

# Crystallographic and NMR Studies of Platinum(II) and Palladium(II) $\eta^3$ -Methallyl Trichlorostannate Olefin Complexes

Alfredo Musco\* and Roberto Pontellini

*Institute of Chemical Sciences, University of Urbino, I-61029 Urbino, Italy*

Mariella Grassi

*University of Milan, Inorganic and Metallorganic Chemistry, I-20133 Milano, Italy*

Angelo Sironi

*Istituto di Chimica Strutturistica Inorganica, I-20133 Milano, Italy*

Stefano V. Meille

*Dipartimento di Chimica, Politecnico di Milano, I-20133 Milano, Italy*

Heinz Rügger

*Spectrospin AG, CH-8117 Fällanden, Switzerland*

Christian Ammann and Paul S. Pregosin\*

*Inorganic Chemistry, ETH Zürich, CH-8092 Zürich, Switzerland*

Received December 4, 1987

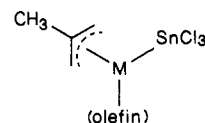
Complexes of the type  $M(\text{SnCl}_3)\{\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2\}$ (olefin) ( $M = \text{Pt}, \text{Pd}$ ; olefin = styrene, ethylene, norbornene) have been prepared and their  $^1\text{H}$ ,  $^{13}\text{C}$ , and, in some cases,  $^{119}\text{Sn}$  and  $^{195}\text{Pt}$  NMR spectra recorded. Two-dimensional  $^1\text{H}$  NOE and  $^{13}\text{C}$ - $^1\text{H}$  correlation methods were used for assignment purposes. The structures for the platinum- (1a) and palladium- (2a) styrene complexes have been determined by X-ray diffraction. The two compounds are isomorphous and crystallize in the triclinic space group  $P\bar{1}$  with cell constants  $a = 8.740$  (2) Å,  $b = 9.338$  (2) Å,  $c = 10.931$  (2) Å,  $\alpha = 72.43$  (1)°,  $\beta = 89.38$  (1)°, and  $\gamma = 73.33$  (2)° for the Pd complex and  $a = 8.698$  (2) Å,  $b = 9.373$  (2) Å,  $c = 11.015$  (2) Å,  $\alpha = 72.32$ °,  $\beta = 89.76$ °, and  $\gamma = 73.30$ ° for the Pt derivative. Both compounds have the olefin C-C vector almost parallel to the coordination plane (20.8 and 23.3° for 1a and 2a, respectively). Analyses of the NMR and crystallographic data lead to the conclusion that the  $\text{SnCl}_3$  and olefin ligands both exercise a moderate trans influence with the former larger than the latter. Back-bonding from the metal to the olefin is suggested to be larger for Pt than Pd.

## Introduction

It is well-known that  $\pi$ -allyl complexes are useful intermediates in organic synthetic reactions.<sup>1</sup> It is also recognized<sup>2</sup> that trichlorostannate complexes of Pt(II) are intermediates in the platinum-catalyzed hydroformylation of olefins.<sup>2,3</sup> In view of our interest in both of these areas<sup>4,5</sup> we have prepared a selection of complexes of types 1 and 2 and consider here some of their interesting structural characteristics. Specifically, we report X-ray crystallographic results for 1a and 2a as well as extensive  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for 1 and 2 from which we make suggestions as to the relative trans influence of each ligand.

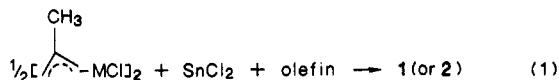
## Results and Discussion

Complexes 1 and 2 are readily prepared by addition of 1 equiv of  $\text{SnCl}_2$  and the olefin to 0.5 equiv of the  $\eta^3$ -



- 1a:  $M = \text{Pt}$ ; olefin = styrene  
 b:  $M = \text{Pt}$ ; olefin = ethylene  
 c:  $M = \text{Pt}$ ; olefin = norbornene  
 2a:  $M = \text{Pd}$ ; olefin = styrene  
 b:  $M = \text{Pd}$ ; olefin = ethylene  
 c:  $M = \text{Pd}$ ; olefin = norbornene

methallyl dimer  $[\text{M}(\mu\text{-Cl})\{\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2\}]_2$ , as shown in eq 1 ( $M = \text{Pd}, \text{Pt}$ ). The complexes are white or pale yellow



solids that afford satisfactory microanalytical data, although in solution they are only moderately stable. For both 1a and 2a crystals suitable for X-ray analysis were obtained via slow recrystallization from ether and methylene chloride-heptane, respectively.

**1. Molecular Structures of 1a and 2a.** Two different ORTEP views of 2a are shown in Figures 1 and 2, drawings of 1a and 2a being visually nondistinguishable. Tables I-III contain experimental data for the two structures; Table IV contains a compilation of bond lengths and angles for our isostructural complexes, whereas Tables V and VI contain comparison data for molecules containing complexed styrene and  $\pi$ -allyl ligands, respectively. The Sn

(1) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon: Oxford, 1982.

(2) Schwager, I.; Knifton, J. F. *J. Catal.* 1976, 45, 256. Knifton, J. F. *J. Org. Chem.* 1976, 41, 793. Bardi, R.; Piazzesi, A. M.; Cavinato, G.; Cavoli, P.; Toniolo, L. *J. Organomet. Chem.* 1982, 224, 407.

(3) Bardi, R.; Piazzesi, A. M.; DelPra, M.; Cavinato, G.; Toniolo, L. *J. Organomet. Chem.* 1982, 235, 107. Rügger, H. J.; Pregosin, P. S.; Scriveranti, A.; Toniolo, L.; Botteghi, C. *J. Organomet. Chem.* 1986, 316, 233.

(4) Giamotti, M.; Musco, A.; Sisti, M.; Grassi, M.; Gatti, G. *Inorg. Chim. Acta*, in press.

(5) Arz, C.; Herbert, I. R.; Pregosin, P. S. *J. Organomet. Chem.* 1986, 308, 373. Herbert, I. R.; Pregosin, P. S.; Rügger, H. *Inorg. Chim. Acta* 1986, 112, 29. Ostojka Starzewski, K. H. A.; Pregosin, P. S.; Rügger, H. *Helv. Chim. Acta* 1982, 65, 785.

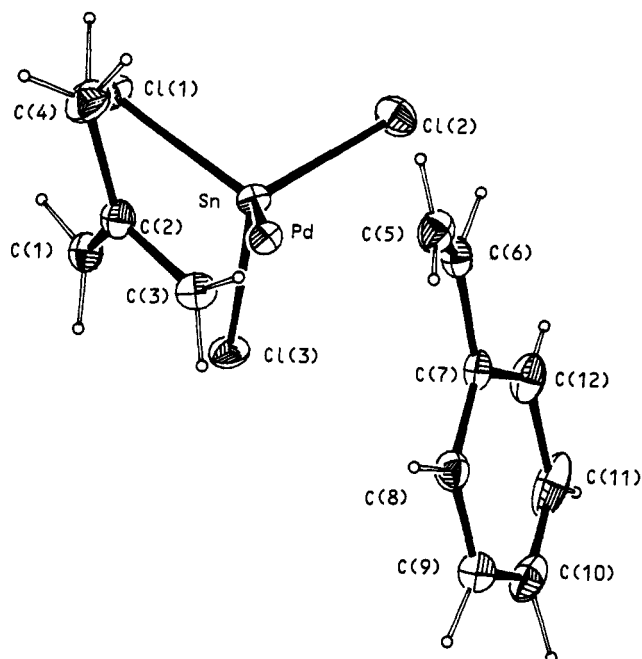


Figure 1. ORTEP view of 1a.

Table I. Crystal Data, Data Collection, and Refinement Details for 1a and 2a

	1a	2a
formula	C <sub>12</sub> H <sub>18</sub> Cl <sub>3</sub> PtSn	C <sub>12</sub> H <sub>18</sub> Cl <sub>3</sub> PdSn
formula mass	579.4	490.7
space group	P1	P1
F(0,0,0)	532	468
a, Å	8.697 (2)	8.740 (2)
b, Å	9.373 (2)	9.338 (2)
c, Å	11.015 (2)	10.931 (2)
α, deg	72.32 (2)	72.43 (1)
β, deg	89.76 (2)	89.38 (1)
γ, deg	73.30 (2)	73.33 (2)
V, Å <sup>3</sup>	816.0 (3)	812.0 (3)
Z	2	2
ρ(calcd), g cm <sup>-3</sup>	2.358	2.007
cryst dimens, mm	0.20 × 0.10 × 0.10	0.22 × 0.12 × 0.08
radiation λ, Å	0.71063 (Mo Kα graphite monochromated)	0.71073 (Mo Kα graphite monochromated)
diffractometer	CAD-4	CAD-4
μ(Mo Kα), cm <sup>-1</sup>	106.7	31.2
temp, °C	298	298
max-min transmissn factors	1.00–0.86	1.00–0.92
2θ range, deg	6–55	6–55
scan mode	ω	ω
scan interval, deg	0.9 + 0.347 tan θ	0.9 + 0.347 tan θ
prescan speed, deg min <sup>-1</sup>	20	20
prescan acceptance, σ(I)/I	1.0	1.0
required σ(I)/I	0.01	0.01
max time for 1 reflctn	70	60
measd, s		
data collected	±h, ±k, ±l	±h, ±k, ±l
unique data collected	2863	2839
unique data used (I ≥ 3 σ(I))	2176	2426
cryst decay	4%	10%
no azim reflctn for abs corr	3	3
final no. of variables	208	208
R	0.0204	0.0160
R <sub>w</sub>	0.0211	0.0172
GOF	0.97	2.22
max peak in final diff Fourier, Å <sup>-3</sup>	1.14 (0.98 Å from Pt)	0.22 (2.05 Å from Pd)

atom, the center of mass for the methallyl anion, and the center of the styrene double bond together with the metal define the coordination planes for our complexes. One can consider the molecules as having irregular planar trigonal geometries. The observed bond angles do not allow the

