(2)	C(21)−O(23)	1.334(7)
C(15)−N(1)	1.273(8)	C(20)−O(22)	1.328(7)
N(1)−C(16)	1.465(8)	O(22)−C(22)	1.457(8)
N(1)−C(17)	1.459(7)	C(23)−O(23)	1.438(9)
C(15)−H(1)	0.86(4)		
N(2)−Pt−N(3)	76.1(2)	C(15)−N(1)−C(16)	120.6(5)
C(15)−N(1)−C(17)	125.8(5)	C(16)−N(1)−C(17)	113.6(5)
Pt−C(15)−N(1)	130.5(4)		

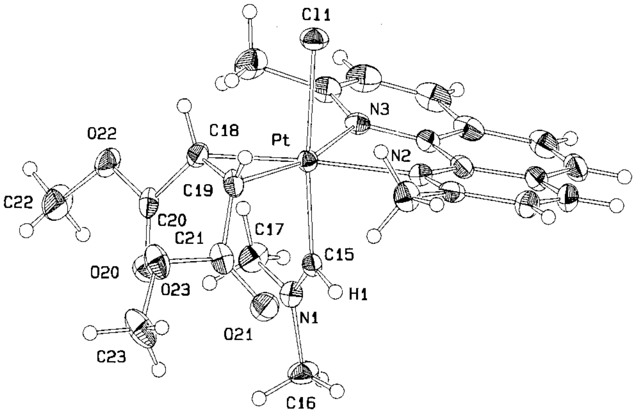

Figure 2. ORTEP drawing (30% probability level) of the cation [PtCl(CHNMe$_2$)(2,9-Me$_2$-1,10-phen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]$^+$, **1a**.

coordinatively saturated environment. In fact, the compounds are stable in nitromethane solution for several days.

No reaction has been observed with water or other neutral oxygen nucleophiles. The complexes react with strong nucleophiles, such as malonate, methoxide, LiOH, and NaBH$_4$. In all cases the metal is reduced and [Pt(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)] is formed, while dimethylformamide is obtained from the carbene moiety. Thus, it appears that an iminium derivative (undergoing successive hydrolysis to the amide) is formed by nucleophilic attack on the metal-bonded carbon.

The reactions effected on **1a** are reported in Scheme 3.

Molecular Structure of the [PtCl(CHNMe$_2$)(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]$^+$ Cation (1a) as Its Chloride Salt Monohydrate. The stereogeometry of the cation **1a** is represented in Figure 2, and relevant bond parameters are listed in Table 2. The coordination geometry around the platinum atom is trigonal bipyramidal, with the dmphen and the double bond of the maleate ester defining the equatorial plane and the chloride and CHNMe$_2$ aminocarbene ligands occupying the axial sites. The ion adopts an asymmetric conformation because neither the CO$_2$Me groups in the maleate ester nor the aminocarbene ligand conforms to a potential C_s symmetry. The interest of this structure lies primarily in the CHNMe$_2$ ligand, found for the first time in a five-coordinate complex. The bond parameters concerning the carbene ligand are as follows: Pt−C 2.006(6) Å, C=N 1.273(8) Å, Pt−C−N 129.6(4)°, Pt−Cl(trans) 2.389(2) Å. The same ligand has been reported in four- and six-coordinate species trans to a chloride. Strictly comparable values have been found in the electron precise octahedral platinum(IV) cation[22] [PtCl$_2$Me(CHNMe$_2$)(6,6′-di-*t*-Bu-2,2′-bipyridine)]$^+$: Pt−C$_{\text{carbene}}$ 1.99(2) Å, C=N 1.31(2) Å, Pt−C−N 131(2)°, Pt−Cl(trans) 2.378(5) Å. Slightly shorter values have been reported for the unsaturated four-coordinate molecule [PtCl$_2$(PPh$_3$)(CHNMe$_2$)]: Pt−C 1.96(1) Å, C=N 1.25(1) Å, Pt−C−N 130.5(4)°, Pt−Cl(trans) 2.347(3) Å.[26] It is evident that the ligand geometry is little affected by the chemical environment, and relevant features of the three species are a substantially localized C=N double bond and predominantly single-bond character of the Pt−C interaction. The above considerations are reinforced by the observation that the carbon−nitrogen distance in the coordinated ligand is in the range of values reported for uncoordinated iminium cations [1.26−1.30 Å].[27,28] In addition the difference between Pt−C$_{\text{carbene}}$ and Pt−C$_{\text{alkyl}}$ average distances in saturated species[6] [2.00 and 2.05 Å, respectively] is slightly larger than the difference between the carbon radii in sp^2 and sp^3 hybridization (0.03 Å). On the other hand evidence that pure σ-donation is not the most appropriate bonding model for the carbene ligand can be drawn from an analysis of its trans influence. The average Pt−Cl distance in five-coordinate species[6] is 2.30 and 2.47 Å, when the trans ligand is another chloride or an alkyl group, respectively. The distance in the present cation [2.389(2) Å] falls between the just cited values, indicating that the carbene ligand acts differently from an alkyl group; that is, a π-bond contribution is to be invoked.

