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Metal insertion into a CH bond as a route to the heterobimetallic μ-methylidene complex $C_5H_5(CO)_2Re(\mu\text{-}CH_2)Pt(PPh_3)_2$

Charles P. Casey*, Yan Wang, Lori M. Petrovich, Todd L. Underiner, Paulette N. Hazin and John M. Desper

Department of Chemistry, University of Wisconsin, Madison, WI 53706 (USA)

Abstract

The reaction of $C_5H_5(CO)_2Re(CH_3)^-Li^+\cdot THF$ (5) with $(Ph_3P)_3Pt[(E)\text{-}C(CH_3){=}CHCH_3]^+CF_3SO_3^-$ (3E) in an attempt to prepare the heterobimetallic complex $C_5H_5(CO)_2(CH_3)RePt[(E)\text{-}C(CH_3){=}CHCH_3](PPh_3)_2$ (**B**) led to the formation of the new heterobimetallic μ-methylene complex $C_5H_5(CO)_2Re(\mu\text{-}CH_2)Pt(PPh_3)_2$ (**4**), which was characterized by X-ray crystallography. A mechanism involving initial generation of intermediate **B** followed by insertion of Pt into a C–H bond and reductive elimination is suggested. The related substituted alkylidene complexes $C_5H_5(CO)_2Re[\mu\text{-}CH(E\text{-}CH_3C{=}CHCH_3)]Pt(PPh_3)_2$ (**9**) and $C_5H_5(CO)_2Re(\mu\text{-}CHCH_3)Pt(PPh_3)_2$ (**11**) were prepared from $Pt(C_2H_4)(PPh_3)_2$ and the appropriate rhenium alkylidene complexes $C_5H_5(CO)_2Re{=}CHR$.

Introduction

We have been exploring the synthesis and reactions of heterobimetallic compounds in an effort to find new types of reactions and catalysts. We found that the rhenium–platinum dihydride $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ (**1**) [1] reduced 2-butyne to the *cis*-alkene rhenium complex $C_5H_5(CO)_2Re(cis\text{-}CH_3CH{=}CHCH_3)$ (**2**) and proposed that the reduction proceeded via platinum hydride addition across the alkyne to give the rhenium–platinum vinyl intermediate $C_5H_5(CO)_2Re(\mu\text{-}H)Pt[(E)\text{-}C(CH_3){=}CHCH_3](PPh_3)_2$ (**A**) (Scheme 1) [2]. In an attempt to test this hypothesis, we reacted $K^+C_5H_5(CO)_2ReH^-$ with $(Ph_3P)_3Pt[(E)\text{-}C(CH_3){=}CHCH_3]^+CF_3SO_3^-$ (**3E**) in an effort to generate **A** by an independent route. The proposed intermediate **A** was not observed but **2** was obtained in high yield, consistent with our hypothesis [3]. We suggested that **A** was generated and that rapid hydride transfer led to **2**.

We thought that by replacing the reactive hydride of intermediate **A** with a methyl group we might be able to observe the related methyl intermediate $C_5H_5(CO)_2(CH_3)RePt[(E)\text{-}C(CH_3){=}CHCH_3](PPh_3)_2$ (**B**). Here we report that attempted generation of **B** led to formation of the new heterobimetallic μ-methylene complex $C_5H_5(CO)_2Re(\mu\text{-}CH_2)Pt(PPh_3)_2$ (**4**), possibly via intermediate **B** (Scheme 2).

Experimental

General procedures

^1H NMR spectra were measured on a Bruker WP200, WP270, AM360 or AM500 spectrometer. $^{13}C\{^1H\}$ NMR spectra were obtained on an AM500 spectrometer operating at 125.76 MHz. $^{31}P\{^1H\}$ NMR spectra were obtained on an AM500 spectrometer operating at 202.46 MHz. $^2H\{^1H\}$ NMR spectra were obtained on an AM360 or AM500 spectrometer operating at 55 or 76 MHz. $^1H\{^{31}P\}$ spectra were obtained on a Varian VXR 500 spectrometer. ^{31}P chemical shifts are referenced to 85% external H_3PO_4. IR spectra were obtained on a Mattson Polaris (FT) spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

Air-sensitive material was manipulated in an inert-atmosphere glove box or by standard high-vacuum and Schlenk techniques. Tetrahydrofuran, hexane and diethyl ether were distilled prior to use from purple solutions of sodium and benzophenone. CH_2Cl_2 was dried over CaH_2.

$Cp(CO)_2Re(CH_3)^-Li^+\cdot THF$ (5)

At −78 °C, THF (10 ml) was condensed into a flask containing $CpRe(CO)_3$ (500 mg, 1.495 mmol) and $LiAlH_4$ (111 mg, 2.925 mmol) and equipped with a reversible frit. When the mixture was stirred at room temperature, gas evolved and the solution turned yellow. The mixture was then heated at 60 °C for 4 h. Solvent was evaporated under high vacuum and the resulting

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*Author to whom correspondence should be addressed.