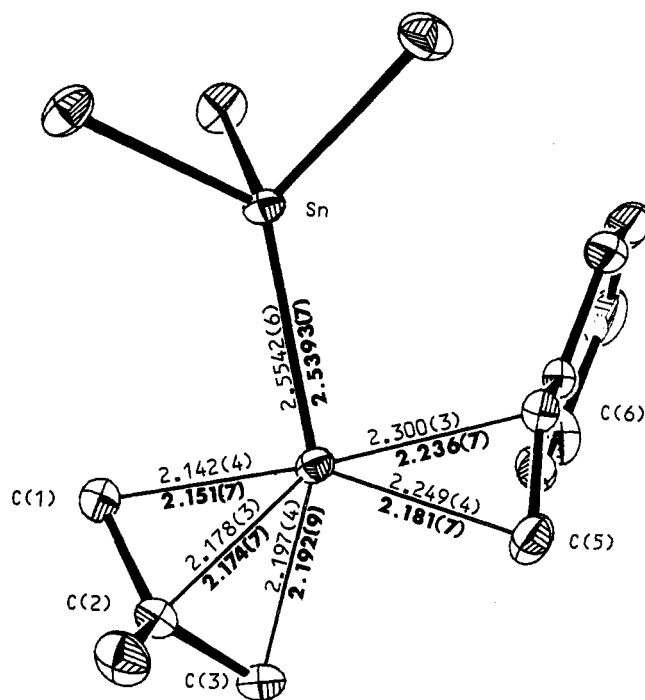


Figure 2. ORTEP picture showing comparison of 1a (bold numbers) and 2a.

Table II. Positional Parameters and Equivalent Thermal Factors for Complex 1a

atom <sup>a</sup>	x	y	z	B <sub>eq</sub> , Å <sup>2</sup>
Sn	-6680 (4)	1225 (5)	20619 (4)	3.66 (4)
Pt	20366 (3)	5346 (3)	24095 (2)	3.42 (2)
Cl1	-28627 (19)	22474 (21)	8476 (16)	5.64 (17)
Cl2	-9673 (24)	-17351 (24)	10986 (18)	6.19 (21)
Cl3	-20097 (20)	-6404 (20)	39099 (15)	5.15 (16)
C1	7329 (81)	27911 (73)	25643 (76)	4.62 (66)
C2	22525 (75)	28654 (69)	21264 (65)	4.69 (63)
C3	35848 (79)	17691 (82)	29398 (79)	4.97 (73)
C4	23972 (117)	38535 (94)	8105 (91)	6.61 (93)
C5	42669 (79)	-12124 (79)	22965 (85)	5.26 (73)
C6	31156 (77)	-19997 (74)	25871 (71)	4.78 (66)
C7	29514 (65)	-30104 (63)	38626 (61)	4.07 (57)
C8	35618 (86)	-28983 (76)	49711 (69)	5.16 (70)
C9	34123 (110)	-39115 (96)	61464 (85)	6.74 (93)
C10	26888 (112)	-50315 (92)	62538 (113)	7.27 (96)
C11	20678 (104)	-51469 (89)	51633 (118)	7.32 (107)
C12	21723 (82)	-41430 (78)	39575 (89)	5.98 (81)

atom <sup>b</sup>	x	y	z	B, Å <sup>2</sup>
H1s	-34 (7)	346 (7)	188 (5)	5 (1)
H1a	56 (8)	255 (7)	338 (6)	6 (2)
H3a	362 (8)	127 (8)	386 (6)	6 (2)
H3s	469 (8)	158 (7)	270 (6)	5 (1)
H41	328 (11)	330 (10)	52 (8)	9 (1)
H42	147 (10)	412 (9)	19 (8)	9 (1)
H43	240 (11)	477 (10)	72 (9)	9 (1)
H51	505 (7)	-140 (7)	301 (6)	4 (1)
H52	455 (9)	-72 (8)	136 (7)	8 (2)
H6	273 (6)	-219 (6)	191 (5)	3 (1)
H8	420 (8)	-209 (7)	490 (6)	6 (1)
H9	393 (8)	-388 (8)	682 (7)	6 (1)
H10	256 (8)	-576 (8)	704 (7)	6 (1)
H11	175 (8)	-585 (8)	503 (6)	6 (1)
H12	156 (8)	-415 (7)	319 (6)	6 (1)

<sup>a</sup> Positional parameters × 10<sup>5</sup>. <sup>b</sup> Positional parameters × 10<sup>8</sup>.  
<sup>c</sup> H1s for syn proton; H1a for anti proton.

definition of a clear-cut "trans" relationship between the ligands. The angle C(1)–M–C(6), 168°, in both complexes comes closest to 180°; however, the C(3)–M–Sn angle, at 153°, deviates significantly from a trans orientation. The small bite angle of the π-allyl ligand, ca. 66°, makes 180°

Table III. Positional Parameters and Equivalent Thermal Factors for Complex 2a

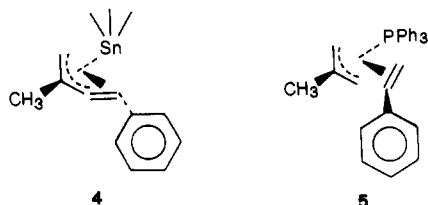
atom <sup>a</sup>	x	y	z	B <sub>eq</sub> , Å <sup>2</sup>
Sn	-7105 (2)	1405 (2)	20336 (2)	3.44 (2)
Pd	20042 (2)	5405 (2)	23787 (2)	3.31 (2)
Cl1	-29301 (9)	22546 (9)	8389 (7)	5.25 (7)
Cl2	-10213 (11)	-17281 (11)	10458 (8)	5.92 (9)
Cl3	-20794 (10)	-6679 (9)	38939 (7)	5.12 (7)
C1	7374 (38)	27777 (37)	25833 (37)	4.51 (30)
C2	22315 (35)	28688 (31)	21487 (28)	4.22 (27)
C3	35804 (36)	17607 (36)	28989 (32)	4.38 (30)
C4	23838 (54)	39067 (45)	8252 (39)	6.25 (40)
C5	42576 (42)	-12801 (41)	22143 (42)	5.29 (35)
C6	31655 (35)	-20644 (33)	25533 (32)	4.45 (28)
C7	29884 (31)	-30245 (29)	38585 (29)	3.99 (25)
C8	36495 (41)	-29168 (35)	49646 (31)	4.87 (30)
C9	35124 (51)	-38815 (43)	61634 (37)	6.37 (39)
C10	27252 (50)	-49839 (44)	62893 (48)	6.88 (42)
C11	20483 (48)	-50968 (41)	52355 (58)	7.62 (52)
C12	21643 (40)	-41231 (37)	40030 4(42)	5.64 (36)

atom <sup>b</sup>	x	y	z	B, Å <sup>2</sup>
H1s	-21 (3)	338 (3)	204 (3)	4 (1)
H1a	66 (4)	249 (4)	337 (3)	5 (1)
H3a	363 (4)	134 (3)	374 (3)	5 (1)
H3s	475 (4)	156 (3)	257 (3)	5 (1)
H41	347 (6)	365 (5)	51 (4)	10 (1)
H42	151 (6)	397 (5)	32 (4)	10 (1)
H43	228 (6)	492 (5)	83 (4)	10 (1)
H51	495 (4)	-126 (3)	272 (3)	4 (1)
H52	441 (5)	-77 (5)	142 (4)	8 (1)
H6	263 (4)	-223 (3)	185 (3)	5 (1)
H8	421 (4)	-211 (4)	487 (3)	7 (0)
H9	399 (4)	-370 (4)	692 (3)	7 (0)
H10	276 (4)	-567 (4)	714 (4)	7 (0)
H11	153 (5)	-576 (4)	525 (4)	7 (0)
H12	165 (5)	-421 (4)	337 (4)	7 (0)

<sup>a</sup> Positional parameters  $\times 10^5$ . <sup>b</sup> Positional parameters  $\times 10^3$ .  
<sup>c</sup> H1s, for syn proton; H1a, for anti proton.

angles difficult to achieve without severely compressing the two remaining ligands. Undoubtedly the most unique aspect of the structures arises from the almost in-plane orientation of the styrene double bond with respect to the coordination plane (20.8 (4)° and 23.2 (2)° for **1a** and **2a**, respectively). This type of arrangement has been recognized as a theoretical possibility<sup>6</sup> and recently observed in some few cases,<sup>7,8</sup> e.g., for the  $\eta^3$ -methallyl complex [Pt(CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>)(PhCH=CH<sub>2</sub>)PPh<sub>3</sub>]PF<sub>6</sub> (**3**).<sup>8a</sup> We note that while in **1a** and **2a** the styrene phenyl ring points toward the *cis*-SnCl<sub>3</sub>, i.e., **4**, the analogous moiety in **3** is adjacent to the  $\pi$ -allyl as shown in **5**. Whereas in **5** the



allyl methyl and the phenyl ring are above the coordination plane, in **4** they are on opposite sides. The dihedral angle between the plane of the methallyl and the coordination plane,  $\sim 114.0$  (6)° and  $116.5$  (3)° for **1a** and **2a**, respectively, is in the usual range. Analyses of the individual coordinated ligand characteristics, relative to literature

(6) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

(7) Rakowsky, M. H.; Woolcock, J. C.; Wright, L. L.; Green, D. B.; Rettig, M. F.; Wing, R. M. *Organometallics* **1987**, *6*, 1211.

