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Transformation of a Terminal Phenylethenylidene Ligand to a μ-η^1,η^4-Phenylethenyl Ligand or a μ-η^1,η^2-Phenylethenyl Ligand: Structural Characterization of a Plausible Intermediate Species of a Fluxional Process

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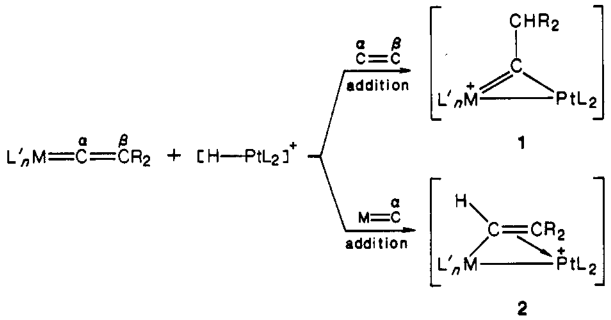
Addition of the Pt-H bond of [*trans*-Pt(H)(PEt$_3$)$_2$(acetone)]$^+$ to a tungsten terminal phenylethenylidene ligand, W=C=C(Ph)(H), occurs with the unexpected regiochemistry of H addition to the α-carbon atom and Pt addition to the tungsten atom to form a heterodinuclear complex containing a bridging styryl ligand. Spectroscopic data of the product in both solution phase and the solid state are consistent with a structure having a μ-η^1,η^4-styryl ligand. Variable-temperature ^{1}H NMR data confirm a dynamic process having a $\Delta G^{\ddagger}$(198 K) of ca. 9.4 kcal/mol for an exchange between equivalent μ-η^1,η^4-styryl structures in analogy to the fluxional behavior of η^3-benzyl ligands. However, the X-ray structure of the product containing CHCl$_3$ of crystallization in the lattice reveals a molecular structure possessing a μ-η^1,η^2-styryl ligand: {PtW[μ-η^1,η^2-C(H)=C(H)(Ph)](PEt$_3$)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(CO)$_3$}BF$_4$·CHCl$_3$; triclinic; $P\bar{1}$; $Z = 2$; $a = 15.689$ (3) Å, $b = 16.192$ (4) Å, $c = 11.799$ (2) Å; $\alpha = 93.69$ (2)°, $\beta = 95.66$ (2)°, $\gamma = 89.98$ (2)°. This structure is analogous to a η^1-benzyl structure which is a plausible intermediate for the exchange process of the μ-η^1,η^4-styryl ligand.

Introduction

We have reported previously that the Pt—H and Pt—R bonds of the reagents [*trans*-Pt(R)(PEt$_3$)$_2$(acetone)]$^+$ add regioselectively across the C≡C triple bond of terminal alkynyl ligands to give homo- or heterodinuclear complexes containing μ-alkenylidene ligands.[1a,b] These platinum reagents also add Pt—H or Pt—R bonds regioselectively across M≡C triple bonds of terminal alkylidyne ligands to afford heterodinuclear complexes containing μ-alkylidene ligands.[1c–e] The regiochemistry observed for these Pt-H addition reactions is precisely that expected for having initial coordination of the C-C or M-C multiple bond to the coordinatively unsaturated complex [HPt(PEt$_3$)$_2$]$^+$ followed by 1,2-addition of the polarized bond Pt$^{\delta-}$—H$^{\delta+}$ across the unsaturated bond such that the H ligand adds to the site normally preferred by electrophilic reagents. This mechanism is proposed by analogy to the mechanism deduced by Clark and co-workers for the addition of this platinum-hydride species to alkynes.[2]

An intriguing question arises as to the preferred site of Pt-H addition when a ligand contains both C-C and M-C unsaturated bonds, such as with a terminal alkenylidene ligand. As shown in eq 1, addition of the hydrogen ligand to C(β) of the alkenylidene ligand would give a dinuclear μ-alkylidyne complex, 1,[3] while addition of the hydrogen ligand to C(α) would afford a dinuclear μ-η^1,η^2-alkenyl complex, 2. The formation of a μ-alkylidyne product, 1, might be expected on the basis of the recognized polarity of the Pt-H bond in this reagent (as defined above) and the usual propensity of terminal alkenylidene ligands to undergo electrophilic attack at C(β).[4]



(1)

We now report that the terminal alkenylidene complex *mer*-(OC)$_3$(dppe)W=C=C(Ph)(H), where dppe is Ph$_2$PCH$_2$CH$_2$PPh$_2$ (prepared previously by Templeton and co-workers[4i]), reacts with [*trans*-Pt(H)(PEt$_3$)$_2$(acetone)]$^+$ to give a μ-$\eta^1,\eta^{2\,\mathrm{or}\,4}$-styryl complex obtained by an unexpected regioselective addition of the Pt hydrogen ligand to C(α) of the phenylvinylidene ligand. This result is unexpected because conventional electrophilic reagents add to C(β) of this tungsten alkenylidene complex.[4i] Furthermore, the structural chemistry of the dinuclear product has several interesting features. In solution phase and as a pure solid, this complex contains two bridging carbonyl ligands and a μ-η^1,η^4-styryl ligand where the styryl phenyl ring coordinates to the tungsten atom as a (μ-alkylidene)(η^3-benzyl) ligand. This structure exhibits fluxional behavior in solution analogous to that known for related η^3-benzyl ligands. However, as single-crystalline material containing solvent of crystallization, this dinuclear compound contains terminal carbonyl ligands and a μ-

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η^1,η^2-styryl ligand where the styryl ligand acts formally as a (μ-alkylidene)(η^1-benzyl) ligand. This structure closely corresponds to that expected for a plausible intermediate species in the above fluxional process. In addition, the transformation of the terminal phenylvinylidene ligand to a μ-$\eta^1,\eta^{2 \mathrm{or} 4}$-styryl ligand involves a rearrangement of the initial W–C σ bond to a Pt–C σ bond. This type of structural rearrangement for μ-η^1,η^2-alkenyl ligands has precedent in other systems. A detailed discussion of these results is presented below.

Experimental Section

Materials and Methods. All manipulations were performed under an atmosphere of dry, prepurified nitrogen. Diethyl ether, hexane, pentane, and tetrahydrofuran (THF) were dried over Na/K alloy with benzophenone having been added to the diethyl ether and THF. Methylene chloride was dried over CaH_2, and acetone was dried over $CaSO_4$. All solvents were distilled under nitrogen immediately prior to use.