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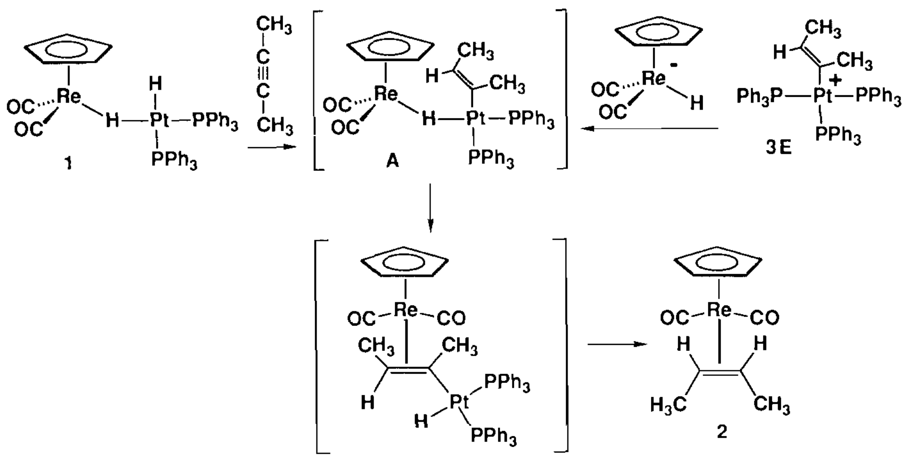
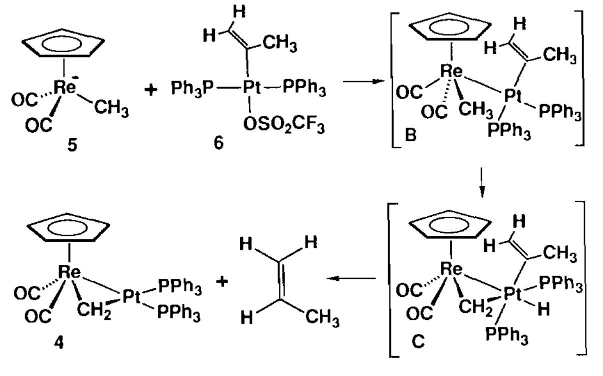


Scheme 1.



Scheme 2.

yellow oil was extracted with 30 ml diethyl ether to give a yellow solution and a white solid. The mixture was filtered and the white solid was rinsed with 2×10 ml ether. The ether solution was concentrated to 4 ml and 15 ml of hexane was added at −78 °C to give a pale yellow precipitate. The solid was isolated by cold filtration, sonicated with 15 ml hexane for 1 h, and filtered to give **5** (479 mg, 79% pure, 66% yield) as a fine yellow powder which was dried under high vacuum for 12 h. ^{1}H NMR showed a 0.93 ± 0.05:1 ratio of THF:**5** (200 MHz, CD_3CN): δ 4.87 (s, C_5H_5, 5.1H), 3.64 (m, THF, 3.6H), 1.79 (m, THF, 3.9H), −0.06 (s, CH_3, 2.9H). ^{1}H NMR (200 MHz, THF-d_8): δ 4.86 (s, C_5H_5), −0.03 (s, CH_3); integration of the Cp peak of **5** versus a weighed amount of C_6Me_6 showed a purity of 79%. ^{13}C NMR (126 MHz, THF-d_8): δ 217.5 (s, CO), 84.8 (d, C_5H_5, J(CH) = 175 Hz), −25.3 (q, CH_3, J(CH) = 122 Hz). IR (THF): 1849(s), 1724(s) cm^{-1}.

Anal. Calc. for $C_{12}H_{16}LiO_3Re$: C, 35.93; H, 4.02. Found: C, 27.27; H, 3.66%. This indicates that the major impurities in **5** are inorganic salts. Plasma emission analysis showed the presence of both Al (4.66%) and Li (2.66% found, 1.7% calc.). This is consistent with the major impurities in **5** being inorganic salts of Li and Al.

Cp(CO)$_2$Re(μ-CH$_2$)Pt(PPh$_3$)$_2$ (4)

A THF solution of *trans*-Pt[C(CH_3)=CH_2](CF_3SO_3)(PPh_3)$_2$ [4] (124 mg, 0.130 mmol) and Cp(CO)$_2$ReCH$_3$Li·THF (**5**) (100 mg, 80% purity, 0.20 mmol) was stirred for 2 h at room temperature. Solvent was evaporated and the residue was purified by column chromatography (silica gel, CH_2Cl_2). The first yellow band was collected and evaporated to give **4** (100 mg, 74%) as a yellow solid. ^{1}H NMR (200 MHz, CD_3COCD_3): δ 7.6–7.2 (m, C_6H_5), 5.13 (dd, J(PH) = 4.7, 1.4 Hz, CH_2), 4.78 (s, C_5H_5); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 206.2 (s, CO), 135.9 (d, J(PC) = 38 Hz, *ipso*-C), 135.7 (dd, J(P'C) = 46 Hz, J(PC) = 2 Hz, *ipso*-C), 134.7 (d, J(P'C) = 13 Hz, *o*-C), 133.8 (d, J(PC) = 12 Hz, *o*-C), 128.0 (d, J(PC) = 4 Hz, *m*-C), 127.9 (d, J(P'C) = 5 Hz, *m*-C), 129.6 (s, *p*-C), 91.9 (d, J(PC) = 56 Hz, J(PtC) = 560 Hz, μ-CH_2), 87.4 (s, Cp); ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 31.6 (d, J(PP) = 12 Hz, J(PtP) = 2878 Hz), 23.0 (d, J(PP) = 12 Hz, J(PtP) = 4307 Hz). IR (CH_2Cl_2): ν(CO) 1925(vs), 1844(s) cm^{-1}. *Anal.* Calc. for $C_{44}H_{37}O_2P_2PtRe$: C, 50.77; H, 3.58. Found: C, 50.47; H, 3.53%.