(8) (a) Ki, K. M.; Kai, Y.; Kasai, N.; Kurosawa, H. *J. Am. Chem. Soc.* **1983**, *105*, 2482. (b) Miki, K.; Yamatoya, K.; Kasai, M.; Kurosawa, H.; Emoto, M.; Urabe, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1520.

Table IV. Bond Lengths (Å) and Selected Bond Angles (deg) in **1a** and **2a**

	Pd	Pt
Bond Lengths		
Sn-M	2.5542 (6)	2.5393 (7)
Sn-Cl1	2.3806 (9)	2.3701 (16)
Sn-Cl2	2.3875 (12)	2.3686 (26)
Sn-Cl3	2.3822 (9)	2.3647 (17)
M-C1	2.142 (4)	2.151 (7)
M-C2	2.178 (3)	2.174 (7)
M-C3	2.197 (4)	2.192 (9)
M-C5	2.249 (4)	2.181 (7)
M-C6	2.300 (3)	2.236 (7)
C1-C2	1.401 (5)	1.418 (10)
C2-C3	1.393 (4)	1.402 (8)
C2-C4	1.508 (5)	1.492 (11)
C5-C6	1.347 (5)	1.389 (11)
C6-C7	1.472 (4)	1.470 (9)
C7-C8	1.388 (5)	1.378 (11)
C7-C12	1.386 (5)	1.394 (11)
C8-C9	1.374 (5)	1.385 (11)
C9-C10	1.368 (7)	1.347 (15)
C10-C11	1.346 (8)	1.365 (18)
C11-C12	1.401 (6)	1.395 (14)
C1-H1s	0.95 (3)	1.10 (5)
C1-H1a	0.83 (3)	0.88 (7)
C3-H3a	0.88 (3)	0.97 (6)
C3-H3s	1.06 (3)	0.97 (6)
C4-H41	1.00 (5)	0.91 (9)
C4-H42	0.93 (6)	0.98 (9)
C4-H43	0.92 (5)	0.83 (10)
C5-H51	0.83 (4)	0.98 (7)
C5-H52	0.89 (4)	1.05 (7)
C6-H6	0.98 (3)	0.90 (6)
C8-H8	1.00 (4)	1.04 (8)
C9-H9	1.01 (4)	0.88 (8)
C10-H10	0.95 (3)	0.95 (6)
C11-H11	0.86 (5)	0.83 (9)
C12-H12	0.87 (4)	1.00 (8)
M-DB	2.173 (5)	2.100 (9)
M-AL	1.912 (6)	1.911 (14)
Bond Angles		
M-Sn-Cl1	121.60 (3)	120.34 (6)
M-Sn-Cl2	122.42 (4)	122.53 (7)
M-Sn-Cl3	117.45 (3)	116.51 (5)
Cl1-Sn-Cl2	96.26 (4)	96.86 (7)
Cl1-Sn-Cl3	96.06 (4)	97.00 (7)
Cl2-Sn-Cl3	97.20 (4)	98.39 (7)
Sn-M-C6	87.84 (9)	86.10 (19)
Sn-M-C5	119.33 (11)	120.23 (21)
Sn-M-C3	154.03 (10)	153.47 (21)
Sn-M-C2	121.45 (9)	121.42 (18)
Sn-M-C1	87.96 (10)	87.74 (20)
C5-M-C6	34.42 (13)	36.62 (27)
C3-M-C6	116.27 (13)	118.34 (27)
C3-M-C5	86.50 (14)	86.10 (28)
C2-M-C6	149.84 (13)	151.19 (26)
C2-M-C5	115.68 (14)	114.62 (26)
C2-M-C3	37.13 (12)	37.46 (27)
C1-M-C6	168.30 (13)	168.19 (28)
C1-M-C5	152.50 (15)	151.01 (28)
C1-M-C3	66.49 (13)	66.31 (29)
C1-M-C2	37.84 (13)	38.28 (26)
C1-C2-C4	121.8 (3)	121.6 (7)
C1-C2-C3	116.7 (3)	114.8 (6)
C3-C2-C4	120.6 (3)	122.9 (7)
C5-C6-C7	126.5 (3)	125.4 (7)
C6-C7-C12	119.1 (3)	118.9 (6)
C6-C7-C8	123.1 (3)	122.5 (6)
C8-C7-C12	117.8 (3)	118.6 (7)
C7-C8-C9	121.2 (3)	120.0 (7)
C8-C9-C10	120.3 (4)	122.1 (9)
C9-C10-C11	119.8 (4)	118.4 (10)
C10-C11-C12	121.1 (4)	121.6 (9)
C7-C12-C11	119.8 (4)	119.2 (8)
SN-M-AL	121.9 (2)	121.7 (4)
SN-M-DB	103.5 (1)	102.9 (3)
AL-M-DB	134.5 (2)	135.4 (5)

<sup>a</sup> DB = middle point of the styrene double bond. <sup>b</sup> AL = center of gravity of the C1, C2, and C3 allylic carbons.

Table V. X-ray Bond Length (Å) Data for Styrene Complexes<sup>a</sup>

complex	M-C	M-C	C-C	ref
M = Pt				
[Pt(SnCl <sub>3</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )-CH <sub>2</sub> (PhCH=CH <sub>2</sub> )]	2.237 (7)	2.182 (7)	1.389 (11)	this work
<i>cis</i> -[PtCl <sub>2</sub> (CH <sub>3</sub> S(O)-(tol- <i>p</i> ))(PhCH=CH <sub>2</sub> )]	2.219 (9)	2.188 (8)	1.360 (11)	30
[Pt(CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> )-(PPh <sub>3</sub> )(PhCH=CH <sub>2</sub> )-PF <sub>6</sub> (3)]	2.301 (12)	2.203 (12)	1.341 (17)	8
<i>cis</i> -[PtCl <sub>2</sub> (PhCH=CH <sub>2</sub> ) <sub>2</sub> ]	2.270 (5)	2.156 (7)	1.382 (9)	31
	2.258 (6)	2.173 (6)	1.398 (9)	
M = Pd				
<i>trans</i> -[PtCl <sub>2</sub> (NC <sub>6</sub> H <sub>4</sub> X)-(p-YC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> )]				
X = NMe <sub>2</sub>	2.262 (16)	2.137 (17)	1.419 (25)	
X = H	2.236 (10)	2.180 (12)	1.454 (17)	
X = NO <sub>2</sub>	2.216 (11)	2.174 (13)	1.374 (18)	
[PtCl <sub>2</sub> (Bu <sup>+</sup> N=CH=NBu <sup>+</sup> )(PhCH=CH <sub>2</sub> )]	2.20 (4)	2.16 (4)	1.53 (5)	33
M = Pd				
Pd{CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> -(SnCl <sub>3</sub> )(PhCH=CH <sub>2</sub> )}	2.300 (3)	2.249 (4)	1.347 (5)	this work
[Pd(Cp)(PPh <sub>3</sub> )(p-YC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> )]X				34
Y = OCH <sub>3</sub> ; X = BF <sub>4</sub>	2.264 (5)	2.182 (5)	1.373 (7)	
Y = H; X = PF <sub>6</sub>	2.255 (5)	2.182 (5)	1.361 (7)	
Y = Cl; X = BF <sub>4</sub>	2.235 (6)	2.187 (6)	1.360 (9)	
[Pd(Cp)(PEt <sub>3</sub> )(PhCH=CH <sub>2</sub> )]BF <sub>4</sub>	2.234 (5)	2.176 (6)	1.369 (8)	35

<sup>a</sup> Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>; all the allyl ligands are η<sup>3</sup>.

