

cis-Hydroxyplatination of Dimethyl Maleate: Modeling the Intermediates in a Catalytic Alkene-Hydration Cycle with Organoplatinum(II)–Hydroxo Complexes

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Abstract: Dimethyl maleate adds to the Pt–OH bonds of *cis*-Pt(OH)(Me)(PPh₃)₂ (**2**), Pt(OH)(Me)(dppe) (**3**), and Pt(OH)(Me)(pdmp) (**5**) [dppe = 1,2-bis(diphenylphosphino)ethane, Ph₂PCH₂CH₂PPh₂; pdmp = *o*-phenylenebis(dimethylphosphine), *o*-C₆H₄(PMe₂)₂] to give *cis*-PtMe{CH(CO₂Me)CH(OH)(CO₂Me)}L₂ [L₂ = 2PPh₃ (**6**), dppe (**7**), pdmp (**8**)]. Crystals of **6** are monoclinic, space group *P2₁/n*, with *a* = 12.658(2) Å, *b* = 21.688(4) Å, *c* = 14.340(2) Å, β = 97.25(1)°, and *Z* = 4. The structure was solved by the heavy atom method and refined by least-squares analysis to *R* = 0.027 and *R_w* = 0.032 based on 4508 unique observed reflections. The platinum atom is planar-coordinated by two *cis*-PPh₃ ligands, a methyl group [*r*(Pt–C) = 2.111(6) Å], and a CH(CO₂Me)CH(OH)(CO₂Me) group [*r*(Pt–C) = 2.152(7) Å]. The *threo*-(*R**,*R**)-configuration of the PtCH(CO₂Me)CH(OH)(CO₂Me) moiety indicates that dimethyl maleate undergoes *syn* addition to the Pt–OH bond of **2**, probably by *cis*-migratory insertion into the Pt–OH bond of a five-coordinate intermediate Pt(OH)(Me)(PPh₃)₂(η²-(*Z*)-MeO₂CCH=CHCO₂-Me). Dimethyl maleate does not insert into the Pt–OH bonds of *trans*-Pt(OH)(Ph)(PEt₃)₂ (**1**) or Pt(OH)(CF₃)(dppe) (**4**), and dimethyl fumarate is inert toward **1**, **2**, and **4**, but it reacts with **5** to give the monomethyl fumarate complex PtMe{(*E*)-OC(O)CH=CHCO₂Me}(pdmp) (**9**). Treatment of **6** or **7** with aqueous acids cleaves their Pt–CH(CO₂-Me)CH(OH)(CO₂Me) bonds forming [PtMe(H₂O)L₂]⁺ and dimethyl maleate, MeO₂CCH₂CH(OH)CO₂Me, thus demonstrating two steps necessary for catalysis of addition of water to dimethyl maleate.

Introduction

The catalytic hydration of terminal alkenes to primary alcohols at ambient temperature and pressure has been listed as one of the challenges of industrial catalysis.² Both enzymes and transition metal complexes can catalyze the hydration of alkenes, mainly those having electron-withdrawing substituents. The enzyme fumarase reversibly converts fumarate to *L*-malate and aconitase reversibly adds water to enzyme-bound *cis*-aconitate to give either isocitrate or citrate.³ Chlororuthenate(II) complexes catalyze the hydration of 1,1-difluoroethylene and vinyl fluoride,⁴ and maleic acid can be converted into malic acid by various compounds of aluminum(III) and chromium(III).⁵ Di-μ-hydroxo complexes [Pd₂(μ₂-OH)₂(L₂)₂]²⁺ (L₂ = dppe, dcpe)⁶ catalyze the hydration of diethyl maleate to diethyl malate, though with low turnover number.⁷ The reported direct anti-Markovnikov hydration of terminal alkenes catalyzed by *trans*-PtHCl(PMe₃)₂ in the presence of aqueous NaOH and a phase-transfer catalyst at 60–100 °C has unfortunately proved to be irreproducible.⁹ Finally, acyclic 1,3-dienes, such as butadiene and isoprene, undergo tail-to-tail dimerization and

addition of water to give octadienols in the presence of palladium catalysts such as Pd(acac)₂/PPh₃ or Pd(PPh₃)₄,¹⁰ under similar conditions, allene gives 3-methyl-2-methylene-3-buten-1-ol.¹¹

In the palladium-catalyzed hydration reactions and in the oxidative hydrolysis of alkenes (the Wacker process), monomeric hydroxopalladium(II) complexes may play an important role.¹² Monomeric hydroxoplatinum(II) complexes Pt(OH)(R)-L₂ (L = various tertiary phosphines; R = H, Me, Ph, CF₃, C₆H₅) catalyze the hydration of nitriles to carboxamides¹³ and, for R = CF₃, in the presence of H₂O₂, the epoxidation of alkenes;¹⁴ moreover, the Pt–O bond undergoes insertion with simple molecules such as CO, CO₂, RCN, and RNC.¹⁵ So far, however, little is known about the reactions of these and related complexes with olefins, although such reactions could play an important part in homogeneously catalyzed olefin hydration. Tetrafluoro-

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(6) Abbreviations: dppe = 1,2-bis(diphenylphosphino)ethane, Ph₂PCH₂CH₂PPh₂; dcpe = 1,2-bis(dicyclohexylphosphino)ethane, Cy₂PCH₂CH₂PCy₂; pdmp = *o*-phenylenebis(dimethylphosphine), *o*-C₆H₄(PMe₂)₂; COD = 1,5-cyclooctadiene, C₈H₁₂; C₆H₉ = 1-cyclohexenyl.

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Table 1. NMR (¹H, ³¹P) Data for *cis*-PtMe{CH^A(CO₂Me)CH^B(OH)(CO₂Me)}L₂ (**6–8**)^a

L ₂	δ (H)						δ (³¹ P)	
	Pt–Me	α-CO ₂ Me	β-CO ₂ Me	OH	H ^A	H ^B	P <i>trans</i> to Me	P <i>cis</i> to Me
2PPh ₃ (6)	0.45 (dd, ³ J _{PH} 7.0, 7.8, ² J _{PH} 62)	3.63 (s, ⁵ J _{PH} 3.9)	3.75 (s)	2.34 (d, ³ J _{HH} 7.0, ⁴ J _{PH} 2.8)	2.97 (ddd, ³ J _{HH} 10.0, ³ J _{PH} 16.6, 10.8, ² J _{PH} 108)	4.74 (ddd, ³ J _{HH} 10.0, ³ J _{H(OH)} 7.0, ⁴ J _{PH} 0.8, ³ J _{PH} 10)	29.3 (d, ² J _{PP} 11, ¹ J _{PP} 2007)	26.4 (d, ² J _{PP} 11, ¹ J _{PP} 2501)
dppe (7) ^b	0.48 (dd, ³ J _{PH} 6.8, 6.8, ² J _{PH} 65)	3.34 (s, ⁵ J _{PH} 4.0)	3.45 (s)	2.64 (d, ³ J _{HH} 8.2, ⁴ J _{PH} 2.6)	3.10 (ddd, ³ J _{HH} 9.4, ³ J _{PH} 9.5, ² J _{PH} 108)	4.03 (ddd, ³ J _{HH} 9.0, ³ J _{H(OH)} 8.2, ⁴ J _{PH} 1.6, ³ J _{PH} 16)	47.5 (s, ¹ J _{PP} 1802)	46.6 (s, ¹ J _{PP} 2404)
pdmp (8) ^{c,d}	1.11–1.22 ^e	3.30 (s)	3.49 (s)	3.39 (br d, ³ J _{HH} 8.3)	3.66 (dt, ³ J _{HH} 8.3, ³ J _{PH} 10.8, 10.8, ² J _{PH} 110)	5.31 (br dd, ³ J _{HH} 8.3, ³ J _{H(OH)} 8.3)	27.6 (s, ¹ J _{PP} 1794)	23.4 (s, ¹ J _{PP} 2318)