X-ray crystallography of Cp(CO)$_2$Re(μ-CH$_2$)Pt(PPh$_3$)$_2$·2 acetone-d$_6$ (4·2 acetone-d$_6$)

Recrystallization from acetone-d_6 gave yellow crystals of Cp(CO)$_2$Re(μ-CH$_2$)Pt(PPh$_3$)$_2$·2 acetone-d_6 (**4**·2 acetone-d_6) suitable for X-ray analysis. Diffraction data were collected on a Nicolet P3f diffractometer. The 6297 measured data for **4** yielded 4229 independent, observed ($F > 4.0\sigma(F)$) data. The structure was solved by direct methods and refined by full-matrix least-squares methods using the SHELXTL PLUS software package. Crystallographic data (Table 1), atomic coordinates (Table 2), selected bond lengths and selected

TABLE 1. Crystallographic data for $Cp(CO)_2Re(\mu\text{-}CH_2)\text{-}Pt(PPh_3)_2 \cdot 2$ acetone-d_6

Formula	$C_{44}H_{37}O_2P_2PtRe \cdot 2C_3D_6O$
Formula weight	1169.1
a (Å)	16.084(5)
b (Å)	20.691(7)
c (Å)	25.397(8)
V (Å^3)	8850(5)
Z	8
Space group	*Pbca*
T (°C)	−160
λ (Å)	0.71073 (Mo Kα)
ρcalc. (g/cm^3)	1.755
μ (mm^{-1})	6.075
Transmission min./max.	0.0536/0.1025
$R(F_o)$	0.0354
$R_w(F_o)$	0.0387

bond angles (Table 3) are presented. See also 'Supplementary material'.

$Cp(CO)_2Re{=}CH(E\text{-}CH_3C{=}CHCH_3)$ (7)

2-Butyne (2.5 mmol) was condensed into a mixture of $Cp_2Zr(H)Cl$ (0.65 g, 2.5 mmol) in 20 ml of benzene at −78 °C. The resulting white suspension was stirred at 25 °C for 2.5 h to give a homogeneous brown solution. (In several preparations, $Cp_2Zr(E\text{-}CH_3C{=}CHCH_3)Cl$ [5] was isolated by filtration and evaporation of benzene, and spectroscopically characterized. ^1H NMR (C_6D_6, 200 MHz): δ 6.01 (qq, $J=6.2$, 1.8 Hz, ZrC=CH), 5.80 (s, C_5H_5), 1.72 (dq, $J=1.8$, 1.0 Hz, $ZrCCH_3$), 1.55 (dq, $J=6.2$, 1.0 Hz, $ZrC{=}CHCH_3$). This material was >90% pure by NMR.) The brown solution of $Cp_2Zr(E\text{-}CH_3C{=}CHCH_3)Cl$ was filtered under nitrogen to remove unreacted $Cp_2Zr(H)Cl$ and placed under 500 mm CO [6]. Pale yellow crystals of the acyl complex $(\eta^5\text{-}C_5H_5)_2Zr(Cl)[\eta^2\text{-}CO(E\text{-}CH_3C{=}CHCH_3)]$ (**8**) began to precipitate after 45 min. After 12 h, the solid was collected by filtration and washed with benzene to give **8** (0.57 g, 68%). ^1H NMR (CD_3CN, 200 MHz): δ 7.49 (qq, $J=7.0$, 1.4 Hz, C=CH), 2.18 (dq, $J=7.0$, 1.0 Hz, $C{=}CHCH_3$), 1.85 (pentet, $J=1.0$ Hz, $ZrCOCCH_3$). This material was used without further purification.

Addition of a slurry of $Cp(CO)_2ReH^-K^+$ (385 mg, 1.11 mmol) [7] at 0 °C in THF to a pale yellow THF solution of **8** (397 mg, 1.17 mmol) at 0 °C gave a deep orange–red solution. Solvent was immediately evaporated under high vacuum and the resulting deep red oil was chromatographed (silica gel, CH_2Cl_2). Evaporation of solvent from the first red band gave a deep red oil from which small crystals formed. Sublimation at 70 °C under high vacuum gave burgundy crystals of **7** (375 mg, 90%), m.p. 96 °C. ^1H NMR (CD_2Cl_2, 200 MHz): δ 15.72 (d, $J=0.9$ Hz, Re=CH), 6.47 (quartet of pentets, $J=7.2$, 0.9 Hz, $C{=}CHCH_3$), 5.72 (s, C_5H_5),

TABLE 2. Atomic coordinates (×10^5) and equivalent isotropic displacement coefficients (pm^{-2}) for $Cp(CO)_2Re(\mu\text{-}CH_2)\text{-}Pt(PPh_3)_2 \cdot 2$ acetone-d_6