Table VI. X-ray Bond Length (Å) Data for Allyl<sup>+</sup> Complexes

complex	M-C <sup>1</sup>	M-C <sup>3</sup>	ref
[M(SnCl <sub>3</sub> )(CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> )-(PhCH=CH <sub>2</sub> )]	2.197 (4)	2.142 (4)	this work
M = Pd			
M = Pt	2.191 (9)	2.150 (7)	
[Pd(μ-Cl){CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> }] <sub>2</sub> <sup>b</sup>	2.123 (7)	2.121 (8)	13
[PdCl{CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> }(CH(PPh <sub>3</sub> )-COCH <sub>3</sub> ) <sup>c</sup>	2.180 (4)	2.126 (4)	14
[PdCl{CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> }(PPh <sub>3</sub> )]	2.211 (6)	2.120 (5)	15a
[Pd(SnCl <sub>3</sub> )(CH <sub>2</sub> CHCH <sub>2</sub> )(PPh <sub>3</sub> )]	both ca. 2.19		15b
[Pt(SnCl <sub>3</sub> )(CH <sub>2</sub> CHCH <sub>2</sub> )(PCy <sub>3</sub> )]	2.170 (5)	2.234 (7)	15c

<sup>a</sup> All the allyl complexes are η<sup>3</sup>. <sup>b</sup> [Pd(μ-Cl){CH<sub>2</sub>C(Bu<sup>+</sup>)CH<sub>2</sub>}]<sub>2</sub> is longer, ca. 2.14 Å. <sup>c</sup> Ylide complex.

data, reveal some interesting features:

**PhCH=CH<sub>2</sub>.** Comparison of the M—C and C=C distances involving styrene (Table IV) reveal that, for M = Pd, they are longer and shorter, respectively, than for M = Pt. Furthermore, the M—C(6) bond length is greater than M—C(5) in both complexes. For M = Pt the M—C separations are quite typical and correspond within experimental uncertainty to pertinent literature data (see Table V). Our data suggest that while π-back-bonding is significant in Pt(II) neutral complexes, it plays a minor role in Pd(II) analogues. Consistent with this idea are the M—C (2.301 (12) and 2.203 (12) Å) and C=C (1.341 (17) Å) separations for the cationic Pt complex 3 which are very similar to those of our Pd complex 2a.

**SnCl<sub>3</sub>.** The M—SnCl<sub>3</sub> separations are 2.538 (1) and 2.554 (1) Å for 1a and 2a, respectively, and thus are significantly longer for the Pd complex. These values are in the middle of the expected range of 2.487 (3)–2.634 (1) Å.<sup>9</sup> Consequently, it is reasonable to conclude that the π-allyl is not labilizing the SnCl<sub>3</sub><sup>-</sup> to any great extent. Where either a strong σ-donor or π-acceptor is present, the Pt—Sn bond separation is often ca. 2.6 Å, e.g., *trans*-Pt(SnCl<sub>3</sub>)-(COPh)(PEt<sub>3</sub>)<sub>2</sub>, 2.634 (1) Å,<sup>9</sup> *trans*-Pt(SnCl<sub>3</sub>)<sub>2</sub>(P(OPh)<sub>3</sub>)<sub>2</sub>, 2.599 (2) Å,<sup>10</sup> and Pt(SnCl<sub>3</sub>)Cl(DIOP), 2.598 Å.<sup>11</sup> Bond

(9) Albinati, A.; von Gunten, J.; Pregosin, P. S.; Rügge, H. J. *J. Organomet. Chem.* 1985, 295, 239.

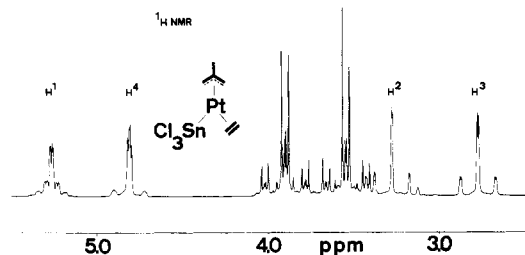


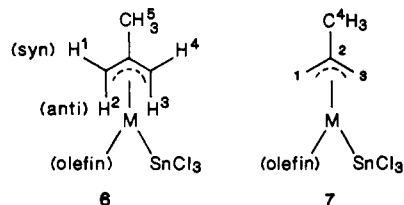
Figure 3. <sup>1</sup>H NMR (250-MHz) spectrum of Pt(SnCl<sub>3</sub>)(CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>)(CH<sub>2</sub>=CH<sub>2</sub>).

lengths and angles within the SnCl<sub>3</sub> conform to literature expectations.<sup>9–12</sup>

**η<sup>3</sup>-CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>.** Assuming that the M—C(terminal) separations reflect the bonding to the π-allyl ligand, we note that (i) this ligand is not symmetrically bound, the M—C bond “trans” to SnCl<sub>3</sub> being somewhat longer, and (ii) both values, i.e., ca. 2.15 Å trans to styrene and ca. 2.19 Å trans to SnCl<sub>3</sub>, suggest the π-allyl fragment is responding electronically to the presence of the two π-acceptors. In support of (ii) we note that the M—C(terminal) distance for the chloro-bridged dimer [Pd(μ-Cl){CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>}]<sub>2</sub> and that for the carbon pseudo trans to Cl in PdCl{CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>}(Ph<sub>3</sub>PCHCOCH<sub>3</sub>) are 2.12–2.13 Å.<sup>13,14</sup> Coordinated tertiary phosphines induce an M—C(terminal) distance of ca. 2.19–2.23 Å<sup>15</sup> (see Table V).

While one must be cautious in view of the large experimental uncertainty in much of the bond length data shown in Tables V and VI, the overall picture for our complexes is suggestive of a coordination sphere with moderate bond lengths, none very long or very short, containing an SnCl<sub>3</sub> ligand, which exerts a mildly labilizing influence.

**2. NMR Spectroscopy. A. <sup>1</sup>H Results.** Although there is an extensive <sup>1</sup>H NMR literature<sup>16</sup> associated with π-allyl complexes, the proton spectra for 1 and 2 are not readily assigned. This problem arises due to the presence of the olefin absorptions that appear close to the four different CH methallyl proton signals, H<sup>1</sup>–H<sup>4</sup> (our nomenclature for the <sup>1</sup>H and <sup>13</sup>C resonances is shown by 6 and 7, respectively). We were fortunate in having several



qualitative empiricisms available with which to begin the

(10) Albinati, A.; Pregosin, P. S.; Rügge, H. *Inorg. Chem.* 1984, 23, 3223.

(11) Consiglio, B.; Pino, P.; Scallone, M. ETH Zürich, unpublished results.

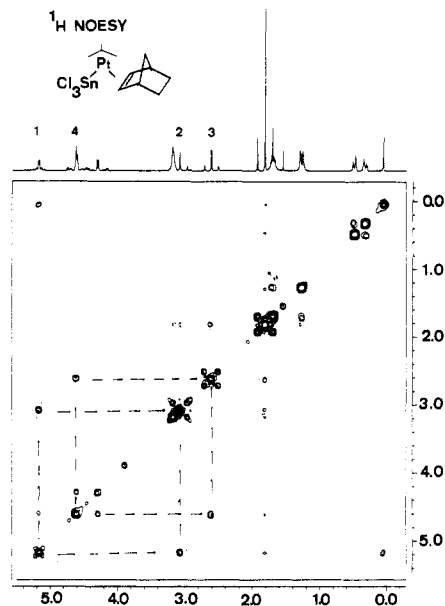
(12) Nelson, J. H.; Alcock, N. W. *Inorg. Chem.* 1982, 21, 1196. Adams, R. D.; Katahira, D. A. *Organometallics* 1982, 1, 53. Koop, D. J.; Bernal, I. *Inorg. Chem.* 1982, 20, 4065. Giandomenico, C. M.; Dewan, J. C.; Lippard, S. J. *J. Am. Chem. Soc.* 1981, 103, 1407. Onaka, S. *Bull. Chem. Soc. Jpn.* 1975, 48, 319. Churchill, M. R.; Lin, K. G. *J. Am. Chem. Soc.* 1974, 96, 74.

(13) Smith, A. E. *Acta Crystallogr.* 1965, 18, 331.

(14) Facchin, G.; Bertani, R.; Calligaris, M.; Nardin, G.; Mari, M. *J. Chem. Soc., Dalton Trans.* 1987, 1381.

(15) (a) Faller, J. W.; Blankenship, C.; Whitmore, B.; Sena, S. *Inorg. Chem.* 1985, 24, 4483. (b) Mason, R.; Robertson, G. B.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* 1968, 1655. (c) Rügge, H.; Clark, H. C., unpublished results.

(16) Faller, J. W. *Adv. Organomet. Chem.* 1977, 16, 211; Faller, J. W. *In Determination of Organic Structures by Physical Methods*; Academic: New York, 1973; Vol. 5, p 75. Vrieze K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Academic: New York, 1975; p 441.



