Double Deprotonation of a Cationic Ruthenium(II) Terminal Vinylidene Complex and Molecular Structures of the Terminal Vinylidene Complex $[(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru({=}C{=}CH_2)]PF_6$ and the Acetylide Complex $(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru(C{\equiv}CSiMe_3)$

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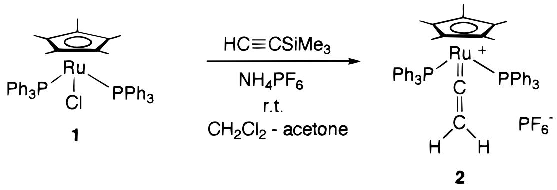
Summary: $(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru(Cl)$ ***(1)*** *reacted with* $HC{\equiv}CSiMe_3$ *in the presence of* NH_4PF_6 *to afford the cationic Ru(II) terminal vinylidene complex,* $[(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru({=}C{=}CH_2)]PF_6$ ***(2)****, in 73% yield. The terminal vinylidene complex* ***2*** *was doubly deprotonated with t-BuLi to generate the reactive lithioacetylide complex,* $(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru(C{\equiv}CLi)$ ***(4)****, which was trapped with* Me_3SiCl *and MeI to give* $(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru(C{\equiv}CSiMe_3)$ ***(5)*** *and* $(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru(C{\equiv}CMe)$ ***(6)*** *in 86 and 39% yields, respectively. The molecular structures of* ***2*** *and* ***5*** *were determined by X-ray crystallography.*

Introduction

Conjugated bases of organic terminal acetylenes have been used as powerful nucleophilic synthons for the preparation of new alkynyl compounds.[1] Wong first reported the deprotonation of a terminal alkynyl ligand of transition metal complexes and the subsequent reaction of the deprotonated terminal alkynyl ligand with transition metal electrophiles to give new types of $FpC_4(M)$ [$Fp = (\eta^5\text{-}C_5H_5)(CO)_2Fe$; M = Fe, Mo, W] complexes.[2] Wong's pioneering efforts have been applied to Gladysz to $(\eta^5\text{-}C_5Me_5)(PPh_3)(NO)Re((C_2)_nH)$ ($n = 1-4$) complexes, and the versatile reactivity of the $(\eta^5\text{-}C_5Me_5)(PPh_3)(NO)Re((C_2)_nLi)$ species as a valuable synthon was demonstrated.[3]

We report here the application of Wong's methodology to a ruthenium analogue, i.e. *in situ* generation of the lithioacetylide complex $(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru(C{\equiv}CLi)$ **(4)** by the double deprotonation of the cationic Ru(II) vinylidene complex $[(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru({=}C{=}CH_2)]PF_6$ **(2)**, which is the conjugate acid of the corresponding terminal acetylide complex, $(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru(C{\equiv}CH)$ **(3)**, and the functionalization of **4** by trapping with electrophiles. At the beginning of this study, we planned the employment of terminal acetylide complexes, RuC_2H. However, the preparation and manipulation of terminal acetylide complexes require precaution for the exhaustive exclusion of moisture and air because of the significant susceptibility of terminal ethynyl complexes toward water and air. Therefore, we have examined the deprotonation of the cationic terminal vinylidene complex **2**, which is inert relatively toward moisture and air. The molecular structures of the terminal vinylidene complex **2** and the acetylide $(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru(C{\equiv}CSiMe_3)$ **(5)** determined by X-ray diffraction are also reported.

Scheme 1



Results and Discussion

The chloro−Ru(II) complex $(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru(Cl)$ **(1)** reacted with (trimethylsilyl)acetylene in the presence of NH_4PF_6 to give the cationic Ru(II) terminal vinylidene complex $[(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru({=}C{=}CH_2)]PF_6$ **(2)**, as air- and moisture-stable mustard-yellow crystals in 73% yield (Scheme 1). The desilylation forming the terminal vinylidene complex is probably explained by the significant susceptibility of the $C(sp^2)-Si$ bond toward moisture described about a Re(I) complex by Bianchini *et al.*[4] A similar observation is reported in the preparation of Fe(II)[5] and Ru(II)[6] complexes. Recently, Puerta *et al.* isolated a Ru(II) (trimethylsilyl)vinylidene without desilylation[7] and a Re(I) analogue as a transient species was also observed.[4] The Re(I) terminal vinylidene complexes were reacted with water to afford the hydroxycarbene complexes.[7] On the contrary, complex **2** never reacted with water or MeOH as a nucleophile and gave no acetyl or carbene complex. The reason for the kinetic inertness toward water may

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[⊗] Abstract published in *Advance ACS Abstracts*, February 15, 1997.