	x	y	z	U_{eq}[a]
Re(1)	48170(2)	7284(2)	64563(1)	203(1)
Pt(1)	50933(2)	−5709(2)	64975(1)	173(1)
C(1)	34857(48)	8949(47)	65921(38)	262(33)
C(2)	38427(49)	14888(46)	64635(40)	266(33)
C(3)	41396(51)	14456(46)	59363(38)	250(33)
C(4)	39463(50)	8288(47)	57470(37)	251(32)
C(5)	35462(49)	4776(44)	61480(37)	222(31)
C(6)	57370(49)	12466(41)	64997(37)	196(20)
O(1)	63118(37)	15632(33)	65333(30)	398(26)
C(7)	50966(52)	4978(45)	71584(42)	276(33)
O(2)	52646(36)	4127(32)	76047(28)	317(24)
C(8)	55503(54)	1065(39)	59939(41)	233(32)
P(1)	42720(13)	−10491(11)	71196(10)	191(7)
C(11)	37154(50)	−17412(43)	68677(39)	231(33)
C(12)	35673(55)	−23150(46)	71321(39)	277(34)
C(13)	31811(62)	−28229(51)	68960(46)	385(40)
C(14)	29012(54)	−27586(50)	63821(46)	371(40)
C(15)	30314(54)	−22039(52)	61058(43)	346(38)
C(16)	34381(49)	−17000(47)	63402(38)	246(32)
C(21)	47445(54)	−13430(43)	77210(35)	226(31)
C(22)	43062(61)	−15060(45)	81696(39)	303(36)
C(23)	47035(65)	−17361(49)	86124(43)	389(39)
C(24)	55124(63)	−18206(47)	86185(41)	360(38)
C(25)	59490(58)	−16748(48)	81708(40)	301(37)
C(26)	55708(53)	−14310(45)	77274(38)	265(34)
C(31)	34364(50)	−5575(41)	73778(36)	200(30)
C(32)	26931(51)	−5662(46)	71464(42)	294(35)
C(33)	20818(58)	−1737(45)	73169(41)	288(35)
C(34)	22130(60)	2438(47)	77402(43)	335(37)
C(35)	29445(58)	2648(45)	79826(39)	280(35)
C(36)	35632(54)	−1343(42)	78054(40)	238(33)
P(2)	56573(13)	−14244(11)	60862(9)	185(8)
C(41)	66306(51)	−12714(44)	57916(38)	235(32)
C(42)	68918(52)	−15975(46)	53381(36)	230(32)
C(43)	76546(52)	−14849(49)	51471(38)	274(35)
C(44)	81536(53)	−10520(49)	53941(38)	279(33)
C(45)	79035(53)	−7319(47)	58424(41)	297(35)
C(46)	71456(52)	−8422(47)	60355(38)	269(33)
C(51)	58787(50)	−21537(43)	64666(37)	225(30)
C(52)	66292(61)	−22589(51)	66798(40)	337(37)
C(53)	67738(68)	−27830(55)	70027(43)	416(42)
C(54)	61738(70)	−32247(54)	71185(42)	418(42)
C(55)	54350(66)	−31190(49)	69158(40)	375(37)
C(56)	52840(54)	−26019(42)	65823(33)	230(30)
C(61)	50585(50)	−17216(41)	55382(32)	192(28)
C(62)	50424(52)	−23578(45)	53701(34)	235(30)
C(63)	45447(53)	−25600(48)	49656(37)	262(31)
C(64)	40472(51)	−21250(45)	47268(38)	247(33)
C(65)	40644(53)	−14817(50)	48733(35)	266(35)
C(66)	45522(47)	−12776(46)	52852(36)	220(31)
C(1S)	10215(72)	41464(62)	10098(51)	605(51)
C(2S)	3470(69)	44804(57)	7412(52)	486(44)
O(1S)	−39(58)	42155(49)	3864(41)	828(42)
C(3S)	1159(75)	51070(63)	9514(59)	726(59)
C(4S)	80387(78)	42668(58)	−1979(55)	606(51)
C(5S)	81695(61)	36394(61)	893(46)	403(44)
O(2S)	83344(47)	31513(42)	−1507(32)	518(32)
C(6S)	81170(71)	36359(65)	6702(47)	557(50)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Selected bond lengths (Å) and angles (°) for $Cp(CO)_2Re(\mu\text{-}CH_2)Pt(PPh_3)_2$

Bond distances (Å)			
Re(1)–Pt(1)	2.730(1)	Re(1)–C(1)	2.295(8)
Re(1)–C(2)	2.273(9)	Re(1)–C(3)	2.291(9)
Re(1)–C(4)	2.332(9)	Re(1)–C(5)	2.337(9)
Re(1)–C(6)	1.887(8)	Re(1)–C(7)	1.905(10)
Re(1)–C(8)	2.135(9)	Pt(1)–C(8)	2.048(9)
Pt(1)–P(1)	2.321(3)	Pt(1)–P(2)	2.261(2)
C(6)–O(1)	1.172(11)	C(7)–O(2)	1.182(13)
Bond angles (°)			
Pt(1)–Re(1)–C(8)	47.9(2)	Re(1)–Pt(1)–C(8)	50.7(2)
Re(1)–C(8)–Pt(1)	81.5(4)	C(6)–Re(1)–C(7)	83.4(4)
Pt(1)–Re(1)–C(6)	114.7(3)	Pt(1)–Re(1)–C(7)	71.1(3)
Re(1)–C(6)–O(1)	179.0(8)	Re(1)–C(7)–O(2)	174.0(8)
C(6)–Re(1)–C(8)	84.3(4)	C(7)–Re(1)–C(8)	102.8(4)
Re(1)–Pt(1)–P(1)	110.1(1)	Re(1)–Pt(1)–P(2)	145.4(1)
C(8)–Pt(1)–P(1)	160.2(3)	C(8)–Pt(1)–P(2)	95.1(3)
P(1)–Pt(1)–P(2)	103.4(1)		

2.42 (pentet, $J=1.1$ Hz, Re=CHCCH_3), 1.15 (dq, $J=7.2$, 1.0 Hz, C=CHCH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): δ 279.3 (Re=CH), 205.7 (CO), 160.5 (Re=CH*C*), 139.3 (Re=CHC=*C*), 91.9 (C_5H_5), 17.2, 16.8 (CH_3s); IR (CH_2Cl_2): 1960(s), 1878(s), cm^{-1}. HRMS calc. for $C_{12}H_{13}O_2Re$, 376.0474; found, 376.0481.