**Figure 4.** 2-D  $^1\text{H}$  NOESY spectrum for  $\text{Pt}(\text{SnCl}_3)(\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{norbornene})$ . Cross peaks for the geminal interaction are indicated.

assignments: (1) the anti protons  $\text{H}^2$  and  $\text{H}^3$  usually appear at higher field than the syn protons  $\text{H}^1$  and  $\text{H}^4$ ; (2) NMR-active ligand atoms trans to coordinated  $\text{SnCl}_3$  couple to the  $^{117,119}\text{Sn}$  spin with relatively large  $^nJ(\text{Sn},\text{X})$  values ( $\text{X} = ^1\text{H}, ^{13}\text{C}, ^{31}\text{P}, \dots$ ).<sup>18</sup> Consequently, we can assign the  $^1\text{H}$  spectrum of  $\text{Pt}(\text{SnCl}_3)(\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{CH}_2=\text{C}-\text{H}_2)$ , shown in Figure 3. Interestingly, the ethylene protons form an AA'XX' spin system since, despite rapid rotation, there is no symmetry element permitting equivalence with respect to these protons. An examination of the  $^1\text{H}$  data for the anti protons in Table VII reveals that  $^3J(\text{Sn},\text{H}^2)$  is ca. 76 Hz whereas we do not observe an analogous coupling to  $\text{H}^3$ . However, we find that the syn protons,  $\text{H}^1$  and  $\text{H}^4$ , do not always follow this trend in  $^3J(\text{Sn},\text{H})$  to the same extent, and in some cases we observe values of 40–50 Hz for both  $\text{H}^2$  and  $\text{H}^3$ . This potential ambiguity was resolved by the two-dimensional  $^{13}\text{C}$  NMR methods described in the next section; however, an equally valid approach applies  $^1\text{H}$  2-D NOE spectroscopy (see Figure 4) since protons attached to the same carbon exhibit substantial Overhauser enhancements due to the geminal arrangement. Interestingly, both  $\text{H}^2$  and  $\text{H}^3$  have larger  $^2J(\text{Pt},\text{H})$  values than do  $\text{H}^1$  and  $\text{H}^4$  and that for  $\text{H}^4$  is often not resolved. Since this finding cannot be related to the trans influence phenomena, it seems likely that the anti and syn protons have different geometric positions with respect to platinum. This idea is supported by a neutron diffraction study for  $\text{Ni}(\eta^3-\text{C}_3\text{H}_5)_2$ <sup>19</sup> which shows the anti proton bent away from the nickel, whereas the syn proton has moved out of the  $\pi$ -allyl plane toward the metal. Perhaps this difference in geometry is also (partly) responsible for empiricism 1 on chemical shifts.

(17) (a) Clark, H. C.; Hampden-Smith, M. J.; R uegger, H. *Organometallics*, in press. (b) Mann, B. E.; Shaw, B. L.; Shaw, G. *J. Chem. Soc. A* 1971, 3536. (c) Mabbott, D. J.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* 1977, 294. (d) Boag, N.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1980, 1200. (e) *Ibid.* 1980, 1208. (f) *Ibid.* 1980, 1220.

(18) (a) Clark, H. C.; Ferguson, G.; Hampden-Smith, M. J.; R uegger, H.; Ruhl, E., submitted for publication. (b) Ostoja Starzowski, K. H. A.; Pregosin, P. S. *Catalytic Aspects of Metal Phosphine Complexes*; Advances Chemistry 176; American Chemical Society: Washington, D.C., 1982; p 23.

(19) Goddard, R.; Kruger, C.; Mark, F.; Stansfield, R.; Zhang, X. *Organometallics* 1985, 4, 285.

**Table VII.**  $^1\text{H}$  NMR Data ( $\delta$ ) for  $\text{M}(\text{SnCl}_3)(\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{olefin})$

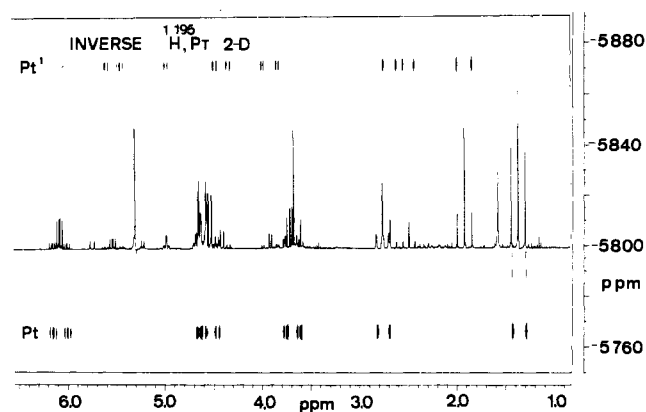
olefin	$\text{H}^1$	$\text{H}^2$	$\text{H}^3$	$\text{H}^4$	$\text{CH}_3$	olefin
<b>M = Pt</b>						
$\text{CH}_2=\text{CH}_2^b$	5.27 [16] (40)	3.27 [51] (76)	2.77 [62] n.o.	4.81 [44] n.o.	1.92 [59]	3.90, 3.54 [59], [59]
norbornene <sup>c</sup>	3.6, 1	1	2.1	3.6, 2.1		
	5.21 [17] (41)	3.12 [53] (80)	2.64 [50] n.o.	4.62 [43] n.o.	1.82 [59]	4.62, 4.33 [67], [67]
styrene <sup>d</sup>						
major isomer	4.66 [20] (40)	3.68 [57] (76)	2.76 [53] (8)	4.58 [45] n.o.	1.37 [53]	6.09, 3.73 (cis), 4.54 (trans) [58], [57], [53]
minor isomer	3.5 [19] (45)	0.8, 0.8 [48] (79)	2.2 [53]	3.5, 2.2 [46] <sup>e</sup>	1.91 [63]	5.54, 3.92 (cis), 4.41 (trans) [62], [62], [56]
<b>M = Pd</b>						
$\text{CH}_2=\text{CH}_2^f$	5.47 (51)	3.59 (88)	3.20 (14)	4.95 (27)	1.87	4.40 <sup>g</sup>
norbornene <sup>h</sup>	3.2, 1.5 5.34 (52)	3.36 (92)	2.97 (12)	4.66 (24)	1.69	5.26, 5.15
styrene <sup>h</sup>	3.1, 2.0 4.83 (44)	4.01 (70)	3.03 n.o.	4.56 (19)	1.09	6.78 4.06 (cis) 5.11 (trans)

<sup>a</sup>  $\text{CDCl}_3$  solutions for the Pt complexes;  $\text{CD}_2\text{Cl}_2$  for the Pd analogues.  $J(\text{Pt},\text{H})$  values (Hz) in brackets.  $J(\text{Sn},\text{H})$  values (Hz) in parentheses. Values below the parentheses represent  $J(\text{H},\text{H})$  (Hz); n.o. = not observed. For styrene, cis refers to H nucleus cis to the  $\alpha$ -proton. <sup>b</sup>  $\text{CH}_2=\text{CH}_2$  protons afford an AA'XX' spin system. <sup>c</sup> Aliphatic resonances: bridging  $\text{CH}^A\text{H}^B$ ,  $\delta$  0.35 ( $\text{H}^A$ , endo to double bond), 0.59 ( $\text{H}^B$ , exo to double bond), 1.29 (exo protons of  $\text{CH}_2\text{CH}_2$  bridge), (endo protons of  $\text{CH}_2\text{CH}_2$  bridge), 3.18 (methine H). <sup>d</sup> For olefin signals  $^3J(\text{H},\text{H})_{\text{trans}} = 13$  Hz,  $^3J(\text{H},\text{H})_{\text{cis}} = 9$  Hz, and  $^2J(\text{H},\text{H})_{\text{gem}} = 2$  Hz. <sup>e</sup> Under Pt satellites of  $\text{H}^1$  in major isomer. <sup>f</sup> 193 K. <sup>g</sup> 240 K, AB system for two olefinic protons; aliphatic resonances:  $\delta$  0.08, 0.65 (bridging  $\text{CH}^A\text{H}^B$ ), 1.07, 1.56 (bridging  $\text{CH}_2\text{CH}_2$ ), 3.08 (methine H). <sup>h</sup> 193 K.

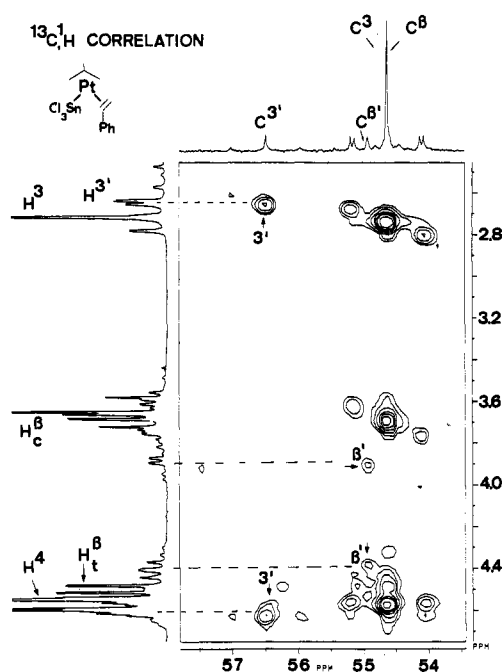
Olefin proton resonances are also listed in the table and follow literature patterns;<sup>20,21</sup> i.e., these are shifted to high-field relative to the uncoordinated ligand. The protons of all three olefins couple to  $^{195}\text{Pt}$  with values ranging from 50 to 60 Hz.  $\text{Pt}(\text{SnCl}_3)(\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{PhCH}=\text{CH}_2)$  presents a special problem in that there are two isomers in solution and consequently twice as many  $^1\text{H}$  signals. The spectrum can be simplified and individual resonances associated with its corresponding  $^{195}\text{Pt}$  absorption via  $^{195}\text{Pt}$ ,  $^1\text{H}$  inverse 2-D spectroscopy (see Figure 5). In this methodology *only* signals coupled to  $^{195}\text{Pt}$  appear, and the two rows of  $^1\text{H}$  signals project onto a  $^{195}\text{Pt}$  axis. There are complex exchange processes involved in isomer interconversion that we shall discuss elsewhere; however, the similarity of the two  $^{195}\text{Pt}$  resonances,  $\delta -5770$  and  $-5875$ , (relative to  $\text{H}_2\text{PtCl}_6$ ) is consistent with isomeric complexes.