^a Measured in CD₂Cl₂, except where stated otherwise; coupling constants in Hz. Quoted multiplicities do not include ¹⁹⁵Pt satellites. ^b δ 1.7–2.4 (br m, PCH₂). ^c Measured in C₆D₆. ^d δ 1.45 (d, 3H, PMe, ²J_{PH} 8.8, ³J_{PH} 17.9), 1.81 (d, 3H, PMe, ²J_{PH} = 9.2, ³J_{PH} = 18.4). ^e Overlaps PMe₂ resonances.

roethylene inserts into the Pt–O bond of Pt(OMe)(Me)(dppe) to give Pt(CF₂CF₂OMe)(Me)(dppe), which has been fully characterized by spectroscopic methods and by single-crystal X-ray analysis.^{16,17} Although full details have not been published, the initial product of insertion of C₂F₄ into the Pt–OH bond of Pt(OH)(Me)(dppe), Pt(CF₂CF₂OH)(Me)(dppe), is reported to rearrange to the O-bonded species Pt(OCF₂CF₂H)(Me)(dppe), formally resulting from insertion into the O–H bond.¹⁵ Recently, the insertion of ethylene into the Ir–OH bond or Ir(OH)(Ph)(PMe₃)(η⁵-C₅Me₅) to give the β-hydroxyethyl complex Ir(CH₂CH₂OH)(Ph)(PMe₃)(η⁵-C₅Me₅) has been reported.¹⁸ We describe here the stoichiometric insertion of dimethyl maleate, (Z)-MeO₂CCH=CHCO₂Me, into Pt–OH bonds and show that it probably proceeds by a *cis* migration of hydroxide to the coordinated olefin.

Experimental Section

Reactions were performed under an atmosphere of nitrogen with use of standard Schlenk techniques and of solvents that had been distilled, dried, and degassed. The following instruments were used to obtain NMR spectra: Varian XL200E (¹H at 200.0 MHz, ¹³C at 50.29 MHz, ³¹P at 80.98 MHz, and ¹⁹F at 188.20 MHz), Varian Gemini (¹H at 300.1 MHz), Jeol FX-200 (¹H at 200.0 MHz and ¹³C at 50.1 MHz), and Jeol FX-60 (³¹P at 24.2 MHz). Chemical shifts (δ) are reported in ppm to high frequency of internal Me₄Si (¹H and ¹³C{¹H}), internal CFC₃ (¹⁹F{¹H}), or external 85% H₃PO₄ (³¹P{¹H}). Coupling constants (*J*) are in Hz. Quoted multiplicities do not include ¹⁹⁵Pt satellites. The NMR spectroscopic data for complexes **6–8** are summarized in Table 1. IR spectra were recorded as KBr disks in the range 4000–250 cm⁻¹ on Perkin-Elmer 683 and 1800 spectrometers. Melting points (uncorrected) were determined in nitrogen-filled capillaries on a Gallenkamp melting-point apparatus. Elemental analyses were performed in-house.

Starting Materials. Dimethyl maleate was dried and distilled over 4 Å molecular sieve prior to use. All other chemicals were AR grade and were used without further purification. The crystalline 1:1 adduct of hydrogen chloride with dimethylacetamide, DMA·HCl, was prepared by bubbling HCl gas slowly into a 10% solution of DMA in benzene. The resulting white precipitate was washed with benzene and ether and stored in a desiccator. The ligand pdmp¹⁹ and the complexes Pt₂-Me₄(μ₂-SMe₂)₂,²⁰ *trans*-PtI(Me)(PPh₃)₂,²¹ *trans*-PtBr(CF₃)(PPh₃)₂,²² *trans*-Pt(OH)(Ph)(PET₃)₂,^{13c,23} and Pt(OH)(Me)(dppe)²⁴ were prepared by the appropriate literature procedures. The preparations of other starting materials are described below.

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(a) **PtBr(CF₃)(dppe)**. This was prepared in 60% yield from PtBr(CF₃)(PPh₃)₂ and dppe in benzene, following the procedure described in ref 22 for the corresponding *cis*-Ph₂PCH=CHPPh₂ complex. It formed colorless microcrystals from CH₂Cl₂/ether. ¹⁹F{¹H} NMR (CD₂Cl₂): δ -21.5 (dd, ³J_{PF} = 57.8, 13.4, ²J_{PF} = 572). ³¹P{¹H} NMR (CD₂Cl₂): δ 42.8 (dq, ³J_{PF} = 13.4, ²J_{PP} = 5.8, ¹J_{PP} = 3930, P *trans* to Br), 39.7 (dq, ³J_{PF} = 57.1, ²J_{PP} = 5.8, ¹J_{PP} = 1821, P *trans* to CF₃). Anal. Calcd for C₂₇H₂₄BrF₃P₂: C, 43.68; H, 3.26; P, 8.34; Br, 10.76. Found: C, 43.90; H, 3.32; P, 8.53; Br, 10.98.

(b) **Pt(OH)(CF₃)(dppe)** (**4**). The procedure followed that of ref 22 for the corresponding *cis*-Ph₂PCH=CHPPh₂ complex. After recrystallization from CH₂Cl₂/C₆H₆, the product was obtained as colorless microcrystals in 81% yield. ¹H NMR (CD₂Cl₂): δ 1.90 (s, OH). ¹⁹F{¹H} NMR (CD₂Cl₂): δ -28.6 (dd, ³J_{PF} = 55.0, 9.2, ²J_{PF} = 589). ³¹P{¹H} NMR (CD₂Cl₂): δ 33.3 (dq, ³J_{PF} = 9.5, ²J_{PP} = 4.6, ¹J_{PP} = 3271, P *trans* to OH), 35.2 (dq, ³J_{PF} = 58.4, ²J_{PP} = 4.6, ¹J_{PP} = 2067, P *trans* to CF₃). IR (KBr, cm⁻¹): 3620 m [ν(OH)]. Anal. Calcd for C₂₇H₂₅F₃O₂Pt·0.5C₆H₆: C, 50.14, H, 3.93; P, 8.62. Found: C, 49.91; H, 3.80; P, 8.45.

(c) ***cis*-Pt(OH)(Me)(PPh₃)₂** (**2**). We found that the reported method of preparation²⁵ gave the acetyl complex *cis*-PtMe(CH₂COMe)(PPh₃)₂, which was presumably formed by reaction of the initially formed hydroxo complex with the acetone used as solvent; we therefore modified the procedure as follows.