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Table 1. Crystal and Intensity Collection Data for 2 and 5

compd	**2**·Et$_2$O	**5**·C$_6$H$_6$
chem Formula	C$_{52}$H$_{57}$F$_6$OP$_3$Ru	C$_{57}$H$_{60}$SiP$_2$Ru
fw	1006.01	936.22
cryst system	monoclinic	monoclinic
space Group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	10.813(5)	14.548(3)
b, Å	20.867(9)	21.169(2)
c, Å	22.02(1)	16.399(4)
β, deg	103.71(3)	91.64(2)
V, Å^3	4826.92	5048.28
Z	4	4
D_{calcd}, g cm^{-}3	0.20 × 0.08 × 0.08	0.26 × 0.20 × 0.18
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
rfln (hkl) limits	$0 \le h \le 14$ $0 \le k \le 29$ $-31 \le l \le 23$	$0 \le h \le 20$ $0 \le k \le 26$ $-23 \le l \le 23$
tot. no. of rflns measd	13 343	3 698
no. of unique rflns	13 064	13 376
no. of rflns used in LS	7271	9273
LS params	766	760
R	0.0487	0.0407
R_w	0.0511	0.0456
max peak in final Fourier map, e Å$-^3$	0.76	0.42
min peak in final Fourier map, e Å^{-3}	−0.56	−1.07

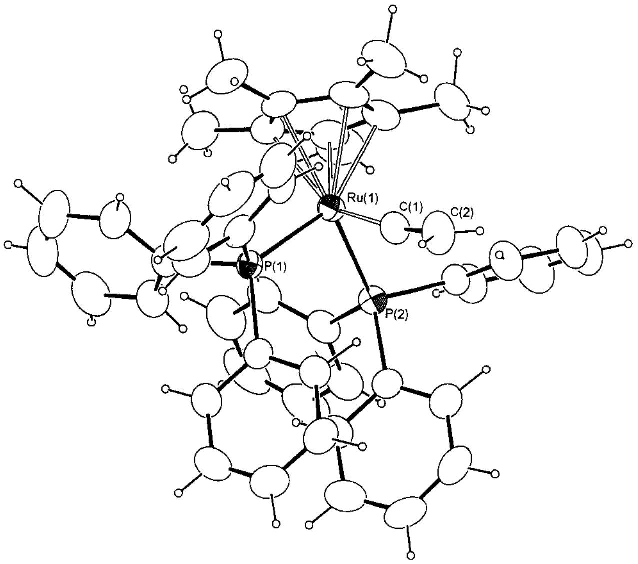
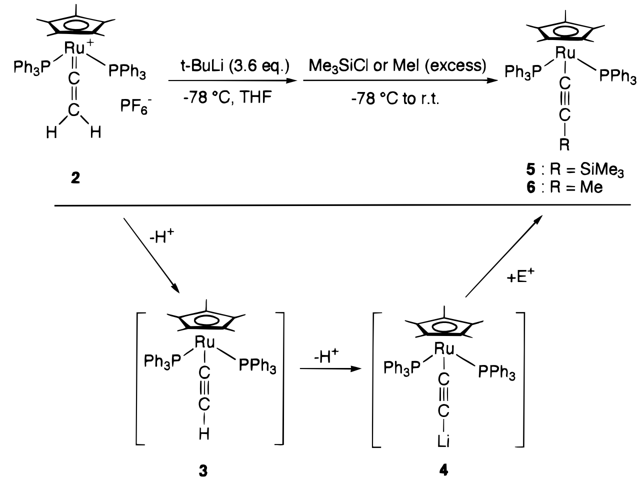


Figure 1. Molecular structure of **2**. A Et$_2$O molecule which was incorporated in the crystal and a PF$_6$ counteranion are omitted for clarity. Selected bond distances (Å): Ru(1)−P(1), 2.362(2); Ru(1)−P(2), 2.355(2); Ru(1)−C(1), 1.843(5); C(1)−C(2), 1.297(8); Ru(1)−C(Cp* ring), 2.31 (av); C−C(Cp* ring), 1.42 (av); C(Cp* ring)−C(Me), 1.50 (av). Selected bond angles (deg): P(1)−Ru(1)−P(2), 99.2(1); P(1)−Ru(1)−C(1), 89.8(2); P(2)−Ru(1)−C(1), 89.5(2); Ru(1)−C(1)−C(2), 172.2(5).

be explained by the steric hindrance and the electron-donating ability of the auxiliary ligands. The C=C stretching vibration in the IR spectrum ($\nu_{\mathrm{C=C}}$ 1616 cm^{-1}) and the Ru=*C* ^{13}C resonance at very low field in the NMR spectrum (349.94 ppm, $^2J_{\mathrm{PC}}$ = 15.2 Hz) of **2** are characteristic features of vinylidene complexes.[6,8]