Infrared (IR) spectra were recorded on a Perkin-Elmer 727 spectrophotometer as solutions in a 0.10-mm sodium chloride cavity cell by using the solvent as a reference, and a polystyrene film was used as the calibration standard. Solid-state IR spectra were recorded on the same instrument as KBr pellets. ^{1}H NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz) or an IBM NR-300 spectrometer (300 MHz), using the ^{2}H signal of the solvent as an internal lock frequency. Chemical shifts (in δ) were measured with respect to the residual solvent peak as an internal reference. ^{31}P NMR spectra were recorded on an IBM NR-200 spectrometer operating at a frequency of 81 MHz. Chemical shifts were measured with respect to the external reference 85% H_3PO_4. For measurement of NOE difference spectra, 1024 scans of each irradiation spot were acquired before subtraction, and 1.0 Hz of exponential line-broadening was used. 2D-COSY spectra were obtained by using the standard Bruker microprogram. 256-1K spectra were recorded by using a 90–τ–45 pulse sequence. Sine-bell apodization, magnitude calculation, and symmetrization were employed. Variable-temperature spectra were recorded on a Bruker AM-400 spectrometer in 10 °C increments, from −40 to −100 °C, using CD_2Cl_2 as the solvent. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Bis(diphenylphosphino)ethane (dppe), phenylacetylene, phenylacetylene-2-^{13}*C*, potassium tetrachloroplatinate, silver tetrafluoroborate, triethylphosphine, and tungsten hexacarbonyl were used as obtained from commercial sources. The compounds *trans*-$(PEt_3)_2PtHCl$,[5] *trans*-$(PEt_3)_2PtDCl$,[6] and *mer*-(dppe)$(OC)_3W{=}C{=}C(H)(Ph)$[4i] were prepared according to literature methods.

Preparation of {PtW[μ-C(CHC$_6$H$_5$)(H)](dppe)(CO)$_3$(PEt$_3$)$_2$}BF$_4$ (5a). A 0.20-mmol solution of **4a** was prepared in 10 mL of acetone from 0.092 g of *trans*-$(PEt_3)_2PtHCl$ and 0.038 g of $AgBF_4$. This solution was filtered through Celite in a Schlenk frit into a stirred solution of 0.20 mmol of **3a** in 5 mL of acetone. A color change from deep green to bright orange was observed after 3 min. The solution was allowed to stir at 25 °C for 1 h. The solvent was removed at reduced pressure. The resulting residue was washed with 2 × 10 mL diethyl ether and was dried in vacuo. Crystallization at −15 °C from CH_2Cl_2/hexane solution afforded 0.18 g (72% yield) of orange crystals. Upon drying under a stream of nitrogen at 25 °C, the crystals rapidly lost solvent of crystallization from the lattice and yielded a bright orange powder: mp 206–207 °C; IR (CH_2Cl_2) ν(CO) 1945 (s), 1860 (s, br) cm^{-1}; IR (KBr pellet) ν(CO) 1930 (s), 1840 (s, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15 (m, 18, CH_3), 1.85–2.10 (m, 12, CH_2), 2.20–3.05 (m, 4, PCH_2CH_2P), 5.15 (d, 2, ortho Ph, J = 7.5 Hz), 5.65 (m, 1, CHPh), 6.30 (m, 1, μ-CH), 6.60 (t, 2, meta Ph, J = 7.5 Hz), 6.95 (t, 1, para Ph, J = 7.5 Hz), 7.15–7.75 (m, 20, 4Ph); $^{31}P\{^1H\}$ NMR (5% $CDCl_3/CHCl_3$) δ 39.5 (m, Ph_2PCH_2, $^2J_{^{195}Pt-^{31}P}$ = 55.0 Hz, $^1J_{^{183}W-^{31}P}$ = 216.6 Hz), 29.5 ("t", Ph_2PCH_2, "J"$_{^{31}P-^{31}P}$ = 9.4 Hz, $^2J_{^{195}Pt-^{31}P}$ = 61.8 Hz, $^1J_{^{183}W-^{31}P}$ = 229.4 Hz), 21.8 (m, PEt_3 $^1J_{^{195}Pt-^{31}P}$ = 4065.6 Hz), 12.5 ("d", PEt_3, "J"$_{^{31}P-^{31}P}$ = 16.4 Hz, $^1J_{^{195}Pt-^{31}P}$ = 2662.0 Hz). Anal. Calcd for $C_{49}H_{61}BF_4O_3P_4PtW$: C, 45.71; H, 4.77; F, 5.90; P, 9.62. Found: C, 45.58; H, 4.67; F, 5.86; P, 9.58.

Table I. Crystallographic Data for Complex 5a•CHCl$_3$

formula	$C_{50}H_{62}BCl_3F_4O_3P_4PtW$
mol wt	1407.02 daltons
cryst system	triclinic
space group	$P\bar{1}$
a, Å	15.689 (3)
b, Å	16.192 (4)
c, Å	11.799 (2)
α, deg	93.69 (2)
β, deg	95.66 (2)
γ, deg	89.98 (2)
V, Å^3	2956.3
Z	2
D_{calcd}, g cm^{-3}	1.570
cryst size, mm	0.30 × 0.25 × 0.20
μ(Mo Kα), cm^{-1}	46.33
X radiatn	λ = 0.71073 Å (graphite monochromater)
temp, °C	23 (1)
hkl space explored	$h,\pm k,\pm l$
2θ range, deg	0–45
no. of reflns measd	7965
no. of unique data	7701
no. of unique data used	4934, $I > 3\sigma(I)$
scan type	ω–2θ
scan mode	fixed scan rate of 4°/min (in ω)
bkgd time	peak counting time/bkgd counting time rate = 2:1
abs cor	empiricial ψ-scan correctn
transmissn factors	(relative values scaled to smallest cryst dimensn)
max	0.9981
min	0.7236
av	0.8825
no. of stds used	3
intensity decay	none
no. of variables refined	318
R	0.073
R_w[a]	0.091

[a] $R_w = \{[\sum w(|F_o| - |F_c|)^2]/\sum w|F_o|^2\}^{1/2}$ where w is $1/\sigma(F_o)^2$.

Preparation of {PtW[μ-C(CHC$_6$H$_5$)(D)](dppe)(CO)$_3$(PEt$_3$)$_2$}BF$_4$ (5b). The above procedure for preparing complex **5a** was followed except that *trans*-$(PEt_3)_2PtDCl$ was substituted for *trans*-$(PEt_3)_2PtHCl$. The ^{1}H NMR spectrum indicates intensity loss for the resonance at δ 6.30.

Preparation of {PtW[μ-^{13}C(CHC$_6$H$_5$)(H)](dppe)(CO)$_3$(PEt$_3$)$_2$}BF$_4$ (5c). The compound *mer*-(dppe)$(OC)_3W{=}{}^{13}C{=}CHPh$ (**3b**) was prepared by Templeton's method,[4i] using phenylacetylene-2-^{13}C. This terminal alkenylidene complex was reacted with cation **4a** under the same conditions as for the nonlabeled analogue, **3a** (see above): ^{1}H NMR ($CDCl_3$) δ 6.30 (m, $^1J_{^{13}C-^1H}$ = 148.20 Hz, μ-^{13}CH). Other resonances remained essentially unchanged as compared to the spectral data of **5a**.