To a stirred suspension of *trans*-PtI(Me)(PPh₃)₂ (0.64 g, 0.74 mmol) in acetone (25 mL) was added AgBF₄ (0.15 g, 0.77 mmol). The mixture was kept in the absence of light for 1 h, the precipitated AgI was removed by centrifugation, and the clear, colorless solution was evaporated to dryness *in vacuo*. The off-white residue was treated with THF (10 mL) and the cloudy suspension was stirred at room temperature for 10 min. The solvent was removed *in vacuo* and the THF treatment was repeated several times. Finally, to the THF solution was added dropwise a solution of KOH (0.06 g, 1.1 mmol) in H₂O (1.5 mL), giving immediately a clear, pale-yellow solution with a small amount of black solid. The mixture was stirred at room temperature for 48 h, and the solvents were removed *in vacuo*. Recrystallization of the residue from C₆H₆/ether gave **2** as colorless microcrystals (0.50 g, 83%), mp 208–210 °C (dec). The yield is significantly lowered if the reactants are heated at any stage. ¹H NMR (C₆D₆): δ 1.55 (dd, ³J_{PH} = 8.2, 6.0, ²J_{PH} = 44.4, PtOH), 1.10 (dd, ³J_{PH} = 7.1, 4.4, ²J_{PH} = 64.6, PtMe). ³¹P{¹H} NMR (C₆D₆): δ 26.9 (d, ²J_{PP} = 10.7, ¹J_{PP} = 1745, P *trans* to Me), 18.7 (d, ²J_{PP} = 10.7, ¹J_{PP} = 3608, P *trans* to OH). IR (Nujol, cm⁻¹): 3610 w [ν(OH)]. Anal. Calcd for C₃₇H₃₄O₂Pt: C, 59.12; H, 4.56; P, 8.24. Found: C, 58.67; H, 4.43; P, 7.94.

(d) **PtMe₂(pdmp)**. Although this compound can be made by addition of pdmp to PtMe₂(COD), higher yields were obtained by the following procedure. To a rapidly stirred suspension of Pt₂Me₄(μ₂-SMe₂)₂ (2.00 g, 3.48 mmol) in toluene (40 mL) was added pdmp (1.37 g, 6.92 mmol). The mixture was stirred at room temperature for 0.5 h and solvent was removed *in vacuo*. The resulting white solid was washed with three portions of hexane (20, 10, and 10 mL) and dried *in vacuo*. The yield of PtMe₂(pdmp) was 2.48 g (84%). ¹H NMR (CD₂Cl₂): δ 7.76, 7.56 (br m, C₆H₄), 1.65 (d, ²J_{PH} = 8.4, ³J_{PH} = 23.1, PMe₂), 0.49 (t, septn between outer lines = 15.7 Hz, ²J_{PH} = 68.1, PtMe).

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$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 25.3 ($^1J_{\text{PP}} = 1763$). Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{P}_2\text{Pt}$: C, 34.05; H, 5.24; P, 14.63. Found: C, 34.96; H, 5.59; P, 14.75.

(e) **PtCl(Me)(pdmp)**. A solution of $\text{PtMe}_2(\text{pdmp})$ (1.45 g, 3.43 mmol) in CH_2Cl_2 (15 mL) was treated with a solution of $\text{DMA}\cdot\text{HCl}$ (0.40 g, 3.25 mmol), and the mixture was stirred for 0.5 h at room temperature (caution: evolution of methane). Solvent was removed under reduced pressure and the residue was washed with several portions of ether to give $\text{PtCl}(\text{Me})(\text{pdmp})$ as a white solid, which was dried *in vacuo*. The yield was 1.35 g (88%). ^1H NMR (CD_2Cl_2): δ 7.82–7.60 (m, C_6H_4), 1.85 (d, $^2J_{\text{PH}} = 11.3$, $^3J_{\text{PH}} = 51.8$, PMe_2), 1.76 (d, $^2J_{\text{PH}} = 9.5$, $^3J_{\text{PH}} = 16.1$, PMe_2), 0.51 (dd, $^3J_{\text{PH}} = 7.8$, 3.6, $^2J_{\text{PH}} = 53.6$, PtMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 33.8 (d, $^2J_{\text{PP}} = 3$, $^1J_{\text{PP}} = 1730$, P trans to Me), 18.0 (d, $^2J_{\text{PP}} = 3$, $^1J_{\text{PP}} = 4030$, P trans to Cl). Anal. Calcd for $\text{C}_{11}\text{H}_{19}\text{ClP}_2\text{Pt}$: C, 29.77; H, 4.32; Cl, 7.99; P, 13.96. Found: C, 29.93; H, 4.35; Cl, 7.55; P, 13.94.

(f) **Pt(OH)(Me)(pdmp) (5)**. (i) To a suspension of $\text{PtCl}(\text{Me})(\text{pdmp})$ (0.05 g, 0.11 mmol) in THF (10 mL) was added a solution of KOH (0.09 g, 1.6 mmol) in water (1 mL). The mixture was stirred for 3 h at room temperature and evaporated to dryness *in vacuo*, ensuring that most of the water was removed. The residue was extracted with THF (20 mL) and the extract was centrifuged to remove insoluble solids. The solution was evaporated under reduced pressure to a volume of ca. 3 mL and hexane (20 mL) was added with rapid stirring. The resulting colorless solid was washed with hexane (2 \times 5 mL) and dried *in vacuo* to give **5** (0.04 g, 85%).

(ii) A suspension of $\text{PtCl}(\text{Me})(\text{pdmp})$ (0.20 g, 0.45 mmol) in THF (30 mL) was treated with AgBF_4 (0.11 g, 0.57 mmol). The mixture was stirred in the dark for 1 h and centrifuged. The supernatant liquid was treated with a solution of KOH (0.16 g, 2.86 mmol) in water (1 mL), the mixture was stirred for 5 min, and solvent was removed *in vacuo*. The residue was extracted with THF (3 \times 15 mL) and the extract was centrifuged to remove solids. Solvent was removed *in vacuo* to give **5** (0.12 g, 63%). ^1H NMR (C_6D_6): δ 7.23–6.82 (m, C_6H_4), 1.61 (d, $^2J_{\text{PH}} = 9.3$, $^3J_{\text{PH}} = 18.0$, PMe_2), 1.23 (d, $^2J_{\text{PH}} = 10.4$, $^3J_{\text{PH}} = 40.4$, PMe_2), 0.90 (dd, $^3J_{\text{PH}} = 7.6$, 3.6, $^2J_{\text{PH}} = 59.3$, PtMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 29.5 ($^1J_{\text{PP}} = 1857$, P trans to Me), 7.1 ($^1J_{\text{PP}} = 3309$, P trans to OH). IR (THF, cm^{-1}): 3509 m [$\nu(\text{OH})$]. Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{OP}_2\text{Pt}$: C, 31.06; H, 4.74; P, 14.57. Found: C, 30.86; H, 4.64; P, 14.81.

Reactions of Hydroxo Complexes with Dimethyl Maleate. (a) A solution of *cis*- $\text{Pt}(\text{OH})(\text{Me})(\text{PPh}_3)_2$ (**2**) (0.10 g, 0.13 mmol) in benzene (30 mL) was treated with dimethyl maleate (0.20 mL, 1.60 mmol, excess) and the mixture was stirred at room temperature for 3 days. The solvent was removed by evaporation under reduced pressure to give a colorless residue, which was washed with ether (2 \times 5 mL) and benzene/ether (1:2) (2 mL) to give *cis*- $\text{PtMe}\{\text{CH}(\text{CO}_2\text{Me})\text{CH}(\text{OH})(\text{CO}_2\text{Me})\}(\text{PPh}_3)_2$ (**6**) (0.10 g, 84%) as a white powder, mp 151–155 °C dec. The same compound was formed over a period of 1.5 days in THF. Crystals for X-ray analysis were grown by slow diffusion of ether into a solution of **6** in CH_2Cl_2 . IR (KBr, cm^{-1}): 3580 (sharp) [$\nu(\text{OH})$], 1730 s, 1680 s [$\nu(\text{C}=\text{O})$]. Anal. Calcd for $\text{C}_{43}\text{H}_{42}\text{O}_5\text{P}_2\text{Pt}$: C, 55.65; H, 4.73; P, 6.92. Found: C, 56.71; H, 4.63; P, 6.41.