$Cp(CO)_2Re[\mu\text{-}CH(E\text{-}CH_3C{=}CHCH_3)]Pt(PPh_3)_2$ (9)

A solution of $Cp(CO)_2Re{=}CH(E\text{-}CH_3C{=}CHCH_3)$ (**7**) (150 mg, 3.9 mmol) in 8 ml CH_2Cl_2 was added dropwise to a solution of $Pt(C_2H_4)(PPh_3)_2$ [8] (298 mg, 3.9 mol) in 5 ml CH_2Cl_2. The deep red color of the rhenium compound changed to bright yellow in 5 min. After 15 min, the solution was concentrated to 3 ml by evaporation of solvent under vacuum. Hexane was slowly condensed into the solution and a yellow precipitate formed. The precipitate was filtered, washed with hexane, and dried under high vacuum go give **9** (352 mg, 83%). ^1H NMR (CD_2Cl_2, 270 MHz): δ 7.6–7.1 (m, 30H, C_6H_5), 6.75 (dd, $J(PH)=4.2$, 2.2 Hz, CH), 4.89 (s, C_5H_5), 4.13 (bm, C=CH), 1.35 (bs, μ-CHCCH_3), 1.24 (bm, C=CHCH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 23.66 (d, $J(PP)=10$ Hz, $J(PtP)=4427$ Hz), 31.3 (d, $J(PP)=10$ Hz, $J(PtP)=2242$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): δ 207.8, 205.7 (CO); 153, 112 (C=C); 136–127 (C_6H_5); 122.7 (d, $J(PC)=55$ Hz, μ-C); 85.7 (C_5H_5); 20.8, 13.8 (CH_3). IR (CH_2Cl_2): 1924(vs), 1845(s) cm^{-1}. *Anal.* Calc. for $C_{48}H_{43}O_2P_2PtRe$: C, 52.64; H, 3.93. Found: C, 53.03; H, 3.84%.

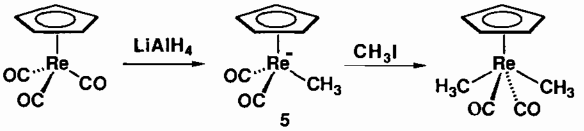
$Cp(CO)_2Re(\mu\text{-}CHCH_3)Pt(PPh_3)_2$ (11)

A benzene solution of $Cp(CO)_2Re{=}CHCH_3$ (**10**) [9] (25 mg, 0.075 mmol) and $Pt(C_2H_4)(PPh_3)_2$ [8] (96 mg, 0.129 mmol) was stirred at room temperature for 3 h. The solution turned from orange to yellow immediately and gas evolution was observed. Solvent was evaporated and the residue was purified by flash column chromatography (silica gel, CH_2Cl_2). The first yellow band was collected and evaporated to give **11** (70 mg, 89%) as a yellow solid. $Cp(CO)_2Re(\mu\text{-}^{13}CHCH_3)Pt(PPh_3)_2$ (**11**-^{13}C) was prepared from $Cp(CO)_2Re{=}^{13}CHCH_3$ (>95% ^{13}C) using a similar procedure. The ^{13}C and ^{31}P spectra are reported for **11**-^{13}C. As determined by ^1H NMR, **11** decomposed in CD_2Cl_2 over two days at room temperature to give $Cp(CO)_2Re(C_2H_4)$. ^1H NMR (500 MHz, 1:1 THF-d_8:CF_2Cl_2): δ 7.7–7.1 (m, C_6H_5), 6.35 (qd, $J(HH)=7.2$ Hz, $J(PH)=6.0$ Hz, CH), 4.70 (s, C_5H_5), 2.18 (td, $J(HH)=7.2$ Hz, $J(PH)=7.2$, 5.2 Hz CH_3). ^1H NMR (500 MHz, 1:1 THF-d_8:CF_2Cl_2, −93 °C): δ 7.7–7.0 (C_6H_5), 6.03 (minor CH), 5.89 (major CH), 4.67 (minor Cp), 4.58 (major Cp), 2.27 (major CH_3), 2.09 (minor CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 206.5 (CO), 205.7 (CO), 136.7 (d, $J(PC)=35.3$ Hz, C_6H_5), 135.0 (d, $J(PC)=13.1$ Hz, C_6H_5), 134.3 (d, $J(PC)=11.3$ Hz, C_6H_5), 129.3 (d, $J(PC)=10.5$ Hz, C_6H_5), 116.8 (d, $J(PC)=56.7$ Hz, $J(PtC)=614.3$ Hz, CH), 84.9 (C_5H_5), 36.7 (d, $J(CC)=34.3$ Hz, CH_3). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 27.6 (dd, $J(CP)=57.0$ Hz, $J(PP)=18$ Hz, $J(PtP)=2605$ Hz), 20.4 (d, $J(PP)=16$ Hz, $J(PtP)=4374$ Hz). *Anal.* Calc. for $C_{45}H_{39}O_2P_2PtRe$: C, 51.23; H, 3.73. Found: C, 50.75; H, 3.89%.