Crystal and Molecular Structural Determination of Complex 5a. Complex **5a** was prepared as stated above and was crystallized as orange prisms from $CHCl_3$/hexane solution (3:1) at −15 °C. The crystals were isolated and stored under a nitrogen atmosphere containing chloroform vapor, and the flask was stored in dry ice. Collection of the X-ray data was performed by Molecular Structure Corp., College Station, TX, as a commercial, technical service. The data crystal was mounted in a glass capillary in a random orientation. An Enraf-Nonius CAD4 computer-controlled, κ-axis diffractometer was used for data collection; and Lorentz, polarization, and empirical absorption corrections were applied to the data. Relevant crystallographic data are provided in Table I.

The phase problem was solved by locating the two heavy atoms Pt and W in a sharpened Patterson function. All nonhydrogen atoms were located from a series of difference syntheses. Refinement was by full-matrix least squares with anisotropic and isotropic thermal parameters. The quantity minimized was

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(6) This Pt–D compound is prepared according to the procedure reported in ref 5 except that D_2O is used as the solvent. The estimated degree of deuterium incorporation is 80–90%.

Table II. Final Atomic Positional Parameters for Complex 5a•$CHCl_3$ in Fractional Coordinates (with Esd's) Including Atomic Multiplicities (*m*) If Other Than Unity

atom	*x*	*y*	*z*	atom	*m*	*x*	*y*	*z*
Pt	0.22006 (10)	0.03997 (10)	0.25508 (12)	C(71)	0.65	0.2081 (33)	0.5329 (31)	0.7313 (39)
W	0.26126 (10)	0.14888 (10)	0.09916 (12)	Cl(1)	0.58	0.3042 (12)	0.5052 (11)	0.7516 (14)
P(1)	0.17871 (64)	−0.08552 (62)	0.17046 (82)	Cl(2)	0.47	0.1413 (19)	0.4592 (18)	0.7295 (24)
P(2)	0.22045 (71)	0.01701 (77)	0.44189 (85)	Cl(3)	0.48	0.1770 (17)	0.6014 (17)	0.8459 (21)
P(3)	0.37727 (62)	0.23169 (60)	0.04562 (78)	Cl(11)	0.19	0.1839 (30)	0.4278 (29)	0.6794 (37)
P(4)	0.17875 (66)	0.29193 (63)	0.07662 (82)	Cl(12)	0.23	0.1142 (41)	0.5427 (42)	0.8347 (51)
O(1)	0.2313 (15)	0.0861 (15)	−0.1542 (20)	C(72)	0.35	0.4151 (64)	0.5936 (61)	0.1774 (80)
O(2)	0.0629 (17)	0.1124 (16)	0.0738 (20)	Cl(4)	0.35	0.4680 (25)	0.5228 (22)	0.2244 (29)
O(3)	0.3881 (15)	−0.0202 (15)	0.0893 (19)	Cl(5)	0.35	0.3385 (20)	0.5852 (15)	0.0768 (20)
C(10)	0.2396 (23)	0.1199 (23)	−0.0582 (31)	Cl(6)	0.35	0.3470 (22)	0.5957 (20)	0.2864 (27)
C(20)	0.1308 (28)	0.1211 (25)	0.0942 (33)	B		0.18037	0.68978	0.49456
C(30)	0.3389 (22)	0.0421 (21)	0.1010 (27)	F(1)		0.18731	0.60363	0.47929
C(40)	0.2525 (23)	0.3657 (22)	0.0241 (28)	F(2)		0.18164	0.72210	0.61955
C(50)	0.3448 (22)	0.3445 (21)	0.0778 (27)	F(3)		0.25541	0.74585	0.49995
C(01)	0.2433 (27)	0.1550 (26)	0.3109 (33)	F(4)		0.12712	0.76104	0.46039
C(02)	0.3362 (24)	0.1747 (23)	0.3156 (28)					
C(03)	0.3694 (25)	0.2599 (23)	0.3651 (29)					
C(04)	0.4665 (27)	0.2584 (25)	0.3817 (32)	C(34)		0.6621 (29)	0.2144 (31)	0.2067 (36)
C(05)	0.4983 (30)	0.3343 (31)	0.4367 (37)	C(35)		0.6227 (27)	0.1352 (26)	0.1820 (32)
C(06)	0.4390 (30)	0.3897 (27)	0.4594 (34)	C(36)		0.5289 (24)	0.1414 (23)	0.1324 (29)
C(07)	0.3517 (31)	0.3991 (28)	0.4522 (36)	C(41)		0.3962 (21)	0.2211 (21)	−0.1074 (26)
C(08)	0.3118 (25)	0.3243 (26)	0.3983 (31)	C(42)		0.3862 (27)	0.2902 (27)	−0.1713 (37)
C(11)	0.2487 (26)	−0.1878 (25)	0.2129 (31)	C(43)		0.3978 (30)	0.2692 (30)	−0.2826 (40)
C(12)	0.3403 (33)	−0.1943 (31)	0.1791 (40)	C(44)		0.4266 (26)	0.1945 (28)	−0.3239 (33)
C(13)	0.1725 (23)	−0.0978 (22)	0.0111 (29)	C(45)		0.4436 (24)	0.1236 (25)	−0.2645 (33)
C(14)	0.1510 (25)	−0.1806 (25)	−0.0506 (31)	C(46)		0.4276 (22)	0.1462 (22)	−0.1469 (28)
C(15)	0.0767 (25)	−0.1221 (23)	0.1930 (29)	C(51)		0.1316 (24)	0.3418 (25)	0.2021 (30)
C(16)	0.0051 (25)	−0.0465 (24)	0.1931 (31)	C(52)		0.1525 (28)	0.4176 (29)	0.2431 (37)
C(21)	0.1578 (27)	−0.0639 (27)	0.4843 (35)	C(53)		0.1088 (33)	0.4511 (31)	0.3483 (41)
C(22)	0.1522 (28)	−0.0791 (27)	0.6150 (36)	C(54)		0.0564 (32)	0.4007 (33)	0.3857 (38)
C(23)	0.1703 (29)	0.1226 (27)	0.5273 (34)	C(55)		0.0297 (35)	0.3186 (36)	0.3469 (46)
C(24)	0.0794 (37)	0.1440 (34)	0.4884 (44)	C(56)		0.0743 (26)	0.2990 (25)	0.2496 (34)
C(25)	0.3306 (36)	0.0052 (34)	0.5145 (44)	C(61)		0.0875 (24)	0.3069 (23)	−0.0383 (30)
C(26)	0.3812 (34)	−0.0596 (34)	0.4759 (43)	C(62)		0.1045 (24)	0.2758 (23)	−0.1474 (32)
C(31)	0.4914 (24)	0.2262 (25)	0.1072 (30)	C(63)		0.0325 (28)	0.2919 (25)	−0.2337 (33)
C(32)	0.5369 (27)	0.2954 (25)	0.1377 (32)	C(64)		−0.0376 (27)	0.3332 (26)	−0.2140 (35)
C(33)	0.6187 (30)	0.2795 (28)	0.1844 (35)	C(65)		−0.0501 (30)	0.3658 (29)	−0.1032 (41)
				C(66)		0.0150 (28)	0.3571 (25)	−0.0128 (34)