(b) A suspension of $\text{Pt}(\text{OH})(\text{Me})(\text{dppe})$ (**3**) (0.10 g, 0.16 mmol) in benzene (20 mL) was treated with dimethyl maleate (0.40 mL, 3 mmol, excess) and the mixture was stirred at room temperature for 5 days. Removal of solvent *in vacuo* gave initially a yellow oil, which after a few hours turned into an off-white solid. This was shown by NMR spectroscopy (see text and Table 1) to be mainly $\text{PtMe}\{\text{CH}(\text{CO}_2\text{Me})\text{CH}(\text{OH})(\text{CO}_2\text{Me})\}(\text{dppe})$ (**7**), together with unidentified impurities. An analytically pure sample was obtained by crystallization from CH_2Cl_2 /ether, but the yield was only 0.02 g (16%). IR (KBr, cm^{-1}): 3430 w br [$\nu(\text{OH})$], 1730 s, 1670 s [$\nu(\text{C}=\text{O})$]; (CH_2Cl_2) 3589 m [$\nu(\text{OH})$], 1735 s, 1684 s [$\nu(\text{C}=\text{O})$]. Anal. Calcd for $\text{C}_{33}\text{H}_{36}\text{O}_5\text{P}_2\text{Pt}$: C, 51.50; H, 4.71; P, 8.05. Found: C, 51.31; H, 4.46; P, 7.94. The same product was obtained by treatment of **3** (0.15 g, 0.24 mmol) dissolved in THF (20 mL) with dimethyl maleate (0.04 mL, ca. 0.3 mmol) for 7 days.

(c) To a solution of $\text{Pt}(\text{OH})(\text{Me})(\text{pdmp})$ (**5**) (0.03 g, 0.07 mmol) in benzene (10 mL) was added dimethyl maleate (0.10 mL, 0.80 mmol). The mixture was stirred at room temperature for 12 days and solvent was removed by evaporation *in vacuo*. The residue was dissolved in benzene (5 mL) and the solution was centrifuged to remove some solid (mainly unchanged **5**, as shown by NMR spectroscopy). Addition of

hexane precipitated $\text{PtMe}\{\text{CH}(\text{CO}_2\text{Me})\text{CH}(\text{OH})(\text{CO}_2\text{Me})\}(\text{pdmp})\cdot\text{H}_2\text{O}$ (**8**) as a white powder (0.01 g, 25%). IR (CH_2Cl_2 , cm^{-1}): 3450 w br [$\nu(\text{OH})$], 1717 s, 1652 s [$\nu(\text{C}=\text{O})$]. Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{O}_6\text{P}_2\text{Pt}$: C, 34.76; H, 5.15; P, 10.54. Found: C, 34.54; H, 4.53; P, 10.14.

Under the same conditions, *trans*- $\text{Pt}(\text{OH})(\text{Ph})(\text{PEt}_3)_2$ (**1**) and $\text{Pt}(\text{OH})\text{-(CF}_3)_2(\text{dppe})$ (**4**) did not react with dimethyl maleate.

Reaction of Pt(OH)(Me)(pdmp) (5) with Dimethyl Fumarate. A suspension of **5** (0.05 g, 0.12 mmol) in benzene (20 mL) was treated with dimethyl fumarate (0.17 g, 1.18 mmol), and the mixture was stirred for 20 days. The volume of the solution was reduced to ca. 5 mL *in vacuo* and hexane (20 mL) was added with rapid stirring. The resulting white solid was washed with hexane (2 \times 10 mL) and dried *in vacuo*. The yield of $\text{PtMe}\{E\text{-OC}(\text{O})\text{CH}=\text{CHCO}_2\text{Me}\}(\text{pdmp})$ (**9**) was 0.05 g (77%). ^1H NMR (C_6D_6): δ 7.77 (d, $^3J_{\text{HH}} = 15.7$, =CH), 7.36 (d, $^3J_{\text{HH}} = 15.7$, =CH), 6.98 (m, C_6H_4), 3.28 (s, CO_2Me), 1.75 (d, $^2J_{\text{PH}} = 9.7$, $^3J_{\text{PH}} = 15.8$, PMe_2), 1.22 (d, $^2J_{\text{PH}} = 11.1$, $^3J_{\text{PH}} = 49.9$, PMe_2), 1.14 (dd, $^3J_{\text{PH}} = 8.1$, 2.9, $^2J_{\text{PH}} = 47.2$, PtMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 33.0 ($^1J_{\text{PP}} = 1801$, P trans to Me), 10.1 ($^1J_{\text{PP}} = 3975$, $\text{P trans to O}_2\text{CCH}=\text{CHCO}_2\text{Me}$). IR (CH_2Cl_2 , cm^{-1}): 1721 s, 1620 s [$\nu(\text{C}=\text{O})$]. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_4\text{P}_2\text{Pt}$: C, 35.76; H, 4.50; P, 11.53. Found: C, 35.77; H, 4.46; P, 11.42.

There was no observable reaction between $\text{Pt}(\text{OH})(\text{Me})(\text{dppe})$ and dimethyl fumarate at room temperature. In an NMR tube at 50–55 °C with C_6D_6 as the solvent several species formed. The presence of the dppe analogue of **9** was evident from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: δ 49.0 ($^1J_{\text{PP}} = 1791$, P trans to Me), 36.4 ($^1J_{\text{PP}} = 4189$, $\text{P trans to O}_2\text{CCH}=\text{CHCO}_2\text{Me}$).