(20) Kurosawa, H.; Asada, N. *Organometallics* 1983, 2, 251.

(21) Meester, M. A.; Stufkens, D. J.; Vrieze, K. *Inorg. Chim. Acta* 1975, 15, 137; 1976, 16, 191; 1977, 21, 251. Fritz, H.; Sellmann, P. *J. Organomet. Chem.* 1966, 6, 558.



**Figure 5.** 2-D (400-MHz)  $^{195}\text{Pt}$ ,  $^1\text{H}$  reverse measurement<sup>36</sup> for  $\text{Pt}(\text{SnCl}_3)(\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{PhCH}=\text{CH}_2)$  correlating the two  $^{195}\text{Pt}$  signals (Pt major; Pt', minor) to their respective protons. The two rows of cross peaks project onto the  $^{195}\text{Pt}$  chemical shift axis at the resonance frequency of the metal. Note there are only cross peaks for the  $^{195}\text{Pt}$  isotopomers.



**Figure 6.** Section (slice) through a  $^{13}\text{C}$ ,  $^1\text{H}$  2-D correlation (400-MHz  $^{13}\text{C}$  signals, horizontal;  $^1\text{H}$  signals, vertical) for  $\text{Pt}(\text{SnCl}_3)(\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{styrene})$ . The cross peaks for the primed styrene resonances (minor isomer) and  $\text{H}^3$  signals (minor isomer) are marked. Although  $\text{C}^{\beta}$  and  $\text{C}^{\alpha}$  of the major isomer overlap, the four visible cross peaks resolve this ambiguity.

**B.  $^{13}\text{C}$  Results.** In view of the complexity of the  $^1\text{H}$  spectra and occasional ambiguity with respect to coupling constants, we chose to use  $^{13}\text{C}$  measurements both to confirm our bonding views and to assign  $^1\text{H}$  resonances. Whereas conventional one-dimensional spectra help with the former, the latter is accomplished via 2-D proton-carbon correlations such as that shown in Figure 6. These measurements allow us to correlate the methallyl  $\text{CH}_2$  groups pairwise, in that each  $\text{CH}_2$  will correlate to one syn and one anti proton. Thus, the initial assignment of the anti protons permits the identification of the two  $\text{CH}_2$  carbons that then point directly to their respective syn protons. Additionally, from our  $^{13}\text{C}$  measurements, we find that  $^2J(\text{Sn},\text{C})_{\text{trans}} > ^2J(\text{Sn},\text{C})_{\text{cis}}$ , an extension of point 2, above, and that  $\delta(\text{C}^1) > 10$  to low field of  $\delta(\text{C}^3)$ . We note that the  $^1J(\text{Pt},\text{C-olefin})$  and  $^1J(\text{Pt},\text{CH}_2\text{-allyl})$  values are often similar and cluster about 100 Hz, with one or two exceptions, but that  $\delta(^{13}\text{C})$  values vary considerably as one

**Table VIII.**  $^{13}\text{C}$  NMR Data<sup>a</sup> ( $\delta$ ) for the Complexes

	olefin	C <sup>1</sup>	C <sup>3</sup>	CH <sub>3</sub>	C <sup>2</sup>
M = Pt					
ethylene <sup>b</sup>	68.1 (79)		58.3 (106)	23.5 (33)	125.5 (43)
norbornene <sup>c</sup>	69.3 (88)		57.4 (99)	23.1 (33)	124.0 (40)
styrene <sup>d</sup>					
major	78.3 (98)		54.8 (102–105)	22.6 (36)	127.8
minor	75.6 (100)		56.7 (108)	23.6 (30)	
M = Pd					
ethylene <sup>e</sup>	81.8		68.8	23.7	132.5
norbornene <sup>f</sup>	82.5		68.3	23.6	131.0
styrene <sup>g</sup>	91.0		65.0	21.4	g

<sup>a</sup> Relative to TMS. Values in parentheses refer to  $J(\text{Pt},\text{C})$  (Hz). <sup>b</sup>  $^2J(\text{Sn},\text{C}^1) = 213$  Hz,  $\delta(\text{CH}_2=\text{CH}_2) 56.5$  (104 Hz). <sup>c</sup>  $^2J(\text{Sn},\text{C}^1) = 228$  Hz. In  $\text{CD}_2\text{Cl}_2$  the olefin carbons have  $\delta 79.6$  (168 Hz) and 78.4 (170 Hz). <sup>d</sup>  $^2J(\text{Sn},\text{C}^1) = \text{ca. } 223$  Hz (major isomer);  $\delta(\beta\text{-C}) 54.8$  (102–105 Hz),  $\delta(\alpha\text{-C}) 76.6$  (99 Hz). The  $\beta$ -styrene and  $\text{C}^3$  carbons overlap. <sup>e</sup> 243 K,  $\delta(\text{CH}_2=\text{CH}_2) 78.4$ . <sup>f</sup> 243 K, olefin carbons at  $\delta 98.4$  and 97.3. <sup>g</sup> 193 K,  $\delta(\alpha\text{-carbon}) 95.7$ ,  $\delta(\beta\text{-carbon}) 70.8$ . There are unassigned signals at  $\delta 134.4$  and 131.9 that represent the ipso aromatic and  $\text{C}^2$  carbons.

might expect.<sup>22,23</sup> These  $^{13}\text{C}$  differences are conveniently considered in terms of bonding to the metal.

**C. Trans Influence of the Ligands.** Earlier work, using Pt–Cl bond lengths, suggested a similar trans influence for both  $\text{SnCl}_3$  and olefin ligands.<sup>24</sup> With use of our Pt–C<sup>1</sup> and Pt–C<sup>3</sup> separations, in both 1a and 2a, it would seem that the  $\text{SnCl}_3$  is somewhat stronger than styrene, with respect to trans influence, since Pt–C<sup>1</sup> is several hundredths of an angstrom longer than Pt–C<sup>3</sup>. This finding is in agreement with (i) the  $^1J(\text{Pt},\text{C}^1)$  and  $^1J(\text{Pt},\text{C}^3)$  data, in that the former is at least 10 Hz less than the latter, and (ii) the carbon chemical shifts data (see Table VIII) since C<sup>1</sup> is at lower field than C<sup>3</sup> (the dimers  $[\text{M}(\mu\text{-Cl})(\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2)]_2$  (M = Pd, Pt) have  $\delta 61.7$  (Pd)<sup>22</sup> and 45.9 (Pt) ( $^1J(\text{Pt},\text{C}) = 280$  Hz) respectively). It is presumptuous to attempt more than a qualitative interpretation of these  $^{13}\text{C}$  data as both cis and trans effects may be operating and our data suggest that the nature of the olefin is not trivial; however, since  $\text{Pt}(\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{Cp})$  has  $\delta 28.2$  ( $^1J(\text{Pt},\text{C}) = 391$  Hz<sup>17f</sup>) (strong Pt–allyl bonding) and  $\text{PtCl}(\eta^3\text{-C}_3\text{H}_5)(\text{PCy}_3)$  shows  $\delta 69.5$  ( $^1J(\text{Pt},\text{C}) = 39$  Hz) (weaker allyl bonding for the carbon trans to phosphorus<sup>17d</sup>), our values suggest moderate labilizing of the ground-state metal–allyl carbon bonds.

We can also estimate the trans influence of the methallyl ligand via  $^1J(\text{Pt},\text{Sn})$  and  $^1J(\text{Pt},\text{C-olefin})$ . The values of ca. 27 KHz for  $^1J(\text{Pt},\text{Sn})$  (see Experimental Section) in a total range of ca. 3–37 KHz<sup>9,10,24</sup> suggest a modest trans influence for C<sup>1</sup>, i.e., a relatively strong Pt–Sn bond, whereas the  $^1J(\text{Pt},\text{C})$  values of ca. 100 Hz imply that the olefin is not quite so strongly coordinated (e.g., trans- $\text{PtCl}_2(\text{L})(\text{C}_2\text{H}_4)$  has  $^1J(\text{Pt},\text{C}) = 165$  and 217 Hz for L = pyridine and pyridine *N*-oxide, respectively<sup>22</sup>). These coupling constant trends are in qualitative agreement with our crystallo-

(22) Mann, B. E.; Taylor, B. F. *<sup>13</sup>C NMR Data for Organometallic Compounds*; Academic: London, 1981.