$\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$. The variance σ^2 was based on counting statistics and included the usual instability term (4%). Atomic scattering factors used were those tabulated by Cromer and Mann,[7] and the anomalous-dispersion factors used were those of Cromer and Liberman.[8] The disorder present in atoms C(71), C(72), Cl(1)–Cl(6), Cl(11), and Cl(12) was treated by assigning fractional occupation parameters. The percentage of occupation was estimated from peak integration. Atoms B and F(1)–F(4) were located as diffuse areas of electron density. Positional coordinates were calculated on the basis of electron density maxima, and large isotropic thermal parameters were initially assigned to each atom. Isotroptic refinement of these atoms proceeded toward convergence for several least-squares cycles, but further refinement led to positional drifts that would not converge. The positional and thermal parameters were fixed at the values that were obtained after six cycles of least-squares refinement. These positions afforded an average B–F distance of 1.47 Å and an average F–B–F angle of 106.3°.

Refinement proceeded to convergence with anisotropic thermal parameters for atoms Pt, W, Cl(4)–Cl(6), and P(1)–P(4), isotropic thermal parameters for Cl(1)–Cl(3), Cl(11)–Cl(12), C(01)–C(72), and O(1)–O(3), and fixed parameters for the BF_4^- counterion. Of the 7701 reflections recorded, 4934 reflections were used in the final calculations as $I < 3\sigma(I)$ data were omitted. The average and maximum shift-to-error ratios for the final refinement cycle were 0.001 and 0.025, respectively. Maximum and minimum residual $\Delta\rho$ values were 1.7 and 0.3 Å^{-3}, near Cl(2) and C(34), respectively. Least-squares refinement, structure factors, electron density, least-squares planes and bond distances and angles were calculated with the X-ray 67 programs as implemented and updated on the Vanderbilt DEC-1099 computer.[9]

A list of final atomic positional parameters is provided in Table II. Selected interatomic distances and angles are given in Table III. A complete listing of final atomic positional and thermal parameters, interatomic distances and angles, selected least-squares planes data, and final observed and calculated structure factors are included as supplementary material.

Results

When the known tungsten terminal alkenylidene complex **3a**[4i] is treated with the cationic platinum–hydride species **4a**, the heterodinuclear product compound **5a** is formed in 72% yield (see eq 2). Solution IR spectra show ν(CO) metal carbonyl bands at 1945 and 1860 cm^{-1}, thus confirming the presence of terminal and bridging carbonyl ligands. Solid-state IR spectra of **5a** as a KBr pellet show similar carbonyl C–O stretching bands at 1930 and 1840 cm^{-1}.

The ^{1}H and ^{31}P NMR data of **5a** are consistent with the structure shown. An analysis of the ^{1}H NMR spectra of **5a** and its isotopically labeled derivatives **5b** and **5c** permits a more complete characterization of the structure of the bridging hydrocarbyl ligand and reveals certain details about the formation of this ligand. The proton resonances associated with the bridging hydrocarbyl ligand of **5a** lie within the spectral range of δ 5.0–7.0, as shown in spectrum A of Figure 1. The ortho, meta, and para protons of the phenyl substituent give resonances of expected multipl-

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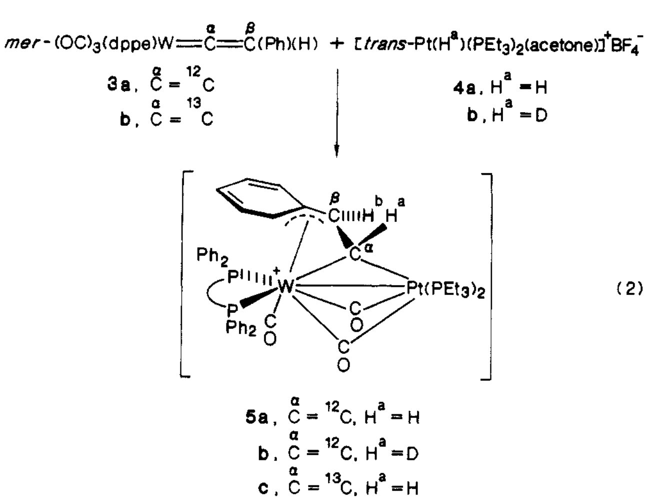
(9) (a) Stewart, J. M. *X-ray 67 Program System for X-ray Crystallography*, Technical Report Tr-67-58; Computer Science Center, University of Maryland: College Park, MD, 1967. (b) Johnson, C. K. ORTEP-II, Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.



(2)

icities at relatively high-field chemical shifts (δ 5.15, 6.60, and 6.95, respectively). The doublet resonance for the ortho protons at δ 5.15 appears at much higher field than that expected for a typical phenyl proton resonance. However, this chemical shift value is quite characteristic for ortho-proton environments of η^3-benzyl ligands.[10] The values of the chemical shifts of the meta- and para-proton resonances are also consistent with those expected for typical η^3-benzyl ligands.[11] Resonances for the alkenyl protons H^a and H^b appear as complex multiplets at δ 5.65 and 6.30. A two-dimensional COSY spectrum confirms the presence of J_{H-H} coupling between the phenyl proton nuclei and between the two alkenyl proton nuclei. Coupling between the alkenyl proton nuclei and the phenyl proton nuclei is not observed.