Reactions of cis-PtMe{CH(CO₂Me)CH(OH)(CO₂Me)}L₂ [L₂ = 2PPh₃ (6**), dppe (**7**)] with Aqueous Acids.** One drop of aqueous acid [HBF_4 (43%) or HPF_6 (60%)] was added to a solution of **6** or **7** (0.05 g) in CD_2Cl_2 or THF-*d*₈ (0.5 mL) in a 5 mm NMR tube, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded immediately. The resulting cationic aquaplatinum(II) complexes $[\text{PtMe}(\text{H}_2\text{O})\text{L}_2]^+$ were characterized *in situ*. $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-*d*₈) (addition of $\text{HPF}_6(\text{aq})$ to **7**): δ 46.2 ($^1J_{\text{PP}} = 1771$, P trans to Me), 33.1 ($^1J_{\text{PP}} = 4182$, $\text{P trans to H}_2\text{O}$). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in THF-*d*₈ was identical to that obtained when one drop of $\text{HPF}_6(\text{aq})$ was added to $\text{Pt}(\text{OH})(\text{Me})(\text{dppe})$ (**3**) in THF-*d*₈ to give $[\text{PtMe}(\text{OH}_2)(\text{dppe})]\text{PF}_6$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) (addition of $\text{HBF}_4(\text{aq})$ to **6**): δ 31.5 ($^1J_{\text{PP}} = 3140$). The spectrum recorded in CD_2Cl_2 was identical to that obtained when **2** was treated similarly to generate *trans*- $[\text{PtMe}(\text{OH}_2)(\text{PPh}_3)_2]\text{BF}_4$. The CD_2Cl_2 solution formed by acidification of **2** was washed with water. The organic phase was dried (MgSO_4) and filtered, and the solvent was removed under reduced pressure to give dimethyl maleate, $\text{MeO}_2\text{CH}_2\text{CH}(\text{OH})\text{CO}_2\text{Me}$, as a colorless oil (ca. 80%). The compound is readily hydrolyzed to the free acid in aqueous solution, so isolation must be carried out as quickly as possible. ^1H NMR (CD_2Cl_2): δ 4.47 (dd, 1H, $^3J_{\text{HH}} = 6.5$, 4.5, CH), 3.73 (s, 3H, CO_2Me), 3.65 (s, 3H, CO_2Me), 3.30 (vbr s, OH), 2.78 (dd, 1H, $^2J_{\text{HH}} = 16.3$, $^3J_{\text{HH}} = 4.5$, CHH), 2.74 (dd, 1H, $^2J_{\text{HH}} = 16.3$, $^3J_{\text{HH}} = 6.5$, CHH). IR (cm^{-1} , neat): 3480 vs br [$\nu(\text{OH})$], 1740 vs [$\nu(\text{C}=\text{O})$], 1300–1160 vs br, 1110 vs, 1045 s [$\nu(\text{C}-\text{O})$]. Anal. Calcd for $\text{C}_6\text{H}_{10}\text{O}_5$: C, 44.45; H, 6.22. Found: C, 44.23; H, 6.51.

Crystallography. Data were collected on a colorless crystal of dimensions 0.07 \times 0.23 \times 0.25 mm. Reflection intensities were recorded on a Philips PW 1100/20 diffractometer using graphite monochromated Mo $K\alpha$ radiation. Lattice parameters were calculated from a least-squares analysis of setting angles for 25 reflections [$40 < 2\theta < 45^\circ$, $\lambda(\text{Mo } K\alpha) = 0.70930 \text{ \AA}$]. A total of 6163 unique reflections, of which 4508, with $I \geq 3\sigma(I)$, were treated as observed, was collected by means of θ - 2θ scans of width $(0.9 + 0.346 \tan\theta)^\circ$ in θ at a rate of 1.0 deg min^{-1} with 10 s background counts on each side of every scan; $2\theta_{\text{max}} = 48^\circ$ with $-14 \leq h \leq 14$, $0 \leq k \leq 23$, and $0 \leq l \leq 16$. Three check reflections measured every 120 min showed a 9% decrease in intensity during data collection, so a decomposition correction was applied to all data.²⁶ Data were corrected for absorption ($A^* = 2.364 - 1.289$). A summary of crystallographic data is given in Table 2. The structure was solved by heavy-atom techniques (SHELXS-86).²⁷ Refinement was performed by full-matrix least-squares methods with anisotropic displacement factors for all non-hydrogen atoms. Hydrogen

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(27) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M.; Krüger, C.; Goddard, R., Eds.; Oxford University Press: London, 1985; p 175.

Table 2. Summary of Crystallographic Data for (R^*,R^*) -*cis*-PtMe{CH(CO₂Me)CH(OH)(CO₂Me)}(PPh₃)₂ (6)

chemical formula	C ₄₃ H ₄₂ O ₅ P ₂ Pt
fw	895.83
space group	monoclinic, <i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	12.658(2)
<i>b</i> , Å	21.688(4)
<i>c</i> , Å	14.340(2)
β, deg	97.25(1)
<i>V</i> , Å ³	3905.2
<i>Z</i>	4
<i>T</i> , K	293
<i>ρ</i> _{calc} , g cm ⁻³	1.524
<i>μ</i> , cm ⁻¹	37.5
<i>F</i> (000)	1792
<i>R</i> ^a	0.027
<i>R</i> _w ^b	0.032
<i>S</i> ^c	1.11

^a *R* = (Σ||*F*_o| - |*F*_c||)/Σ|*F*_o|, ^b *R*_w = [Σ*w*(|*F*_o| - |*F*_c||)²/Σ*w*|*F*_o|²]^{1/2}.
^c *S* = goodness of fit = [Σ*w*(|*F*_o| - |*F*_c||)²/(*m* - *n*)]^{1/2}, where *m* = number of unique reflections and *n* = number of variables.

atoms (from the Δ*F* map for the methyl ligand, and at calculated positions for the phenyl and CH(CO₂Me)CH(OH)(CO₂Me) groups) were positioned geometrically and were not refined; the OH hydrogen atom was not located. Refinement on *F*, 460 parameters, gave the *R* values shown in Table 2, with the weighting scheme *w* = [σ²(*F*) + 0.0004*F*²]⁻¹, maximum shift/error ratio = 0.1, and maximum and minimum heights in the final difference map of +1.26 and -0.90 e Å⁻³, with all major features near the platinum atom. Atomic scattering factors for the neutral atoms, and real and imaginary dispersion terms were used,²⁸ and data reduction and refinement computations were performed with XTAL 2.6.²⁹ Positional and isotropic displacement parameters of non-hydrogen atoms are listed in Table 3.

Results

Precursors. The known planar platinum(II) hydroxo complexes *trans*-Pt(OH)(Ph)(PEt₃)₂ (1), *cis*-Pt(OH)(Me)(PPh₃)₂ (2), and Pt(OH)(R)(dppe) [R = Me (3), CF₃ (4)] are made by the standard method,¹⁵ or a slight modification thereof, from the appropriate halide (Scheme 1). The new hydroxo complex *cis*-Pt(OH)(Me)(pdmp) (5) can be made either in this way or by direct reaction of aqueous KOH with PtCl(Me)(pdmp) in THF. Its ³¹P{¹H} NMR spectrum shows a pair of singlets at δ 29.5 (¹*J*_{PtP} = 1857 Hz, *P trans* to Me) and δ 7.1 (¹*J*_{PtP} = 3309 Hz, *P trans* to OH), the Pt-P coupling constants being normal for hydroxoplatinum(II) complexes.²⁴ As is often the case for hydroxoplatinum(II) complexes, the OH signal could not be located in the ¹H NMR spectrum, but the IR spectrum in THF showed a ν(OH) band at 3590 cm⁻¹.

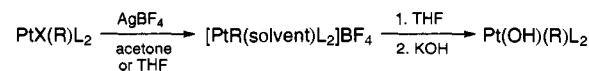
Although 2 has been isolated from *trans*-PtI(Me)(PPh₃)₂,²⁵ its configuration was not assigned. The ³¹P{¹H} NMR spectrum consists of a pair of doublets (²*J*_{PP} = 10.7 Hz) with ¹⁹⁵Pt satellites at δ 26.9 (¹*J*_{PtP} = 1745 Hz) and δ 18.7 (¹*J*_{PtP} = 3608 Hz). These can be assigned on the basis of the Pt-P coupling constants to the phosphorus atoms *trans* to Me and OH, respectively, in a *cis*-planar arrangement. In agreement, the Pt-Me resonance in the ¹H NMR spectrum appears at δ 1.10 in C₆D₆ as a doublet of doublets with ¹⁹⁵Pt satellites, indicative of coupling to two chemically inequivalent phosphorus atoms (³*J*_{PH} = 4.4, 7.1 Hz, ²*J*_{PH} = 64.6 Hz). In this case, the OH resonance is observed at δ 1.55 (C₆D₆) and shows well-resolved coupling to both ³¹P and ¹⁹⁵Pt. The ³¹P{¹H} NMR spectrum of the solvento intermediate [PtMe(acetone)(PPh₃)₂]BF₄ in CD₂Cl₂ shows just a singlet at δ 32.8 (¹*J*_{PtP} = 3161 Hz) and therefore