(23) Akermarck, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* 1987, 6, 620.

(24) Albinati, A.; Moriyama, H.; Rügger, H.; Pregosin, P. S.; Togni, A. *Inorg. Chem.* 1985, 24, 4430.

graphic studies. We note that several groups<sup>17e,18a</sup> have measured  $^1J(\text{Pt},\text{P})$  values in excess of 4 KHz when a tertiary phosphine is coordinated trans to a  $\pi$ -allyl carbon, suggesting a weak  $\sigma$ -donor role for the  $\pi$ -allyl ligand.<sup>25</sup> Taking all the trans influence NMR data together, once again we reach the conclusion that the bonding in our coordination sphere is neither especially strong nor weak.

On the basis of crystallography, we suggested small differences in  $\pi$ -back-bonding to the olefin between **1a** and **2a** and the NMR data in Tables VII and VIII enhance this argument. Comparison of the  $^{13}\text{C}$  data for analogous Pt and Pd compounds shows that both the olefin and  $\pi$ -allyl ligand resonances appear at higher field for Pt than Pd. This  $^{13}\text{C}$  trend for Pt and Pd has been recognized, is also valid for the Rh, Ir pair,<sup>22</sup> and relates to the ability of the metal to  $\pi$ -bond to the ligand. In view of the bonding differences one might expect a more labile coordination sphere for Pd, and this is indeed the case. Relatively sharp NMR spectra for complexes of this metal required temperatures below 240 K, and we shall expand on these and other dynamics shortly. Finally, it has been suggested that in-plane double bonds are unstable.<sup>7</sup> We see no special evidence for this in our complexes, either in solution or in the solid state, and suspect that the statement may be valid for the special class of chelate olefin studied.

### Experimental Section

The complexes were prepared under an atmosphere of dinitrogen purified by passage through BASF catalyst R3-11. Solvents were dried and degassed prior to use. Elemental analysis were performed at Dipartimento di Chimica Organica, Università di Milano, Milano, Italy. The complexes ( $\text{C}_4\text{H}_7\text{MCl}$ )<sub>2</sub> (M = Pd, Pt) were prepared according to reported methods.<sup>26</sup>

**Preparation of Pd(SnCl<sub>3</sub>)(CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>)(C<sub>2</sub>H<sub>4</sub>).** SnCl<sub>2</sub> (0.200 g, 1.05 mmol) was added to a toluene (10 mL) solution of [PdCl(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>] (0.205 g, 0.50 mmol). The mixture was stirred for 30 min at room temperature to yield a yellow suspension. Ethylene was bubbled through this suspension, and a colorless solution was obtained. On standing the off-white microcrystalline material that separated out was filtered under an ethylene atmosphere, washed with pentane, and dried for a short time in vacuo to afford 0.250 g of product. The compound is very air-sensitive and must be stored at -30 °C under nitrogen. Anal. Calcd for C<sub>6</sub>H<sub>11</sub>PdSnCl<sub>3</sub>: C, 17.39; H, 2.66. Found: C, 16.93; H, 2.58.

**Preparation of Pd(SnCl<sub>3</sub>)(CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>)(norbornene).** SnCl<sub>2</sub> (0.200 g, 1.05 mmol) was added to a stirred solution of [PdCl(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>] (0.205 g, 0.50 mmol) in toluene (10 mL). A yellow suspension formed. After 30 min norbornene (0.200 g, 2.1 mmol) dissolved in toluene (2.5 mL) was added. A clear pale yellow solution was obtained, which shortly thereafter deposited an off-white solid. The toluene was siphoned off and the solid material washed with toluene and dried in high vacuum (0.450 g). The compound is very air sensitive. At room temperature CH<sub>2</sub>Cl<sub>2</sub> solutions decompose within a few minutes. Anal. Calcd for C<sub>11</sub>H<sub>17</sub>PdSnCl<sub>3</sub>: C, 27.48; H, 3.54. Found: C, 27.24; H, 3.44.

**Preparation of Pd(SnCl<sub>3</sub>)(CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>)(styrene).** SnCl<sub>2</sub> (0.106 g, 0.54 mmol) was added to [PdCl(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>] (0.102 g, 0.26 mmol) dissolved in 6 mL of CH<sub>2</sub>Cl<sub>2</sub>. After the solution was stirred for 30 min a yellow solid formed which dissolved upon addition of styrene (2.08 g, 20 mmol) to yield a yellow-green solution. Slow diffusion of heptane at -30 °C afforded well-shaped yellow green crystals (0.215 g). The compound decomposes slowly if left at room temperature in both the solid and the solution states. Anal. Calcd for C<sub>12</sub>H<sub>16</sub>PdSnCl<sub>3</sub>: C, 29.37; H, 3.06. Found: C, 29.47; H, 2.98.

(25) Pregosin, P. S. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; VCH: 1987; Vol. 8, p 465. Kunz, R. W.; Pregosin, P. S. *NMR Basic Principles and Progress*; Springer-Verlag: Berlin, 1979; Vol. 16.

(26) Mabott, D. J.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans* 1977, 294.

**Preparation of Pt(SnCl<sub>3</sub>)(CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>)(C<sub>2</sub>H<sub>4</sub>).** SnCl<sub>2</sub> (0.193 g, 1.02 mmol) and [PtCl(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>] (0.282 g, 0.49 mmol) dissolved in toluene (5 mL) were stirred for 15 min at room temperature. An orange-yellow suspension formed. Ethylene was bubbled through the suspension resulting in a clear pale yellow solution. When the mixture was left standing at room temperature, pale yellow well-shaped crystals separated out that were washed with pentane and dried (0.280 g). Anal. Calcd for C<sub>6</sub>H<sub>11</sub>PdSnCl<sub>3</sub>: C, 14.3; H, 2.18. Found: C, 14.2; H, 2.01. <sup>119</sup>Sr NMR (93.27 MHz):  $\delta$  1.3 ( $^1J(\text{Pt},\text{Sn}) = 27\,550$  Hz).

**Preparation of Pt(SnCl<sub>3</sub>)(CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>)(norbornene).** [PtCl(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>] (0.290 g, 0.51 mmol) dissolved in 5 mL of toluene and solid SnCl<sub>2</sub> (0.210 g, 1.10 mmol) were stirred at room temperature. After 15 min the yellow-orange suspension was treated with norbornene (0.564 g, 6 mmol) dissolved in 4 mL of toluene. A pale yellow solution was obtained. The small excess of SnCl<sub>2</sub> was filtered off and the solution reduced in volume to 6 mL. At -30 °C a white microcrystalline material precipitated and this was collected, washed with cold toluene, and dried in high vacuum (0.360 g). Anal. Calcd for C<sub>11</sub>H<sub>17</sub>PtSnCl<sub>3</sub>: C, 23.2; H, 2.99. Found: C, 23.05; H, 3.04. <sup>119</sup>Sr NMR (93.27 MHz):  $\delta$  2.5 ( $^1J(\text{Pt},\text{Sn}) = 27\,515$  Hz).

**Preparation of Pt(SnCl<sub>3</sub>)(CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>)(styrene).** [PtCl(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>] (0.120 g, 0.21 mmol) dissolved in 5 mL of toluene and solid SnCl<sub>2</sub> (0.085 g, 0.45 mmol) were stirred at room temperature for 15 min. Styrene (0.208 g, 2 mmol) was added, and a pale yellow solution was obtained. After filtration of the small excess of SnCl<sub>2</sub> the solution was evaporated. The yellow oily residue was dissolved in diethyl ether (5 mL). At -30 °C, pale yellow crystals precipitated and were collected (0.167 g). Anal. Calcd for C<sub>12</sub>H<sub>16</sub>PtSnCl<sub>3</sub>: C, 24.87; H, 2.59. Found: C, 25.13; H, 2.68. <sup>119</sup>Sr NMR (93.27 MHz):  $\delta$  8.7 ( $^1J(\text{Pt},\text{Sn}) = 28\,376$  Hz) (major isomer),  $\delta$  -4.8 ( $^1J(\text{Pt},\text{Sn}) = 26\,936$  Hz) (minor isomer).

**X-ray Diffraction.** The data for the analysis of both structures were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Crystal data and data collection parameters are summarized in Table I. Lattice parameters were obtained in both cases from a least-squares refinement of 25 reflections ( $18 \leq 2\theta \leq 26$ ). A set of three reflections was centered every 300 data to check the orientation of the crystal. Three standard reflections were monitored every 2 h during the collection, both crystals being slightly unstable. The data were consequently corrected for decay while the empirical absorption correction was based on  $\psi$  scans of three suitable reflections at  $\chi$  values close to 90°. The SDP programs<sup>27</sup> were used for crystal decay and absorption corrections and for the data reduction (Lp corrections applied).

The positions of Pd and Sn atoms in **2a** were determined from a Patterson synthesis while the structure of **1a** was solved by isomorphous substitution. Other atoms were located by standard Fourier methods. Only reflections with  $I > 3\sigma(I)$  were used in the refinement carried out by blocked-matrix least squares using the SHELX package.<sup>28</sup> Reflections (120), (130), (101), (201), (002) and (012) were omitted from the refinement of complex **2a**. Atomic scattering factors corrected for anomalous dispersion effects<sup>29</sup> and for all non-hydrogen atom anisotropic temperature factors were used. Hydrogen atoms were all located from Fourier

(27) *Enraf-Nonius Structure Determination Package, SDP*, Enraf-Nonius: Delft, The Netherlands, 1980.