The correct assignment of the alkenyl proton resonances is evident from the ^1H NMR spectra of the isotopically labeled molecules **5b** and **5c**. Complex **3a** reacts with the Pt–D reagent **4b** (having ca. 80–90% deuterium abundance[6]) to give a monodeuteriated product **5b**. The ^1H NMR spectrum of this complex is shown in spectrum B of Figure 1. The nearly total loss of resonance intensity for the multiplet at δ 6.30 indicates that one of the alkenyl protons is derived entirely from the regioselective addition of the platinum hydride or deuteride reagent to **3a**. The other alkenyl proton resonance at δ 5.65 appears as a more narrow resonance in this monodeuteriated complex in comparison to the analogous resonance of the protiated complex (spectrum A) due to reduced coupling between the alkenyl proton and deuterium nuclei. Complex **3b**, where C(α) is labeled as ^{13}C, reacts with the Pt–H reagent **4a** to give the product **5c**. The ^1H NMR spectrum of this complex is shown as spectrum C of Figure 1. The alkenyl proton resonance centered at δ 6.30 is now split into two resonances due to $^1J_{^{13}C-^1H}$ coupling of 148.2 Hz. These results confirm the assignment of the alkenyl proton resonances. The alkenyl proton resonances at δ 6.30 and 5.65 can be assigned to the proton sites H^a and H^b, respectively. Furthermore, the alkenyl proton H^a is derived solely from the Pt–H reagent.

The assignment of the phenyl proton resonances of the styryl ligand given above is consistent with the higher symmetry of an exchange-averaged spectrum resulting from a fluxional process involving site exchange between two equivalent η^3-benzyl structures. A NOE-difference spectrum of **5a** at ca. +20 °C reveals essentially equal enhancement of the intensities of the resonances for H^a

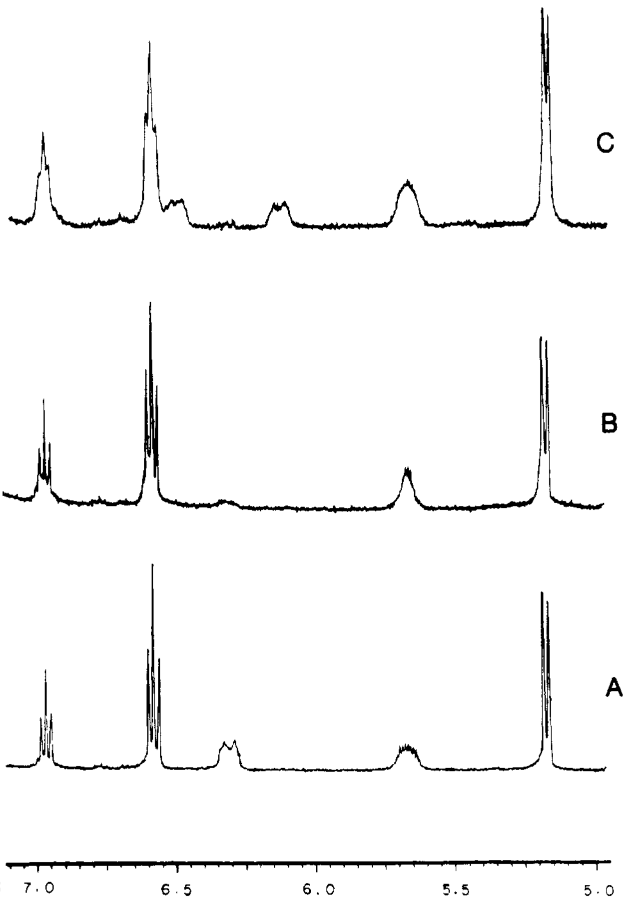


Figure 1. ^1H NMR spectra at 400 MHz for complexes **5a–c** in $CDCl_3$ solution for the frequency range of δ 5.0–7.0: spectrum A, **5a**; spectrum B, **5b** with a deuterium incorporation abundance of 80–90%; spectrum C, **5c**.

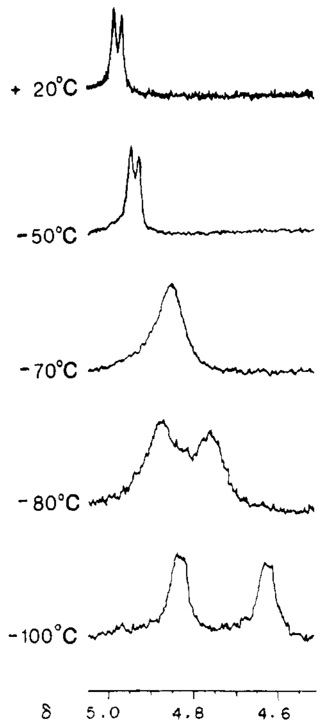


Figure 2. Variable temperature ^1H NMR spectra at 400 MHz of **5a** in CD_2Cl_2 solution showing spectral changes of the ortho-proton resonance of the phenyl substituent of the styryl ligand.

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[10] For example, the exchange-averaged resonances for the ortho protons in (η^3-benzyl)Mo(CO)$_2$(η-C_5H_5) complexes containing benzyl or symmetrically substituted benzyl ligands fall in the range of δ 5.50–5.85.[11]

[11] (a) King, R. B.; Fronzaglia, A. *J. Am. Chem. Soc.* **1966**, *88*, 709–712. (b) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1339–1346.

Table III. Selected Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations for Complex 5a•$CHCl_3$

Interatomic Distances			
Pt–W	2.751 (2)	P(2)–C(21)	1.76 (5)
Pt–P(1)	2.271 (10)	P(2)–C(23)	2.12 (4)
Pt–P(2)	2.258 (10)	P(2)–C(25)	1.87 (5)
Pt–C(01)	1.96 (4)	P(3)–C(50)	1.92 (4)
W–P(3)	2.418 (10)	P(3)–C(31)	1.87 (4)
W–P(4)	2.668 (10)	P(3)–C(41)	1.86 (3)
W–C(10)	1.88 (4)	P(4)–C(40)	1.84 (4)
W–C(20)	2.09 (4)	P(4)–C(51)	1.86 (4)
W–C(30)	2.12 (4)	P(4)–C(61)	1.90 (4)
W–C(01)	2.54 (4)	O(1)–C(10)	1.22 (4)
W–C(02)	2.71 (3)	O(2)–C(20)	1.08 (5)
P(1)–C(11)	2.05 (4)	O(3)–C(30)	1.28 (4)
P(1)–C(13)	1.87 (4)	C(01)–C(02)	1.49 (6)
P(1)–C(15)	1.76 (4)	C(02)–C(03)	1.53 (5)
Interatomic Angles			
W–Pt–P(1)	112.1 (3)	W–C(10)–O(1)	167 (3)
W–Pt–P(2)	145.9 (3)	W–C(20)–O(2)	167 (3)
W–Pt–C(01)	62.6 (12)	W–C(30)–O(3)	173 (3)
P(1)–Pt–P(2)	101.7 (4)	Pt–C(01)–W	74.2 (12)
P(1)–Pt–C(01)	171.4 (12)	Pt–C(01)–C(02)	111 (3)
P(2)–Pt–C(01)	84.4 (12)	W–C(01)–C(02)	80 (2)
Pt–W–P(3)	142.9 (2)	W–C(02)–C(01)	67 (2)
Pt–W–P(4)	121.4 (2)	W–C(02)–C(03)	123 (2)
Pt–W–C(01)	43.2 (10)	C(01)–C(02)–C(03)	120 (3)
Pt–W–C(02)	63.0 (8)	C(02)–C(03)–C(04)	109 (3)
P(3)–W–P(4)	81.1 (3)	C(02)–C(03)–C(08)	121 (3)
P(3)–W–C(01)	115.4 (10)	C(04)–C(03)–C(08)	129 (3)
P(3)–W–C(02)	85.6 (8)		
P(4)–W–C(01)	91.1 (10)		
P(4)–W–C(02)	99.9 (8)		
C(01)–W–C(02)	32.7 (12)		