Table 3. Non-Hydrogen Positional and Isotropic Displacement Parameters for (R^*,R^*) -*cis*-PtMe{CH(CO₂Me)CH(OH)(CO₂Me)}(PPh₃)₂ (6)

	<i>x/z</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^a
Pt	0.22641(2)	0.16045(0)	0.24938(1)	0.0338(1)
P(1)	0.3245(1)	0.08742(6)	0.3415(1)	0.0357(7)
C(111)	0.2772(4)	0.0618(2)	0.4511(4)	0.042(3)
C(112)	0.1904(5)	0.0221(3)	0.4471(5)	0.057(4)
C(113)	0.1505(5)	0.0043(3)	0.5288(6)	0.071(5)
C(114)	0.1985(7)	0.0239(4)	0.6137(5)	0.077(5)
C(115)	0.2848(7)	0.0621(4)	0.6190(5)	0.075(5)
C(116)	0.3243(5)	0.0819(3)	0.5381(4)	0.057(4)
C(121)	0.3420(4)	0.0129(2)	0.2841(4)	0.042(3)
C(122)	0.3015(5)	0.0062(3)	0.1903(4)	0.057(4)
C(123)	0.3176(7)	-0.0492(4)	0.1462(5)	0.078(5)
C(124)	0.3702(6)	-0.0973(3)	0.1948(7)	0.082(6)
C(125)	0.4051(6)	-0.0909(3)	0.2881(7)	0.076(5)
C(126)	0.3922(5)	-0.0365(3)	0.3338(5)	0.057(4)
C(131)	0.4554(4)	0.1175(3)	0.3840(4)	0.041(3)
C(132)	0.4599(5)	0.1799(3)	0.4078(4)	0.053(4)
C(133)	0.5554(6)	0.2071(3)	0.4443(5)	0.072(5)
C(134)	0.6467(6)	0.1739(4)	0.4578(5)	0.078(5)
C(135)	0.6425(5)	0.1120(4)	0.4360(5)	0.069(5)
C(136)	0.5484(5)	0.0838(3)	0.3983(5)	0.053(4)
P(2)	0.3486(1)	0.18035(7)	0.1474(1)	0.0367(8)
C(211)	0.4773(5)	0.1408(3)	0.1520(5)	0.053(4)
C(212)	0.4838(6)	0.0848(4)	0.1092(7)	0.091(6)
C(213)	0.580(1)	0.0526(5)	0.116(1)	0.134(9)
C(214)	0.669(1)	0.0767(7)	0.164(1)	0.15(1)
C(215)	0.6639(7)	0.1314(7)	0.2068(7)	0.116(8)
C(216)	0.5685(5)	0.1645(4)	0.2020(5)	0.073(5)
C(221)	0.2937(5)	0.1660(3)	0.0245(4)	0.048(3)
C(222)	0.1944(5)	0.1393(3)	0.0050(4)	0.053(4)
C(223)	0.1530(6)	0.1266(4)	-0.0871(5)	0.075(5)
C(224)	0.2080(8)	0.1412(5)	-0.1600(6)	0.108(7)
C(225)	0.3065(9)	0.1658(6)	-0.1411(6)	0.148(9)
C(226)	0.3498(7)	0.1775(5)	-0.0495(6)	0.115(7)
C(231)	0.3907(4)	0.2614(2)	0.1539(4)	0.041(3)
C(232)	0.3569(5)	0.2993(3)	0.2209(5)	0.063(4)
C(233)	0.3910(6)	0.3611(3)	0.2299(6)	0.073(5)
C(234)	0.4570(6)	0.3836(3)	0.1705(6)	0.071(5)
C(235)	0.4917(8)	0.3463(4)	0.1045(6)	0.098(6)
C(236)	0.4581(7)	0.2862(3)	0.0961(5)	0.078(5)
C(3)	0.1326(4)	0.2286(3)	0.1734(4)	0.047(3)
C(41)	0.1169(5)	0.2160(3)	0.3950(5)	0.057(4)
O(411)	0.0639(4)	0.2625(2)	0.3843(4)	0.082(4)
O(412)	0.2011(4)	0.2126(2)	0.4608(4)	0.081(3)
C(413)	0.2326(8)	0.2662(5)	0.5150(7)	0.129(8)
C(42)	0.1019(5)	0.1578(3)	0.3385(5)	0.052(4)
C(43)	-0.0105(5)	0.1538(3)	0.2906(5)	0.064(4)
O(431)	-0.0859(4)	0.1484(3)	0.3583(4)	0.098(4)
C(44)	-0.0190(6)	0.0957(4)	0.2332(6)	0.076(5)
O(441)	-0.0108(6)	0.0434(3)	0.2609(5)	0.134(5)
O(442)	-0.0403(5)	0.1071(3)	0.1431(5)	0.103(4)
C(443)	-0.047(1)	0.0522(7)	0.0829(9)	0.19(1)

^a *U*_{eq} = ¹/₃Σ*U*_{ij}*a*_i**a*_j**a*_k.

Scheme 1



must be *trans*. The first product obtained on treatment of *trans*-[PtMe(THF)(PPh₃)₂]⁺ with aqueous KOH also shows a singlet [δ_P (C₆D₆) 30.0, ¹*J*_{PtP} = 3273 Hz] and is probably *trans*-Pt(OH)(Me)(PPh₃)₂; in THF it isomerizes over a period of hours at room temperature to the *cis*-isomer 2.

Reactions. Complexes 1-5 do not react with unactivated olefins such as ethylene, 1-hexene, or cyclohexene. However, an excess of the more electrophilic olefin dimethyl maleate reacts with the *cis*-(hydroxo)methyl complexes 2, 3, and 5 in benzene or THF at room temperature over a period of 2-5 days to give colorless, microcrystalline solids of general formula PtMe{CH(CO₂Me)CH(OH)(CO₂Me)}L₂ [L₂ = 2PPh₃ (6), dppe (7), pdmp (8)] arising from apparent insertion of the olefin into

(28) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(29) *XTAL 2.6 Reference Manual*; Hall, S.-R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland: Nedlands, Australia, and College Park, MD, 1989.

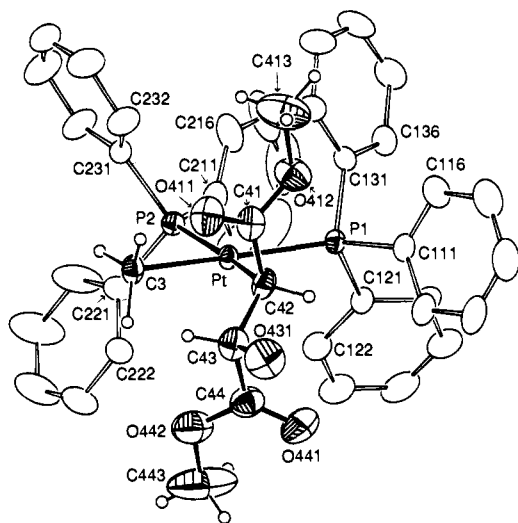


Figure 1. Molecular structure of (R^*,R^*) - $\text{cis-PtMe}\{\text{CH}(\text{CO}_2\text{Me})\text{CH}(\text{OH})(\text{CO}_2\text{Me})\}(\text{PPh}_3)_2$ (**6**), showing the crystallographic labeling scheme.

the Pt-OH bond; there was no observable reaction under the same conditions between dimethyl maleate and both **1** and **4**. Compounds **6–8** can be recrystallized from dichloromethane/ether, **6** being isolated in 84% yield. The other, more soluble compounds are also formed almost quantitatively, as shown by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, but the yields after recrystallization were only *ca.* 20%. The structural formulations rest on ^1H and ^{31}P NMR spectroscopic data (Table 1), IR spectra, and an X-ray structural analysis of **6** (see below).