(28) Sheldrick, G. G. *SHELX Programs*; University of Cambridge; Cambridge England.

(29) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham England, 1974; Vol. IV.

(30) Ball, R. G.; Payne, N. C. *Inorg. Chem.* 1976, 15, 2494.

(31) Albinati, A.; Caseri, W.; Pregosin, P. S. *Organometallics* 1987, 6, 788.

(32) Nyburg, S. C.; Simpson, K.; Wong-Ng, W. *J. Chem. Soc. Dalton Trans.* 1976, 1865.

(33) Van der Poel, H.; van Koten, G.; Kokkes, M.; Stam, C. H. *Inorg. Chem.* 1981, 20, 2941.

(34) Miki, K.; Skiotani, O.; Kai, Y.; Kasai, N.; Kanatani, H.; Kurasawa, H. *Organometallics* 1983, 2, 585.

(35) Miki, K.; Yama, M.; Kai, Y.; Kasai, N. *J. Organomet. Chem.* 1982, 239, 417.

(36) In this methodology the X-nucleus magnetization is detected via  $^1\text{H}$  measurements; see: Benn, R.; Brenneke, H.; Heck, J.; Rufinska, A. *Inorg. Chem.* 1987, 26, 2826. Benn, R.; Brevard, C. *J. Am. Chem. Soc.* 1986, 108, 5622.

Table IX

Distances (Å) of Selected Atoms from the Allyl Plane through C1, C2, and C3 in 1a and 2a

atom	dist from the allyl plane	
	1a	2a
C4	0.210 (9)	0.240 (4)
M	1.7313 (7)	1.7037 (6)
H1s	0.20 (6)	0.15 (3)
H1a	-0.42 (7)	-0.41 (3)
H3a	-0.33 (7)	-0.37 (3)
H3s	0.13 (7)	0.21 (3)

Dihedral Angles (deg) of Selected Planes with the Allyl Plane through C1, C2, and C3 in 1a and 2a

plane	dihedral angle with the allyl plane	
	1a	2a
H1s,C1,C2	12 (3)	11 (1)
H1a,C1,C2	34 (5)	34 (2)
H3a,C3,C2	25 (5)	31 (1)
H3a,C3,C2	9 (3)	14 (1)
C4,C2,C3	9.6 (7)	10.7 (3)
C4,C2,C1	9.5 (7)	10.8 (3)

<sup>a</sup> Esd's in parentheses.

difference maps and refined. In each structure a single average thermal parameter was refined for the three methyl hydrogens, and a second averaged temperature factor was obtained for the five phenyl hydrogens. For the other hydrogen atoms individual isotropic temperature factors were refined.

Table IX shows distances of the  $\pi$ -allyl protons from the plane defined by C1, C2, and C3, as well as some dihedral angles relative to the  $\pi$ -allyl plane. As expected<sup>19</sup> the syn protons move from the plane toward the metal, while the anti protons bend away from the metal.

The complete lists of anisotropic temperature factors (Table S1 for 1a and Table S2 for 2a), bond angles (Table S3 for 1a and Table S4 for 2a), values of  $10F_o$  vs  $10F_c$  (Table S5 for 1a and Table S6 for 2a), least-squares planes (Table S7 for 1a and Table S8 for 2a), together with a list of selected torsion angles and angles between least-squares planes for the two complexes (Table S9), have been deposited as supplementary material.

Routine <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured by using WP-200 and WM-250 MHz Bruker spectrometers. The <sup>119</sup>Sn spectra were measured on the WM-250 MHz spectrometer. Solvents and temperatures are given in the tables. For 1a the <sup>1</sup>H and <sup>13</sup>C and <sup>195</sup>Pt "reverse" NMR spectra<sup>36</sup> were measured by using a 400-MHz spectrometer. The 2-D NOESY and COSY spectra were measured by using standard pulse sequences.<sup>37</sup>

**Acknowledgment.** C.A. thanks Ciba-Geigy, Basel, and the Swiss National Science Foundation for support, and P.S.P. thanks the Johnson Matthey Research Centre, England, for the loan of K<sub>2</sub>PtCl<sub>4</sub>. We are grateful to Dr. C. Anklin, Spectrospin AG, for the <sup>195</sup>Pt, <sup>1</sup>H inverse 2-D measurement. A.M. and M.G. thank the CNR and Ministero PI for financial support.

**Registry No.** 1a (isomer 1), 115419-84-6; 1a (isomer 2), 115509-05-2; 1b, 115419-82-4; 1c, 115419-83-5; 2a, 115419-85-7; 2b, 115419-81-3; 2c, 115436-77-6; SnCl<sub>2</sub>, 7772-99-8; [PdCl(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>], 12081-18-4; [PtCl(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>], 35770-44-6.

**Supplementary Material Available:** Tables containing anisotropic temperature factors (Tables S1 and S2), bond angles (Tables S3 and S4), least-squares planes (Tables S7 and S8), and selected torsion angles (Table S9) (11 pages); listings of structure factors (Tables S5 and S6) (28 pages). Ordering information is given on any current masthead page.

(37) Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* 1983, 22, 350.

## Synthesis and Structures of Bimetallic Titanium and Chromium Carbene Complexes of the Type Cp<sub>2</sub>Ti(Cl)O(CH<sub>3</sub>)CCr(CO)<sub>5</sub>

Eric V. Anslyn, Bernard D. Santarsiero, and Robert H. Grubbs\*

Arnold and Mabel Beckman Laboratory of Chemical Synthesis,<sup>†</sup> California Institute of Technology, Pasadena, California 91125

Received December 22, 1987

$\beta,\beta$ -Dimethyltitanocene metallacyclobutane 1 reacts with M(CO)<sub>5</sub> (M = Cr, Mo) in toluene to yield a titanocene ketene adduct and M(CO)<sub>5</sub>. This reaction produces two intermediates, 3 and 4, with the formula Cp<sub>2</sub>Ti(O)CH<sub>2</sub>CM(CO)<sub>5</sub>. Independent synthesis of 3 and 4 (M = Cr) was achieved by the reaction of Cp<sub>2</sub>Ti(Cl)O(CH<sub>3</sub>)CCr(CO)<sub>5</sub> (9) and NaN(TMS)<sub>2</sub>. Complexes 3 and 4 are formed in a 1:1 ratio, with this ratio changing to 1.3:1 when the methylene group is deuteriated. The fluxional behavior of intermediates 3 and 4 was studied by using variable-temperature <sup>1</sup>H NMR. In contrast, reaction of NaN(TMS)<sub>2</sub> and Cp\*<sub>2</sub>Ti(Cl)O(CH<sub>3</sub>)CCr(CO)<sub>5</sub> (Cp\* = C<sub>5</sub>Me<sub>5</sub>) (preparation from Cp\*<sub>2</sub>TiCl<sub>2</sub> and LiO(CH<sub>3</sub>)CCr(CO)<sub>5</sub>) does not yield complexes analogous to 3 and 4 but instead yields Cp\*<sub>2</sub>Ti(Cl)O(CH<sub>2</sub>)CCr(CO)<sub>5</sub>Na. Cp\*<sub>2</sub>Ti(Cl)O(CH<sub>3</sub>)CCr(CO)<sub>5</sub> exists as two rotational isomers, 11 and 12. The X-ray crystal structure of 11 reveals that the methyl group is wedged between the two permethylcyclopentadienyl ligands. Crystals of 11 are monoclinic, P2<sub>1</sub>/c, with *a* = 12.490 (2) Å, *b* = 13.472 (33) Å, *c* = 17.791 (4) Å,  $\beta$  = 109.83 (2)°, and *Z* = 4. The reaction of Cp\*<sub>2</sub>TiCl<sub>2</sub> and 2LiO(CH<sub>3</sub>)CCr(CO)<sub>5</sub> yields Cp\*<sub>2</sub>Ti(O(CH<sub>3</sub>)CCr(CO)<sub>5</sub>)<sub>2</sub> (13). The X-ray crystal structure of 13 reveals that the methyl group of each Fischer carbene moiety is wedged between the permethylcyclopentadienyl ligands. Crystals of 13 are monoclinic, P2<sub>1</sub>/n, with *a* = 9.958 (2) Å, *b* = 32.226 (8) Å, *c* = 11.998 (3) Å,  $\beta$  = 108.21 (2)°, and *Z* = 4.

### Introduction

Insertion reactions are some of the most common and important reactions in organometallic chemistry. Aside

from being mechanistically interesting, they have proven useful in organic synthesis and have been postulated in catalytic cycles. A subset of the broad group of insertion reactions is the insertion of carbon monoxides of group VIB metal carbonyl complexes into early-transition-metal alkyl, aryl and hydride bonds.<sup>1,2</sup> Several examples of this

<sup>†</sup> Contribution No. 7641.