and H^b (the measured enhancements are 13.3% and 12.6%, respectively) when irradiating the doublet resonance at δ 5.15 for the ortho protons of the styryl ligand. The result is consistent with the occurrence of such a dynamic process. Molecular models of a styryl fragment as the rotomer having symmetry-equivalent ortho protons reveal that the distances from the ortho protons to both H^a and H^b are essentially equal (ca. 3.5 Å).

The occurrence of a η^3-benzyl ligand undergoing a fluxional process is confirmed by a variable-temperature ^1H NMR study of **5a**. At −100 °C, the ortho-proton resonances of the styryl ligand appear as two well-separated doublets, and the corresponding meta-proton resonances appear as two overlapping triplets. A set of spectra showing the shape of the ortho-proton resonance at various temperatures is provided in Figure 2. A chemical shift dependence on temperature is observed. Although the spectrum at −100 °C may not represent the slow-exchange limiting spectrum, the spectrum is now consistent with the expected asymmetry of the η^3-benzyl structure **5a**. Assuming a coalescence temperature of −75 °C, the calculated value of $\Delta G^\ddagger$ (198 K) is 9.4 kcal/mol.

Single crystals of compound **5a** were grown to establish unambiguously its molecular structure by X-ray diffraction. Crystals grown at −15 °C from solutions containing methylene chloride can be isolated as dry single crystals. However, these crystals in the absence of methylene chloride vapor spontaneously fragment to a powder upon warming to near room temperature presumably due to the rapid release of solvent of crystallization. More thermally stable single crystals of **5a** are obtained by crystallization from chloroform/hexane solution. The ^1H NMR spectrum of a bulk sample of these crystals confirms the presence of chloroform of crystallization. Deterioration of the surfaces of these single crystals occurs upon exposure to ambient conditions for ca. 20 min due, presumably, to loss of chloroform. Solution and solid-state (ground sample in KBr) IR spectra of this material are identical with those of **5a** in the carbonyl-stretching region of the spectrum.

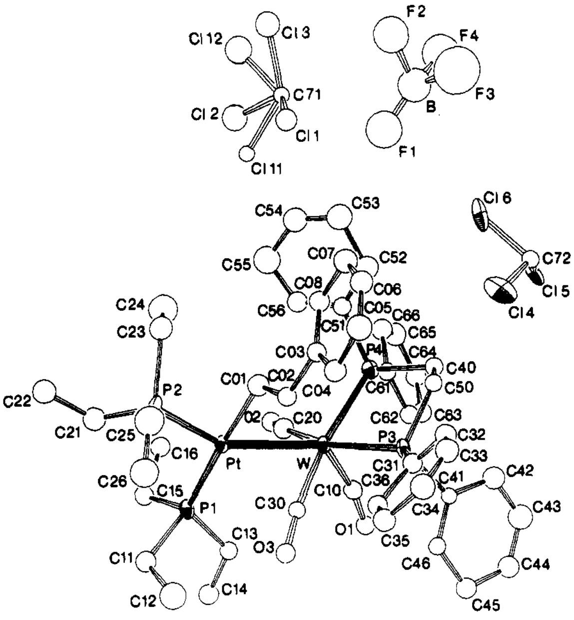

Figure 3. An ORTEP view of complex **5a**·$CHCl_3$ with thermal ellipsoids at 30% probability.

X-ray diffraction intensity data were collected on a crystal of **5a** grown from chloroform/hexane solution. The crystal was mounted in a glass capillary during data collection. A summary of relevant crystallographic data is provided in Table I. A list of final atomic positional parameters is provided in Table II, and selected interatomic distances and angles are listed in Table III. An ORTEP diagram of **5a**·$CHCl_3$ is shown in Figure 3.

The molecular structure of the heterodinuclear cation is related to the structure shown above for **5a**. The $Pt(PEt_3)_2$ moiety is connected to the $W(CO)_3(dppe)$ fragment by a Pt–W single bond having a length of 2.751 (2) Å.[1d,e] The $Pt(PEt_3)_2$ moiety has the expected "Y-shaped" structure with a P(1)–Pt–P(2) angle of 101.7 (4)°.[1a,d,e] The plane defined by [Pt, P(1), P(2)] intersects the plane defined by [W, P(3), P(4)] at a dihedral angle of 82°, and it bisects the $W(CO)_3(dppe)$ moiety nearly symmetrically with the atoms W and C(10) lying nearly in this plane (atomic deviations from coplanarity are 0.22 and 0.12 Å, respectively) and the pairs of atoms: P(3), P(4); C(40), C(50); and C(20), C(30) being nearly symmetrically displaced from this plane (the respective atomic deviations from coplanarity are 1.62, −1.66; −0.86, 0.59; −1.62, 1.87 Å, respectively).

The most important structural details relate to the coordination geometry of the carbonyl ligands and the bridging styryl ligand. The three carbonyl ligands conform to the geometry expected of terminal carbonyl ligands. The more uniquely terminal carbonyl ligand C(10)–O(1) has a W–C distance of 1.88 (4) Å and a W–C–O angle of 167 (3)°. The two carbonyl ligands located in potentially bridging positions C(20)–O(2) and C(30)–O(3) have W–C distances of 2.09 (4) and 2.12 (4) Å, respectively, and W–C–O angles of 167 (3)° and 173 (3)°, respectively. The Pt···C contact distances to C(20) and C(30) are 2.66 (4) and 2.73 (4) Å, respectively. Even with consideration of the relatively large standard deviations for these distances and angles, the carbonyl ligands C(20)–O(2) and C(30)–O(3) are best characterized as being terminal CO ligands.[12,13]

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(12) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* **1986**, *25*, 805–812.