The ^1H NMR spectrum of **6** shows a pair of singlets due to the inequivalent ester methyl groups at δ 3.63 and 3.75; the former shows a small coupling to ^{195}Pt and is therefore assigned to the CO_2Me group in the α -position to platinum. There is a pair of multiplets at δ 2.97 and 4.74 ($J_{\text{HH}} = 10.0$ Hz) due to the methine protons; the former shows a typical two-bond coupling to ^{195}Pt (108 Hz) and couplings to the phosphorus atoms (16.6, 10.8 Hz), hence it must be due to the proton H^{A} attached to the platinum-bound carbon atom. The presence of the CHOH function is evident both from a ^{195}Pt coupled doublet in the ^1H NMR spectrum at δ 2.34 ($^3J_{\text{HH}} = 7.0$ Hz, $^4J_{\text{PtH}} = 2.8$ Hz) and from a strong O-H stretching band at 3580 cm^{-1} in the IR spectrum (KBr disk). The IR spectrum also shows typical ester $\text{C}=\text{O}$ stretching bands at 1730 and 1680 cm^{-1} . The ^1H NMR spectra of **7** and **8** are essentially similar to that of **6**, though the typical Pt-Me resonance, which appears as a doublet of doublets with ^{195}Pt satellites at *ca.* δ 0.5 in **6** and **7**, could not be located in **8**, probably because it is less shielded and is masked by PMe_2 resonances. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **6–8** confirm the presence of *cis*-inequivalent phosphorus atoms. The resonance corresponding to P *trans* to methyl shows a Pt-P coupling of 1800 – 2000 Hz, whereas for the other resonance the Pt-P coupling is 2300 – 2500 Hz, typical of $^1J_{\text{PtP}}$ *trans* to a σ -bonded carbon atom carrying an electron-withdrawing substituent such as CO_2Me or COMe .²⁴

The X-ray study confirms that **6** is a typical square-planar platinum(II) complex. A diagram of the structure is shown in Figure 1, and selected bond lengths and bond angles are given in Table 4. The Pt-CH₃ and Pt-CH(CO₂Me)CH(OH)(CO₂Me) bond lengths differ significantly [$2.111(6)$ and $2.152(7)$ Å, respectively]; the lengthening effect on the Pt-C (sp^3) separation of the electron-withdrawing CO_2Me and $\text{CH}(\text{OH})(\text{CO}_2\text{Me})$ substituents is similar to that exerted by the COPh group in $\text{Pt}(\text{C}_6\text{H}_9)(\text{CH}_2\text{COPh})(\text{dppe})$.³⁰ In agreement with the

Table 4. Selected Bond Distances (Å) and Angles (deg) in (R^*,R^*) - $\text{cis-PtMe}\{\text{CH}(\text{CO}_2\text{Me})\text{CH}(\text{OH})(\text{CO}_2\text{Me})\}(\text{PPh}_3)_2$ (**6**)

Pt-P(1)	2.320(1)	Pt-P(2)	2.300(2)
Pt-C(3)	2.111(6)	Pt-C(42)	2.152(7)
C(41)-O(411)	1.212(8)	C(41)-O(412)	1.333(8)
C(41)-C(42)	1.498(9)	O(412)-C(413)	1.43(1)
C(42)-C(43)	1.502(9)	C(43)-O(431)	1.45(1)
C(43)-C(44)	1.50(1)	C(44)-O(441)	1.20(1)
C(44)-O(442)	1.31(1)	O(442)-C(443)	1.47(2)
P(1)-Pt-P(2)	97.80(5)	P(1)-Pt-C(3)	176.3(2)
P(1)-Pt-C(42)	91.3(2)	P(2)-Pt-C(3)	85.4(2)
P(2)-Pt-C(42)	170.0(2)	C(3)-Pt-C(42)	85.4(2)

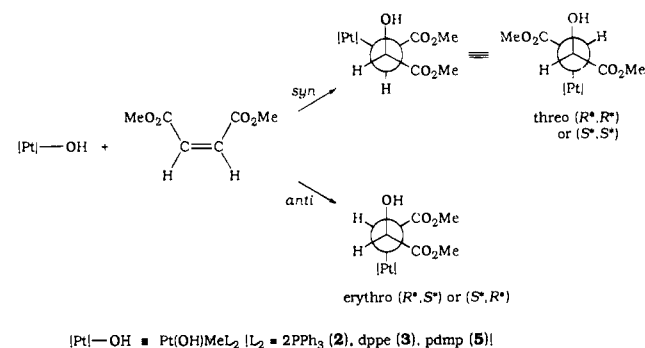


Figure 2. Possible stereochemistry of addition of hydroxoplatinum(II) complexes to dimethyl maleate.

trend evident from the Pt-P coupling constants, the Pt-P distance *trans* to Me [$2.320(1)$ Å] is significantly greater than that *trans* to $\text{CH}(\text{CO}_2\text{Me})\text{CH}(\text{OH})(\text{CO}_2\text{Me})$ [$2.300(2)$ Å], indicative of the higher *trans* influence of the methyl group. Bond lengths and angles within the $\text{CH}(\text{CO}_2\text{Me})\text{CH}(\text{OH})(\text{CO}_2\text{Me})$ and PPh_3 groups are unexceptional.

Although the adjacent chiral carbon centers in the $\text{PtCH}(\text{CO}_2\text{Me})\text{CH}(\text{OH})\text{CO}_2\text{Me}$ group imply the possibility of diastereomers, the ^1H and ^{31}P NMR spectra of **6–8** show the presence of only one species; the reactions of dimethyl maleate with **2**, **3**, and **5** are, therefore, completely (>95%) stereoselective. If the Pt-OH group undergoes *syn* addition to dimethyl maleate, the product will be the *threo* complex, whereas *anti* addition will give the *erythro* isomer (Figure 2). The X-ray structure of **6** shows that the $\text{PtCH}(\text{CO}_2\text{Me})\text{CH}(\text{OH})(\text{CO}_2\text{Me})$ group has the (R^*,R^*) -absolute configuration, i.e. it is priority-reflective,³¹ corresponding to the *threo* complex. Thus the stereochemistry of addition of the Pt-OH group of **2** to dimethyl maleate is *syn*; the same is likely to be true also for **3** and **5**.

Monitoring of the reactions of **3** and **5** with dimethyl maleate in C_6D_6 by ^{31}P NMR spectroscopy gave no evidence for any intermediate. In the case of **2**, however, although formation of **6** is apparent even after 0.5 h, a singlet at δ 29.7 ($^1J_{\text{PtP}} = 3281$ Hz) also appears immediately on mixing the reagents; this disappears slowly as **6** is formed. We believe that this peak is due to *trans*-Pt(OH)(Me)(PPh₃)₂, which is formed as the kinetic product of reversible displacement of PPh₃ from **2** (probably that *trans* to methyl) by dimethyl maleate and subsequent re-entry of PPh₃. Addition of PPh₃ (1:1 or 10:1) suppresses (though not completely) the formation of *trans*-Pt(OH)(Me)(PPh₃)₂ but does not affect the formation of **6**.