The bonding parameters of the dmphen and maleate ligands are normal:[6] Pt−N$_{\text{av}}$ 2.19, Pt−C$_{\text{av}}$ 2.07, C=C 1.428(9) Å. It should be noted that the carbonyl oxygens of the CO$_2$Me appendages in the maleate ester face the aminocarbene ligand and establish short interligand

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(26) Barefield, E. K.; Carrier, A. M.; Sepelah, D. J.; Van Derveer, D. G. *Organometallics* **1982**, *1*, 103.

(27) Knop, O.; Cameron, T. S.; Bakshi, P. K.; Kwiatkowski, W.; Choi, S. C.; Adhikesavalu, D. *Can. J. Chem.* **1993**, *90*, 3139.

(28) Clark, G. R.; Shaw, G. L.; Surman, P. W. J.; Tailor, M. J.; Steele, D. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3139.

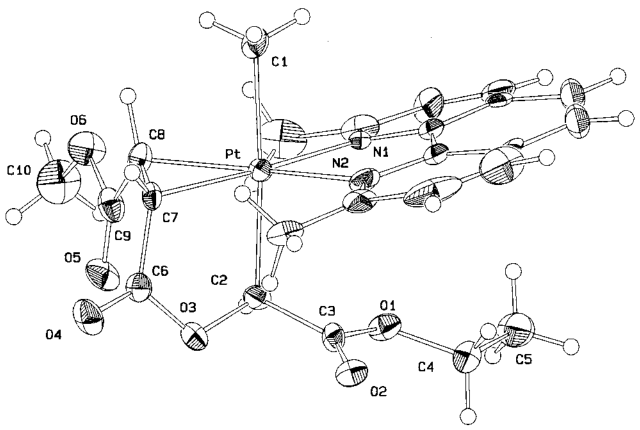

Figure 3. ORTEP drawing (30% probability level) of the molecule [PtMe(dmphen){η^1,η^2-CH(CO$_2$Et)O$_2$CCH=CHCO$_2$Me}], **2a**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [PtMe(dmphen)-{η^1,η^2-CH(CO$_2$Et)O$_2$CCH=CHCO$_2$Me}], 2a

Pt−C(8)	2.10(1)	C(8)−C(7)	1.45(1)
Pt−C(7)	1.99(1)	C(6)−O(4)	1.18(1)
Pt−C(1)	2.118(7)	C(6)−O(3)	1.34(1)
Pt−C(2)	2.140(7)	O(3)−C(2)	1.48(2)
Pt−N(2)	2.14(1)	C(2)−C(3)	1.47(1)
Pt−N(1)	2.17(1)	C(3)−O(2)	1.20(1)
C(8)−C(9)	1.49(2)	C(3)−O(1)	1.343(9)
C(9)−O(5)	1.16(1)	O(1)−C(4)	1.49(1)
C(9)−O(6)	1.38(1)	C(4)−C(5)	1.59(3)
C(10)−O(6)	1.43(1)	C(7)−C(6)	1.52(2)
N(1)−Pt−N(2)	76.3(2)	O(3)−C(2)−C(3)	106(1)
C(7)−C(6)−O(3)	115.8(9)	C(1)−Pt−C(2)	175.9(4)
Pt−C(2)−O(3)	108.4(8)	Pt−C(2)−C(3)	110.5(6)
C(6)−O(3)−C(2)	117.5(7)		

contacts: O(21)···C(15) 2.90, O(20)···C(15) 3.10, O(20)···N(15) 3.03 Å. Therefore the molecular conformation favors a possible intramolecular attack on the carbene carbon (vide infra).