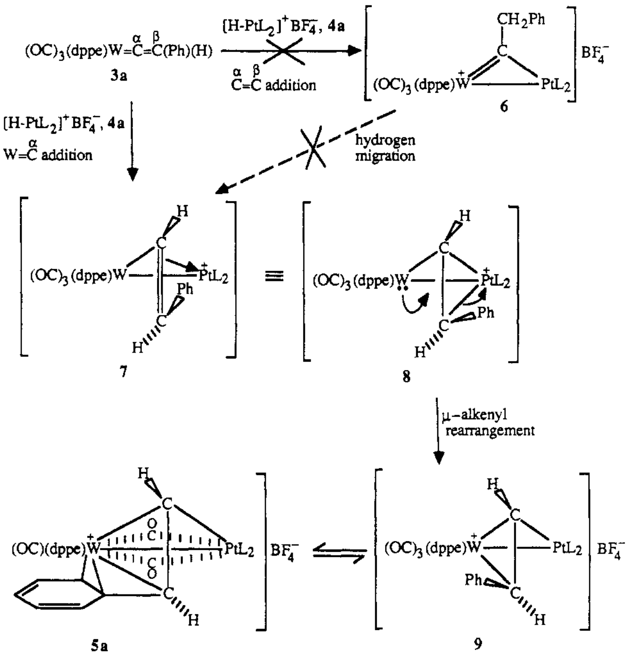
The bridging styryl ligand of **5a** is σ-bonded to the Pt atom. The Pt–C(01) distance of 1.96 (4) Å is similar to the Pt–C distances of 2.01 (2) and 2.04 (3) Å observed in Pt–W complexes containing μ-alkylidene ligands.[1d,e] The Pt–C(01)–C(02) and C(01)–C(02)–C(03) angles of 111 (3)° and 120 (3)°, respectively, are consistent with the expected geometry for a styryl group. The W–C(01) and W–C(02) distances of 2.54 (4) and 2.71 (3) Å indicate a weak π-coordination of the styryl/alkene bond to the tungsten atom. Normal W–C σ-bond distances to μ-alkylidene ligands are significantly smaller than these values [typical W–C(μ-alkylidene) distances are ca. 2.20 Å].[1d,e] The average value of the four W–C(η^2-alkene) distances in *trans*-(η^2-methyl acrylate)$_2$W(CO)$_4$ is 2.30 Å,[14] which is slightly longer than normal W–C(μ-alkylidene) σ-bond lengths. The average C–C distance of these η^2-methyl acrylate ligands is 1.41 (2) Å; the corresponding distance of the styryl ligand in **5a** is 1.49 (6) Å. The weak and unsymmetrical π-coordination of the styryl alkene bond to the tungsten atom probably results from geometrical restraints imposed upon the position of this ligand due to contact interactions between the styryl ligand and hydrogen atoms of the dppe ligand and due to its σ-coordination to the platinum atom. Although the carbon atoms C(01) through C(08) of the styryl ligand are nearly coplanar [the maximum atomic deviation from coplanarity is 0.13 Å for atom C(01) and the Pt atom is displaced only 0.27 Å from this plane], *the phenyl substituent remains uncoordinated to the tungsten atom.* The W···C(03) contact distance is 3.77 (4) Å, and the W···C(04) and W···C(08) contact distances are greater than 4.10 Å.

The BF_4^- counterion and the $CHCl_3$ molecule of crystallization have been refined as disordered entities. The BF_4^- ion is located in nearly a single fixed site, while the $CHCl_3$ molecule is located in two sites with relative populations of 35% and 65%. The $CHCl_3$ molecule weighted at 65% has additional disorder which is modeled best by two molecular fragments. The average values of the B–F distances and F–B–F angles are 1.47 Å and 106.3°, and the average values for the intramolecular C–Cl distances and Cl–C–Cl angles are 1.66 Å and 110°, respectively.

Discussion

A postulated mechanism for the formation of complex **5a** is shown in Scheme I. If the cationic platinum–hydride reagent **4a** acts as a source of H^+ and the neutral coordinatively unsaturated species PtL_2, then the dinuclear μ-alkylidyne complex **6** should form from proton addition at C(β) followed by PtL_2 insertion into the W–C triple bond.[4i] Likewise, complex **6** could be formed by a regioselective 1,2-addition of the Pt–H bond to the C(α)=C(β) bond if the hydride ligand adds to C(β). However, spectroscopic data of the product compound are inconsistent with structure **6**. Furthermore, if **6** were formed as an intermediate species having a lifetime longer than the rate of rotation of the benzyl substituent, then the μ-alkenyl product **7** formed by hydrogen migration should have equivalent deuterium population in the alkenyl proton sites when the Pt–D reagent **4b** is used. This rearrangement of **6** to **7** does not occur because the isolation of products **5b** and **5c** demonstrates deuterium incorporation solely in the alkenyl site, H^a, of **5b**. The conversion of cationic, dinuclear μ-alkylidyne complexes, like **6**, to dinuclear μ-alkenyl compounds by a hydrogen migration as considered above has been demonstrated independently for diiron complexes by Casey and Hoel.[15]

Scheme I. Postulated Mechanism for the Formation of Complex 5a (Where L = PEt$_3$)



We suggest that the Pt—H bond of **4a** adds regioselectively across the W=C(α) bond of **3a** to give **7** directly. Although both nucleophilic and electrophilic attack at C(β) of terminal alkenylidene ligands are known reactions,[4] the presumed polarity of the Pt–H bond of $Pt^{\delta-}$–$H^{\delta+}$ might indicate that this reaction is another example of an unusual electrophilic addition to C(α) of a terminal alkenylidene ligand.[16] Alternatively, the W=C unsaturated bond might coordinate more strongly to the $HPtL_2^+$ species than would the alkenylidene C=C double bond in forming the expected η^2-complex as an intermediate prior to insertion into the Pt—H bond.[2]

Compound **7** is a dinuclear, μ-alkenyl complex[15,17] that can be represented as a π-bonded ligand, **7**, or as the "all-σ" representation **8**. In these formally equivalent representations, the μ-alkenyl ligand is σ-bonded to the tungsten atom and π-bonded to the platinum atom. The rearrangement of **8** to **9** reverses this bonding mode of the μ-alkenyl ligand so that in **9**, the μ-alkenyl ligand is σ-bonded to the platinum atom and π-bonded to the tungsten atom. Analogous rearrangements of μ-alkenyl ligands in dinuclear complexes are known.[15a,18]

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[13] The asymmetrically bridging carbonyl ligands of the two similar Pt-W complexes, $\{(\eta\text{-}C_5H_5)(OC)_2W[\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4Me\text{-}p)(H)]Pt(PEt_3)_2\}BF_4$[1d] and $\{(HBpz_3)(OC)_2W[\mu\text{-}\eta^1,\eta^2\text{-}C(H)(NEt_2)]Pt(PEt_3)_2\}BF_4$,[1e] have the following coordination geometries, respectively: W–C distances of 1.99 (3) and 2.08 (4) Å; W–C–O angles of 157 (2)° and 155 (2)°; and Pt–C distances of 2.23 (3) and 2.28 (2) Å. The Pt–C(20) and Pt–C(30) contact distances of **5a** are 0.38–0.50 Å longer than the corresponding Pt–C distances to the bridging carbonyl ligands of these complexes.