Results and discussion

We sought a convenient source of the $C_5H_5(CO)_2ReCH_3^-$ anion for the attempted synthesis of **B**. Previously, Yang and Bergman [7] had reported the generation of a mixture of $C_5H_5(CO)_2ReCH_3^-K^+$ and *trans*-$C_5H_5(CO)_2Re(CH_3)_2$ from $C_5H_5(CO)_2ReH_2$ via successive deprotonation, methylation and deprotonation; the preparation of $C_5H_5(CO)_2ReH_2$ in turn involves bromination and reduction of $C_5H_5Re(CO)_3$ and occurs in 31% yield [10]. We have found that the $C_5H_5(CO)_2ReCH_3^-Li^+\cdot THF$ (**5**) reagent can be prepared more conveniently in 66% yield by reduction of $C_5H_5Re(CO)_3$ with $LiAlH_4$. The pale yellow solid obtained is a mixture of lithium and aluminum salts and is approximately 80% pure as determined by NMR analysis and by conversion to *trans*-$C_5H_5(CO)_2Re(CH_3)_2$ with methyl iodide. The impurities in this reagent did not affect the reactions reported here since similar results were obtained with a mixture of $C_5H_5(CO)_2ReCH_3^-K^+$ and *trans*-$C_5H_5(CO)_2Re(CH_3)_2$ prepared as described by Bergman. The first direct reductions of a carbonyl ligand to a methyl group were reported by Treichel and Shubkin in the synthesis of $CpW(CO)_2(PPh_3)CH_3$ and $CpMo(CO)_2(PPh_3)CH_3$ [11].

Similar reductions [12] have been used to synthesize $CpRe(CO)(NO)CH_3$ [13], $CpRe(PPh_3)(NO)CH_3$ [14] and $Cp^*Fe(CO)(PPh_3)CH_3$ [15].



Reaction of $C_5H_5(CO)_2ReCH_3^-Li^+ \cdot THF$ (**5**) with *trans*-$(PPh_3)_2Pt[C(CH_3){=}CH_2](CF_3SO_3)$ (**6**) [4] in THF at room temperature followed by chromatography (silica gel, CH_2Cl_2) led to isolation of the heterobimetallic μ-methylene complex $C_5H_5(CO)_2Re(\mu\text{-}CH_2)Pt(PPh_3)_2$ (**4**) as an air stable yellow solid in 54% isolated yield. **4** was characterized spectroscopically and by X-ray crystallography (Fig. 1, Table 3).

In the X-ray structure of **4**, the platinum has a distorted square planar geometry; the platinum atom lies only 0.10 Å out of the mean plane defined by platinum and its attached atoms. The geometry about the rhenium center is best described as a distorted four legged piano stool; alternatively, it can be viewed as a three legged piano stool with the $CH_2{=}Pt$ unit occupying one site. The structure around the Pt center of **4** is similar to that in $(CO)_5W[\mu\text{-}C(OCH_3)C_6H_5]Pt(PMe_3)_2$ described by Stone and coworkers [16]. The 2.730 Å Re–Pt bond length of **4** is shorter than the 2.859 Å bond length of $(4\text{-}MeC_6H_4N_2)ClRe(\mu\text{-dppm})_2(\mu\text{-}CO)PtCl$ [17] and shorter than the 2.838 Å bond length of $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ (**1**) which we now know has a metal hydride bridge [18].

In the low temperature ^1H NMR spectrum of **4** in acetone-d_6 at −105 °C, separate resonances were seen at δ 5.48 and 4.44 for the inequivalent μ-CH_2 protons. The resonances for the μ-CH_2 protons coalesced at about −70 °C and then sharpened to a single multiplet at δ 5.12 with coupling to different phosphines ($J(PH) = 4.7$ and 1.4 Hz). This temperature dependent ^1H NMR behavior indicates that a fluxional process interconverts the μ-CH_2 protons while maintaining the inequivalence of the phosphine ligands. Line shape analysis (using DNMRC [19]) of the temperature dependent ^1H NMR spectra indicated $\Delta G^{\ddagger} = 8.7 \pm 0.1$ kcal mol^{-1} at −70 °C.

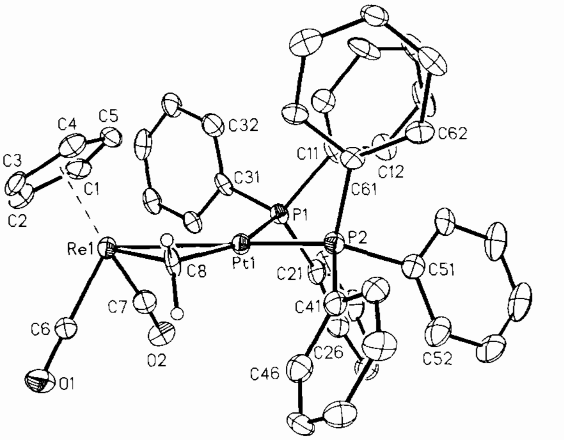
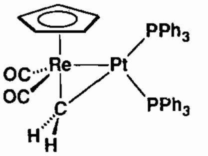


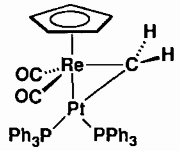
Fig. 1. X-ray structure of $Cp(CO)_2Re(\mu\text{-}CH_2)Pt(PPh_3)_2$.

In the ^{13}C NMR of **4**, the resonance at δ 91.9 (d, $J(PC) = 56$ Hz, $J(PtC) = 560$ Hz) was assigned to the μ-CH_2 carbon on the basis of a DEPT spectrum in which this signal appeared as an inverted doublet. Even at −83 °C, only one ^{13}CO resonance was seen at δ 206.5 ($w_{1/2} = 20$ Hz) even though two different COs would be expected from the X-ray structure. Either the chemical shifts of the COs are not resolved or are similar enough that the fluxional process gives rise to an averaged spectrum at −83 °C. The room temperature ^{31}P NMR of **4** shows two different resonances at δ 31.6 and δ 23.0. This confirms that the fluxional process that exchanges the environments of the two μ-CH_2 protons does not exchange the environments of the two phosphines.