Molecular Structure of [PtMe(dmphen){η^1,η^2-CH(CO$_2$Et)O$_2$CCH=CHCO$_2$Me}] (2a). The stereogeometry of the title compound is shown in Figure 3, and relevant bond parameters are listed in Table 3. The trigonal bipyramidal coordination is adopted with dmphen and maleate double bond in the equatorial plane and two alkyl groups in axial positions, Me and CH(CO$_2$Et)OR. A major stereochemical feature is the coordination of two strong trans influencing sp^3 carbons in opposite sites. We assume that the actual ligand arrangement is stabilized by the formation of a chelate ring connecting equatorial and axial sites. The molecule contains three chiral centers: the olefin carbons C(7) and C(8) and the axial carbon C(2). The crystal consists of the racemic mixture, and the diastereoisomer is defined by the configurations *R*,*S*,*R* of the carbons C(8), C(7), and C(2), respectively, with reference to Figure 3. The two Pt−C(sp^3) distances [2.118, 2.140(7) Å] are slightly different, the shorter value being that of the better donor methyl group. The average Pt−C(sp^3) distance [2.13 Å] is significantly longer than that observed when the opposite ligand is the chloride ion (mean value 2.05 Å).[6] The actual value is in accord with what was recently found for mutually trans methyl groups in the platinum(IV) compounds [PtMe$_4$(CyN=CH−CH=NCy)] [2.14 Å, av][29] and [Pt$_2$Me$_8$(bpym)] [2.13 Å, av].[30] The bond distances for the equatorial ligands Pt−N$_{av}$ 2.15, Pt−C(olefin)$_{av}$ 2.05, and C=C 1.45(1) Å are normal and in accord with the values just discussed for **1a**.

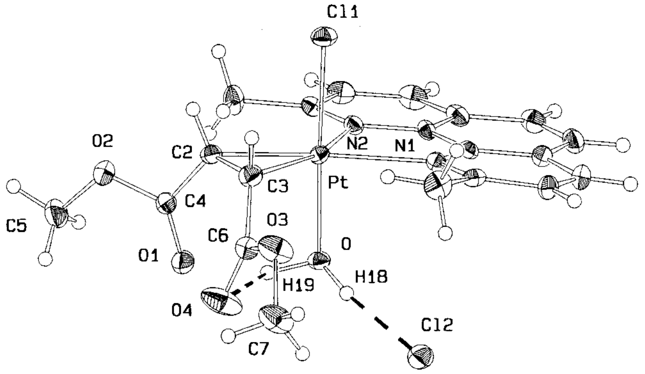

Figure 4. ORTEP drawing (30% probability level) of [PtCl(H$_2$O)(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]Cl.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [PtCl(H$_2$O)(dmphen)-(*Z*-MeO$_2$CCH=CHCO$_2$Me)]Cl·H$_2$O

Pt−O	2.049(5)	C(3)−C(6)	1.47(1)
Pt−C(2)	2.082(7)	C(5)−O(2)	1.45(1)
Pt−C(3)	2.088(8)	C(4)−O(1)	1.229(9)
Pt−N(1)	2.184(6)	C(6)−O(4)	1.20(1)
Pt−N(2)	2.190(6)	C(4)−O(2)	1.312(9)
Pt−Cl(1)	2.269(2)	C(6)−O(3)	1.326(9)
C(2)−C(3)	1.45(1)	C(7)−O(3)	1.45(1)
Cl(2)···O	2.93	O(1)···H(19)	1.65
N(1)−Pt−N(2)	76.3(2)	Cl(1)−Pt−O	177.7(2)
Cl(2)···H(18)−O	163	O−H(19)···O(1)	152