A single-crystal X-ray diffraction study of **2** was performed. The crystallographic data are summarized in Table 1, and the molecular structure of **2** is shown in Figure 1. There have been only a few X-ray structural characterizations of terminal vinylidene complexes, [(η^5-C$_5$H$_5$)(PMe$_2$Ph)$_2$Ru(=C=CH$_2$)]$^+$,[9] {N(SiMe$_2$-CH$_2$PPh$_2$)}Ir(=C=CH$_2$),[10] and [(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$-(Cl)Ru(=C=CH$_2$)]$^+$.[11] The geometry around the Ru(II) atom is a distorted three-leg piano-stool configuration because of the steric repulsion of the triphenylphosphine ligands to each other. The vinylidene ligand is nearly linear [Ru(1)−C(1)−C(2) 172.2(5)°]. The Ru−C(1) distance in **2** is similar to that of related complexes, 1.843(10) Å in [(η^5-C$_5$H$_5$)(PMe$_2$Ph)$_2$Ru(=C=CH$_2$)]$^+$ [9] and 1.882(8) Å in [(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$(Cl)Ru(=C=CH$_2$)]$^+$.[11] The C(1)−C(2) length in **2** is in the typical range, from 1.313(10) Å in [(η^5-C$_5$H$_5$)(PMe$_3$)$_2$Ru(=C=CHMe)]$^+$ [12] to 1.287(13) Å in [(η^5-C$_5$H$_5$)(PMe$_2$Ph)$_2$Ru(=C=CH$_2$)]$^+$.[9]

Scheme 2



Treatment of the terminal vinylidene complex **2** with *t*-BuLi (3.6 equiv) at −78 °C could generate the lithioacetylide complex **(4)** as a very reactive intermediate. The addition of excess (*ca.* 10 equiv) Me$_3$SiCl to the solution of **4** at −78 °C and then warming to room temperature gave the Ru(II) (trimethylsilyl)acetylide complex (η^5-C$_5$Me$_5$)(PPh$_3$)$_2$Ru(C≡CSiMe$_3$) **(5)**, in 86% yield (Scheme 2). Complex **5** showed the C≡C stretching vibration at 1992 cm^{-1} in the IR spectrum and the methyl protons of the trimethylsilyl group at δ 0.18 ppm in the ^{1}H NMR spectrum. The intermediate **4** was also trapped with MeI to give the Ru(II) methylacetylide complex, (η^5-C$_5$Me$_5$)(PPh$_3$)$_2$Ru(C≡CMe) **(6)**. The C≡C stretching vibration in **6** was observed at 2097 cm^{-1} in the IR spectrum, and the methyl proton signal, at δ 2.67 ppm in the ^{1}H NMR spectrum.

The crystal structure of **5** was determined by single-crystal X-ray diffraction. The crystallographic data are summarized in Table 1, and the molecular structure is shown in Figure 2. The distortion from three-leg piano-stool geometry around the Ru(II) atom in **5** is larger than that in **2**. The (trimethylsilyl)acetylide ligand is nearly linear [173.8(4)°]. The distances Ru−C(1), C(1)−C(2), and C(2)−Si in **5** are similar to those of the related *ttt*-(CO)$_2$(PEt$_3$)$_2$Ru(C≡CSiMe$_3$)$_2$[13] [2.062(2), 1.221(2), and 1.812(2) Å, respectively].

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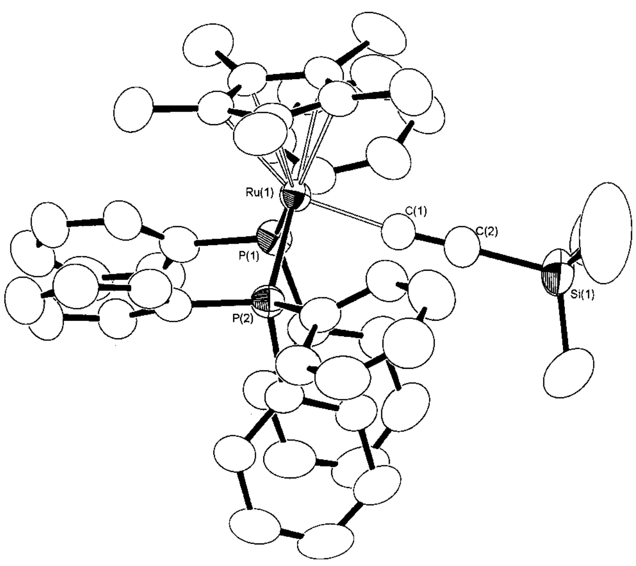

Figure 2. Molecular structure of **5**. A C_6H_6 molecule which was incorporated in the crystal and hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ru(1)–P(1), 2.312(1); Ru(1)–P(2), 2.315(1); Ru(1)–C(1), 2.004(4); C(1)–C(2), 1.213(5); Si(1)–C(2), 1.801(4); Ru(1)–C(Cp* ring), 2.28 (av); C–C(Cp* ring), 1.42 (av); C(Cp* ring)–C(Me), 1.50 (av). Selected bond angles (deg): P(1)–Ru(1)–P(2), 99.1(1); P(1)–Ru(1)–C(1), 85.9(1); P(2)–Ru(1)–C(1), 90.5(1); Ru(1)–C(1)–C(2), 173.8(4).