The insertion of dimethyl maleate into the Pt-OH bonds is irreversible, unlike the corresponding insertion of alkynes.³² Treatment of **6** in benzene with CO (1 bar) displaces one of the PPh₃ ligands and, although the product has not been completely characterized, it is clearly not a hydroxo- or hydroxycarbonyl complex and the $\text{CH}(\text{CO}_2\text{Me})\text{CH}(\text{OH})(\text{CO}_2\text{Me})$ fragment appears to be intact.

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In contrast with dimethyl maleate, dimethyl fumarate does not react with **2**, either at room temperature over a 10-day period or at 50–70 °C over 24 h, although it does catalyze the *cis* to *trans* isomerization of **2**. However, dimethyl fumarate reacts slowly with **5** in benzene to give a colorless half-ester complex $\text{PtMe}\{(\text{E})\text{-OC}(\text{O})\text{CH}=\text{CHCO}_2\text{Me}\}(\text{pdmp})$ (**9**), presumably with elimination of methanol; there was no evidence for the formation of an insertion product analogous to **8**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic parameters are similar to those of **5**, indicating that an O-bonded ligand is present in addition to the methyl group and pdmp. The ^1H NMR spectrum shows just one 3H singlet due to CO_2Me and a pair of doublets at δ 7.36 and 7.77 ($^3J_{\text{HH}} = 15.7$ Hz) arising from the *trans*-olefinic protons. A similar reaction occurs more slowly when **3** is heated with dimethyl fumarate but other unidentified products are also formed.

Discussion

We have established that the Pt–OH bond of *cis*-Pt(OH)-(Me)(PPh₃)₂ (**2**) undergoes stereospecific (>95%) *syn* addition to the C=C bond of dimethyl maleate to give the Pt–C σ -bonded complex *cis*-PtMe{CH(CO₂Me)CH(OH)(CO₂Me)}-(PPh₃)₂ (**6**); the corresponding complexes **7** and **8** containing dppe and pdmp, respectively, are probably formed with the same stereochemistry. A similar addition of the Pt–NHP bond of the hydrido(anilido) complex *trans*-PtH(NHP)(PEt₃)₂ to acrylonitrile to give *trans*-PtH{CH(CN)(CH₂NHP)}(PEt₃)₂ has been observed, although the stereochemistry of this reaction is unknown.³³ The stereochemistry we observe is not consistent with dissociation of OH[−] from the coordination sphere and subsequent external attack on coordinated dimethyl maleate, for which *anti* addition leading to the *threo* product (Figure 2) would be expected. The *syn* addition is most readily explained in terms of a concerted, *cis*-migratory insertion in a five-coordinate intermediate Pt(OH)(Me)L₂(η^2 -Z-MeO₂CCH=CHCO₂Me). We cannot exclude the possibility that insertion is preceded by dissociation of PPh₃ in the case of **2** or by one-ended dissociation of dppe or pdmp in the cases of **3** and **5**. The lability of PPh₃ in **2** is evident from the observation that both dimethyl maleate and dimethyl fumarate catalyze the *cis* to *trans* isomerization of **2**. However, the fact that free PPh₃ slows the isomerization without affecting the insertion seems more consistent with the notion that insertion occurs in a five-coordinate precursor. Our results agree with those of Bryndza *et al.*,^{16,17} who reported that the insertion of C₂F₄ into the Pt–OMe bond of Pt(OMe)(Me)-(dppe) proceeds by reversible formation of a 1:1 adduct and rate-limiting insertion into the Pt–OMe bond, without dissociation of OMe[−] from the coordination sphere. Also in agreement with this work is our failure to observe any insertion of dimethyl maleate into the Pt–Me bonds of **2**, **3**, and **5**.

It is well-known that hard nucleophiles, such as H₂O (OH[−]), R₂NH, OMe[−] (MeOH), O₂CMe[−], and [RCOCHCOR][−], attack olefins coordinated to palladium(II) and platinum(II), in complexes of the type [MCl₃(η^2 -olefin)][−] or MCl₂(η^2 : η^2 -diene), in a *trans* manner, whereas soft nucleophiles, such as H[−] or Me[−] undergo *cis*-migratory insertion.^{34–36} This behavior has been rationalized by ab initio MO calculations on model complexes Pd(H₂O)(nucleophile)₂(C₂H₄).³⁷ In the case of hard nucleophiles, the energy difference between the HOMO based on the metal–nucleophile bond and the LUMO based on the π^* orbital

of the olefin is too large, hence the reaction is charge controlled, whereas for the soft nucleophiles the HOMO is sufficiently high in energy that frontier orbital controlled *cis*-migratory insertion becomes possible. There has, however, been considerable disagreement about the mode of addition of water to olefins in the palladium(II)-catalyzed oxidation of olefins to carbonyl compounds (the Wacker process). Although stereochemical experiments indicate that *trans* addition is likely,³⁶ there is evidence that both *cis*- and *trans*-hydroxypalladation can occur, depending on the nature of the olefin, on the auxiliary ligands, and on the reaction conditions, and that *cis* addition is the key step in the process leading to the carbonyl compounds.³⁸

In the Pt(OH)(R)L₂ and Pt(OMe)(R)L₂ complexes, *cis*-migratory insertions into the Pt–O bond seem to be limited to those alkenes bearing strongly electron-withdrawing substituents (F, CO₂Me). These substituents lower the LUMO of the alkene, presumably providing a better match with the HOMO of the Pt–OH bond. The presence of a strongly electron-donating alkyl ligand may raise the energy of this HOMO, again enabling a closer match with the LUMO of the alkene, although it remains surprising that no insertion is observed into the Pt–Me bond. Replacement of CH₃ by CF₃ acts in the opposite sense, hence insertion into the Pt–O bond is not observed in this case. The failure of dimethyl fumarate to insert into the Pt–OH bonds of **2–5** may be due to steric hindrance to coordination of the C=C bond; thus the Pt–OH bond of the more basic and sterically less hindered complex **5** preferentially attacks a carboxylate carbon atom of dimethyl fumarate, a process analogous to ester hydrolysis.

Finally, since dimethyl maleate, the hydration product of dimethyl maleate, can be obtained by aqueous acid cleavage of the CH(CO₂Me)CH(OH)(CO₂Me) group from **6**, the reactions described here serve as a model for two steps of a hypothetical catalytic cycle for alkene hydration based on coordination of the alkene to a hydroxometal complex. Such a process probably occurs in the reported hydration of diethyl maleate by hydroxopalladium(II) complexes.⁷ Complex **2**, however, does not catalyze the hydration of cyclohexene to cyclohexanol, or of 1-hexene to hexanol, at 60 °C, and precursors that catalyze the hydration of a wider range of alkenes remain to be discovered.

Supporting Information Available: Details of structure refinement for [Pt(CH₃)(C₆H₅O₅)(PPh₃)₂] and tables of atomic coordinates for the hydrogen atoms and displacement parameters, complete listing of bond distances, bond angles, and torsion angles, and selected least squares planes (17 pages); listing of structure factor amplitudes (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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