Molecular Structure of the [PtCl(H$_2$O)(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]$^+$ Cation as Its Chloride Salt Monohydrate.[31] The molecular structure of the title cation is represented in Figure 4, and relevant bond parameters are reported in Table 4. The overall stereogeometry is that usual for this family of compounds[6] and analogous to that just described for **1a** and **2a.** Were it not for the asymmetric conformation of the CO$_2$Me groups in the maleate ligand and the orientation of the hydrogens of the coordinated water, the ion would conform to a C_s symmetry. This cation is chemically related to the cation **1a**, [PtCl(CHNMe$_2$)(dmphen)(*Z*-MeO$_2$CCH=CHCO$_2$Me)]$^+$, from which it derives by substitution of the water molecule for the aminocarbene ligand. The bond distances in the equatorial plane are normal: [Pt−N$_{av}$ 2.19, Pt−C$_{av}$ 2.08, C=C 1.45(1) Å] and in good agreement with the corresponding values in **1a** and **2a**. Expectedly different are the interactions of the axial ligands. The Pt−Cl distance 2.269(2) Å is the shortest found in five-coordinate species (average value 2.30 Å),[6] probably because of the poor donor ability of the trans water oxygen. The Pt−OH$_2$ distance (2.049(5) Å) is normal. Among the numerous determinations

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[29] Hasenzahl, S.; Hausen, H. D.; Kaim, W. *Chem. Eur. J.* **1995**, *1*, 95.

[30] Klein, A.; Kaim, W.; Hornung, F. M.; Fiedler, J.; Zalis, S. *Inorg. Chim. Acta* **1997**, *264*, 269.

[31] Very small amounts of this compound accompanied the synthesis of **1a** in two runs. It was nearly undetectable through NMR spectroscopy, and hence, its spectrum was not attributable with confidence. Attempts of crystallizing crude **1a** afforded by chance very few single crystals of this aquo complex. Analogous species containing a neutral ligand and a halogen have been described.[32]

of the platinum−water interaction the most appropriate comparison is with that reported for [$PtCl_2$(DMSO)(H_2O)] [2.08(2) Å][33] because water and chloride are mutually trans in this molecule. The water ligand is stabilized by two hydrogen bonds, one with a maleate oxygen O(1)···H(19) [1.65(4) Å] and a second with the chloride counterion Cl(2)···H(18) [1.95(3) Å].

Conclusion

This work has demonstrated the synthesis of tbp platinum(II) complexes [PtX(CHY)(*N*,*N*-chelate)(olefin)]$^+$ (X = Cl, Me, or Ph) containing carbene ligands :CHY in apical position. As thoroughly demonstrated elsewhere[6] for complexes with similar coordination environments, the presence of a sterically crowded nitrogen chelate is a requisite necessary for their stability. When Y is NMe_2, i.e., a donor substituent, the complexes can be isolated. On the other hand, their stability seems to be reduced in the presence of electron-withdrawing Y substituents (Y = CO_2Et, $CONMe_2$, CN), as the $C_{carbene}$ atom appears to undergo a fast nucleophilic addition of water. Further rearrangement involving a carbonyl group of the olefin appendages leads to formation of a stable five-coordinate complex containing a η^1,η^2-C,C=C-chelating moiety.

Addition of nucleophiles to [PtCl($CHNMe_2$)(dmphen)(*Z*-$MeO_2CCH{=}CHCO_2Me$)]Cl affords dimethylformamide and the corresponding Pt(0) precursor [Pt(dmphen)(*Z*-$MeO_2CCH{=}CHCO_2Me$)].

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Supporting Information Available: Listing of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for compounds **1a**·H_2O, **2a**, and [PtCl(H_2O)(dmphen)(*Z*-$MeO_2CCH{=}CHCO_2Me$)]Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990240R

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[32] Albano, V. G.; Castellari, C.; De Felice, V.; Panunzi, A.; Ruffo, F. *Organometallics* **1992**, *11*, 3665.

[33] Rochon, F. D.; Kong, P. C.; Melanson, R. *Inorg. Chem.* **1990**, *29*, 2708.