[14] Grevels, F. W.; Lindermann, M.; Benn, R.; Goddard, R.; Krüger, C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1298–1309.

[15] (a) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950–4951. (b) Casey, C. P.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 7197–7198. (c) Casey, C. P.; Fagan, P. J.; Miles, W. H.; Marder, S. R. *J. Mol. Catal.* **1983**, *21*, 173–188. (d) Hoel, E. L. *Organometallics* **1986**, *5*, 587–588.

[16] (a) Werner, H.; Wolf, J.; Müller, G.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 431–432. (b) Wolf, J.; Werner, H. *J. Organomet. Chem.* **1987**, *336*, 413–428.

[17] For other examples of heterodinuclear, μ-alkenyl complexes see the following references and references therein: (a) Moldes, I.; Ros, J.; Mathieu, R.; Solans, X.; Font-Bardia, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1619–1622. (b) Garcia, M. E.; Tran-Huy, N. H.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 2201–2209. (c) Fong, R. H.; Hersh, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 2843–2845.

Complex **9** contains a μ-η^1,η^2-styryl ligand. The tungsten atom has a 18-electron count with three terminal carbonyl ligands, while the platinum atom is four-coordinate and has a 16-electron count. This complex could also be represented as a heterodinuclear compound containing a bridging alkylidene ligand with one of the substituents of the μ-alkylidene carbon atom acting as a η^1-benzyl ligand. Rearrangement of this η^1-benzyl substituent to its η^3-benzyl coordination mode would give the observed product **5a**. In complex **5a**, two of the carbonyl ligands become bonafide bridging carbonyl ligands so that the electron count at tungsten remains 18. The electron count at platinum in **5a** is now also 18.

The fluxional process demonstrated for the η^3-benzyl ligand of **5a** can be represented most easily as an exchange between the two equivalent η^3-benzyl structures of **5a** through the η^1-benzyl intermediate **9**. In going from **9** to **5a**, the plane of atoms defining the eventual η^3-ligand approaches the tungsten atom and displaces the dppe and carbonyl ligands away from its direction of approach and toward the other side of the molecule where two of the carbonyl ligands are placed into bridging positions. Complex **5a** can be represented as a heterodinuclear complex containing a μ-η^1,η^4-styryl ligand or as having a μ-alkylidene ligand where one of the alkylidene substituents acts as a η^3-benzyl ligand. Because of the bonding and structural restraints imposed upon the motion of the μ-styryl ligand, the fluxional process in this system probably does not involve either a [1,5]-sigmatropic shift or a η^3-benzyl rotation mechanism as has been suggested recently for mononuclear, η^3-benzyl complexes.[19] The above proposed mechanism would be consistent with the rather low value of ΔG^{*} for the fluxional process of **5a**.

The solution and solid-state structure (unsolvated material) of **5a** is described best as the η^3-benzyl structure, as shown above. This structure is supported by the presence of a C–O stretching band at a frequency expected for bonafide bridging carbonyl ligands in Pt–W dinuclear complexes[1d,e] and by the very unique and diagnostic chemical shift values observed for the styryl proton resonances of the phenyl substituent. However, the X-ray structural data for **5a** in a lattice containing chloroform of solvation reveal a molecular structure closer to that of **9**. Even within the limits of interpretation resulting from the relatively poor precision of this structural determination, two of the carbonyl ligands are not located in bonafide bridging positions, and the carbon atoms of the phenyl substituent of the styryl ligand are clearly not coordinated to the tungsten atom. In addition, the alkenyl carbon atoms of the styryl ligand are located at positions representing weak, but significant, coordination to the tungsten atom. The W–C(α) distance of 2.54 (4) Å indicates appreciable π-bonding to the tungsten atom. The corresponding W-alkene carbon distances to the chelated, η^2-alkene ligand in the compound *cis*-$(OC)_4$[((*Z*)-η^2-*N*,2,2-trimethyl-3-butenylamino)-*p*-tolylcarbene]tungsten(0) are found in the range of 2.42 (1)–2.49 (1) Å,[20a] and the W-alkene carbon distances to the chelated, η^2-alkene ligand in the complex $(OC)_4W[C(OEt)(CH)(\eta^2\text{-}CH_2CH{=}CH_2)(CH_2CH{=}CH_2)$ are 2.42 (2) and 2.35 (3) Å.[20b] The W–C(β) distance in **5a** of 2.71 (3) Å reflects the unsymmetrical coordination of the styryl ligand to the tungsten atom due to the structural restraints imposed on this η^2-coordination geometry by the σ-bonded attachment of the styryl ligand to the platinum atom and from any interligand steric interactions between the dppe and styryl ligands. Therefore, the structure of **5a** as determined in the solvated lattice closely represents structure **9** which is a plausible structure for the intermediate in the fluxional process exhibited by **5a** in solution. Presumably, the intermolecular packing forces within the solvated lattice of this ionic material are sufficiently strong enough to overcome the energy difference between structures **5a** and **9** (estimated to be at least 10 kcal/mol). Structural distortions observed recently in the ground-state structure of a Zr–allyl complex have been correlated to the unusually facile fluxional processes of this molecule.[21]

Conclusions

Regioselective addition of a Pt—H bond across the W═C bond of a terminal phenylvinylidene ligand occurs to give a heterodinuclear complex containing a μ-η^1,η^4-styryl ligand. This molecule undergoes a fluxional process represented best as the exchange of the η^3-benzyl fragment of the bridging styryl ligand between equivalent sites through a η^1-benzyl fragment structure as an intermediate species. The molecular structure determined for this complex in a lattice containing solvent of crystallization reveals a structure like that expected for the η^1-benzyl intermediate rather than the structure expected for the ground-state structure containing a η^3-benzyl ligand fragment.

Acknowledgment. We thank Dr. Thomas M. Harris for assistance in obtaining COSY spectra. C.M.L. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A platinum metal loan from Johnson Matthey, Inc., is gratefully acknowledged. W.R.T. thanks the Graduate School of Vanderbilt University for a grant in support of this research.

Registry No. **3a**, 88035-90-9; **3b**, 116323-71-8; **5a**, 116323-73-0; **5a**·$CHCl_3$, 116323-80-9; **5b**, 116323-75-2; **5c**, 116323-77-4; *trans*-$(PEt_3)_2PtHCl$, 16842-17-4; *trans*-$(PEt_3)_2PtDCl$, 15636-63-2.

Supplementary Material Available: Tables of final atomic positional and thermal parameters, interatomic distances and angles, and selected least-squares planes data (8 pages); a listing of final observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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