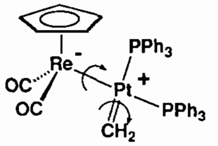
Four different mechanisms might explain the fluxional process. The first two involve conversion of the four legged piano stool geometry around the Re center to a trigonal bipyramidal geometry with either the μ-CH_2(**D**) or the Pt(**E**) *anti* to the Cp ring. A third alternative involves unbridging the μ-CH_2 ligand to give a more polar formally zwitterionic structure (**F**) with lowered barriers to rotation about the Pt–Re and $Pt{=}CH_2$ bonds. A fourth involves rotation of the μ-CH_2 group through a planar carbon intermediate (**G**) but seems unlikely since it fails to interconvert the CO groups.



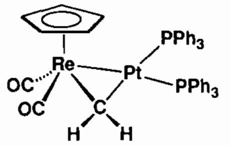
D



E



F



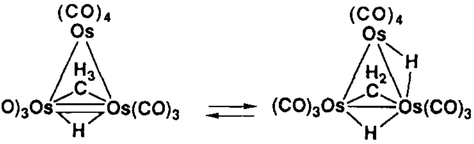
G

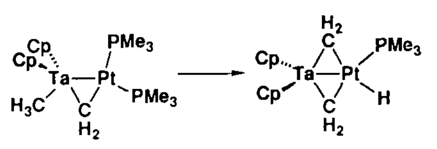
The solvent dependence of the fluxional barrier was examined in an attempt to distinguish between these mechanisms. A substantially lower barrier in polar solvents would be expected if the fluxional process proceeded via zwitterion **F**. Very similar barriers [19] were observed in acetone ($\Delta G^{\ddagger} = 8.7$ kcal mol^{-1} at −70 °C), in 3:1 CF_2Cl_2:THF ($\Delta G^{\ddagger} = 8.7$ kcal mol^{-1} at −70 °C), and in toluene ($\Delta G^{\ddagger} = 8.6$ kcal mol^{-1} at

-70 °C), indicating that the zwitterionic mechanism was unlikely. Based on the results described below for substituted alkylidene complexes, the zwitterion mechanism can be excluded.

The mechanism of formation of **4** was briefly investigated. When the reaction of $C_5H_5(CO)_2ReCH_3^-Li^+\cdot THF$ (**5**) and *trans*-$(PPh_3)_2Pt[C(CH_3){=}CH_2](CF_3SO_3)$ (**6**) [4] in THF-d_8 at -78 °C was monitored by ^1H NMR, μ-methylene complex **4** and $CH_2{=}CHCH_3$ were observed immediately at -78 °C. When the reaction of $C_5H_5(CO)_2ReCD_3^-Li^+\cdot THF$ (**5d**) with **6** in THF was followed by ^2H NMR, $C_5H_5(CO)_2Re(\mu\text{-}CD_2)Pt(PPh_3)_2$ (**4d**) (δ 5.17) and $CH_2{=}CDCH_3$ (δ 5.80) were observed. This establishes a net transfer of deuterium from the methyl group to the vinyl group. Reaction of **5** with $(Ph_3P)_3Pt[(E)\text{-}C(CH_3){=}CHCH_3]^+CF_3SO_3^-$ (**3E**) [4] and with $(Ph_3P)_3Pt[(Z)\text{-}C(CH_3){=}CHCH_3]^+CF_3SO_3^-$ (**3Z**) in THF-d_8 occurred more slowly at room temperature to produce μ-methylene complex **4** and 2-butene with retention of vinyl stereochemistry. The reaction of rhenium methyl anion **5** with the ionic **3E** in THF-d_8 occurred at room temperature and was much slower than the reaction of **5** with the neutral complex **6**. Earlier we had found that the reaction of rhenium hydride anion $C_5H_5(CO)_2ReH^-$ with **3E** was also much slower than the reaction with the neutral complex **6**, and we proposed that this reaction occurred by rate determining dissociation of phosphine from **3E** [3].

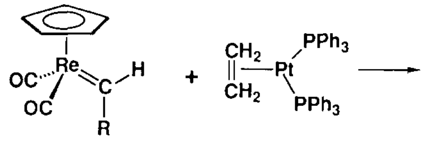
To account for the formation of **4**, we propose the mechanism shown in Scheme 2. Initial formation of intermediate **B** is followed by insertion of platinum into a CH bond of the rhenium methyl group to give intermediate **C**. Reductive elimination of the vinyl group and hydride from platinum then produces the observed μ-methylene complex **4**. The facile intramolecular insertion of a metal into a methyl CH bond is reminiscent of the interconversion of $HOs_3(CO)_{10}CH_3$ and $H_2Os_3(CO)_{10}CH_2$ reported by Calvert and Shapley [20] and of the conversion of $Cp_2(CH_3)Ta(\mu\text{-}CH_2)Pt(PMe_3)_2$ to $Cp_2Ta(\mu\text{-}CH_2)_2Pt(H)(PMe_3)$ [21].



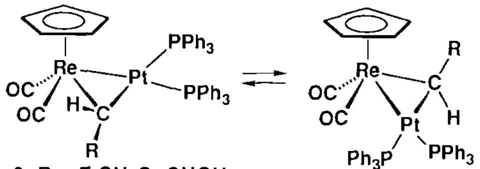


Heterobimetallic μ-CH_2 complexes similar to **4** have been reported. Complexes in which a metal–metal bond is supported by a single μ-CH_2 ligand include $Cp(CO)Co(\mu\text{-}CH_2)Rh(CO)Cp$ [22], $Os_3(CO)_{11}(\mu\text{-}CH_2)Pt(PPh_3)_2$ [23], $Cp(CO)Co(\mu\text{-}CH_2)Pt(PPh_3)_2$ [24] and $(CO)_4Fe(\mu\text{-}CH_2)Pt(PPh_3)_2$ [25]. Heterobimetallic μ-CH_2 complexes containing additional bridging ligands [26] include $Cp^*_2Th(\mu\text{-}\eta^1\text{-},\eta^5\text{-}C_5H_4)(\mu\text{-}CH_2)Ru(Me)Cp$ [27], $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Rh(COD)$ [28], $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Ir(COD)$ [29], $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Pt(CH_3)PMe_3$ [30], $[Cp_2Zr(\mu\text{-}CH_2)(\mu\text{-}Cl)Ru(PPh_3)_2(\mu\text{-}Cl)]_2$ [31], $[Cp_2Ta(\mu\text{-}CH_2)_2Co(PMe_3)Cp]BF_4$ [32] and $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$ [33]. A large number of heterobimetallic complexes having substituted μ-alkylidene ligands have been reported by Stone [34].

The closest reported analog of **4** is $C_5H_5(CO)_2Re[\mu\text{-}C(OCH_3)Ph]Pt(PMe_3)_2$ which was synthesized by Stone from the reaction of a Re carbene complex with a Pt(0) complex [35]. The synthesis of **4** by such a route has not been possible since we have been unable to prepare the requisite $C_5H_5(CO)_2Re{=}CH_2$ complex. For example, attempted hydride abstraction from $C_5H_5(CO)_2ReCH_3^-Li^+\cdot THF$ (**5**) with $(C_6H_5)_3C^+PF_6^-$ failed to produce $C_5H_5(CO)_2Re{=}CH_2$.



7 R = *E*-$CH_3C{=}CHCH_3$
10 R = CH_3



9 R = *E*-$CH_3C{=}CHCH_3$
11 R = CH_3

However, we were able to prepare alkyl and vinyl substituted μ-alkylidene complexes by a route similar to that of Stone [35]. The vinyl rhenium carbene complex $Cp(CO)_2Re{=}CH(E\text{-}CH_3C{=}CHCH_3)$ (**7**) was prepared by reaction of $Cp(CO)_2ReH^-K^+$ with $Cp_2Zr(Cl)[\eta^2\text{-}CO(E\text{-}CH_3C{=}CHCH_3)]$ (**8**) at 0 °C in THF. A similar procedure was used earlier to prepare alkyl substituted rhenium carbene complexes [9]. Reaction of **7** with $Pt(C_2H_4)(PPh_3)_2$ [8] gave an 83% yield of $C_5H_5(CO)_2Re[\mu\text{-}CH(E\text{-}CH_3C{=}CHCH_3)]Pt(PPh_3)_2$ (**9**), which was indefinitely stable at room temperature. In the ^1H NMR spectrum at -80 °C and in the ^{31}P NMR at -53 °C, only one species was observed ($<5\%$ of a second isomer would not have been detected) even though the substituent on the bridging alkylidene carbon could be either *syn* or *anti* to the Cp ring. In the ^1H NMR spectrum, the resonances of the vinyl ligand of **9** broadened somewhat ($w_{1/2}\approx 25$ Hz) at -25 °C and became sharp again at -40 °C. This is consistent with a fluxional process that interconverts one major isomer with a small amount of a minor isomer at −40 °C. We have drawn **9** as the sterically less congested *anti* isomer. The observation of two CO resonances at δ 207.8 and 205.7 in the ^{13}C NMR of **9** is consistent with a fluxional process that interconverts *syn* and *anti* isomers but which does not average the environment of the CO groups. A process proceeding via a geometry similar to that of either **D** or **E** would explain the observations; however, a process proceeding via a geometry similar to that of zwitterion **F** can be excluded since it would have resulted in exchange of the CO environments.

Reaction of $Cp(CO)_2Re{=}CHCH_3$ (**10**) [9] with $Pt(C_2H_4)(PPh_3)_2$ [8] produced the μ-ethylidene complex $C_5H_5(CO)_2Re(\mu\text{-}CHCH_3)Pt(PPh_3)_2$ (**11**) in 89% yield. **11** was somewhat less stable than the vinyl substituted alkylidene complex **9** and decomposed by β hydride elimination to $Cp(CO)_2Re(CH_2{=}CH_2)$ over two days at room temperature in CD_2Cl_2. A 75:25 mixture of two isomers of **11** was observed by ^1H NMR at −93 °C. The Cp peaks of the two isomers appear at δ 4.58 and 4.67 at −93 °C and coalesce at −60 °C. Two different CO resonances at δ 206.5 and 205.7 were seen in the ^{13}C NMR even at room temperature. The major isomer is assigned the less crowded anti configuration as drawn. Again, a fluxional process proceeding via a geometry similar to that of either **D** or **E** explains all of the NMR data.

Supplementary material

Tables of bond lengths, bond angles, anisotropic thermal parameters, hydrogen atom coordinates and isotropic displacement coefficients, and observed and calculated structure factors are available from the authors on request.

Acknowledgements

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