The isolation of **5** and **6** confirms that the terminal vinylidene ligand in **2** was deprotonated twice to form a (μ_2-C≡C)(Ru)/(Li) complex **4** *via* a terminal acetylide ligand. Wong succeeded in isolating new types of Fp-C≡CC≡C(M) complexes (M = Fe, Mo, W) *via* FpC≡C-C≡CLi species which could not detected,[2] while Gladysz described the syntheses of a new types of (Re)C≡C(M) complexes and (Re)C≡CC≡C(M) complexes (M = Pd, Rh) *via* (Re)C≡CLi and (Re)C≡CC≡CLi species which were detected by IR and ^{31}P NMR spectra.[3] We also attempted to react the nucleophilic (Ru)C≡CLi species **(4)** with a transition-metal electrophile, (η^5-C_5Me_5)(CO)$_2$-RuI or *cis*-Pt(PBu$_3$)$_2$Cl$_2$, but the attempts were not successful because of complex side reactions.

The most striking features in **5** are the remarkable inertness of the carbon–silicon bond. Thus, the treatment of **5** with iodoacetophenone in refluxing THF in the presence of Bu$_4$NF (1 equiv) and a catalytic amount (10 mol %) of Pd(PPh$_3$)$_4$ (under the Hiyama coupling conditions)[14] resulted in no conversion. On the other hand, the cyclopentadienyl analogue, (η^5-$C_5H_4SiMe_3$)(PPh$_3$)$_2$Ru(C≡CSiMe$_3$),[15] gave the coupling product, (η^5-C_5H_5)(PPh$_3$)$_2$Ru(C≡CC$_6$H$_4$C(O)Me), in 25% yield (conversion: 50%) under the same conditions.

Experimental Section

All reactions were carried out under an atmosphere of N$_2$ and/or Ar, and workups were performed without precaution to exclude air. NMR spectra were recorded on a Bruker ARX400 spectrometer. IR spectra were recorded on a Perkin-Elmer System 2000 spectrometer. Solvents were purified by distillation from the drying agent prior to use as follows: CH$_2$Cl$_2$ (CaCl$_2$); acetone (anhydrous CaSO$_4$ (Drielite)); CH$_3$CN (CaH$_2$); THF (Na–benzophenone); diethyl ether (LiAlH$_4$). (η^5-C_5Me_5)(PPh$_3$)$_2$RuCl **(1)** was prepared according to the literature.[16] Other reagents were used as received from commercial suppliers.

[(η^5-C$_5$Me$_5$)(PPh$_3$)$_2$Ru(=C=CH$_2$)]PF$_6$ (2). To a solution of (η^5-C_5Me_5)(PPh$_3$)$_2$RuCl **(1)** (2.39 g, 3.0 mmol) and Me$_3$SiC≡CH (1.5 mL, 10.6 mmol) in CH$_2$Cl$_2$ (150 mL) and acetone (90 mL) was added NH$_4$PF$_6$ (1.0 g, 6.1 mmol) at room temperature. The solution was stirred for 3 h. After the solvent had been removed by rotary evaporator, the residue was suspended in benzene (*ca.* 30 mL), collected by filtration, and washed with benzene (10 mL × 3), water (10 mL × 5), and diethyl ether (10 mL × 2). A trace of water contaminating the resulting mustard-yellow powder was removed azeotropically with toluene *in vacuo* at room temperature, giving the title compound **2** as a mustard-yellow solid. An analytically pure sample was obtained by recrystallization from CH$_3$CN–diethyl ether. Mustard-yellow crystals formed. Yield: 1.99 g (73%). Mp: 190 °C (dec). IR (KBr): 1616 cm^{-1} ($\nu_{C=C}$), 841 (ν_{PF_6}). ^{1}H NMR (CD$_3$CN, 400 MHz): δ 1.24 (t, $^4J_{PH}$ = 1.3 Hz, 15H, C$_5$Me$_5$), 4.54 (t, $^4J_{PH}$ = 1.7 Hz, 2H, =CH$_2$), 7.18–7.37 (m, 30H, Ph). ^{13}C NMR (CD$_3$CN, 100 MHz): δ 9.28 (C$_5$*Me*$_5$), 96.98 (=CH$_2$), 104.62 (*C*$_5$Me$_5$), 128.54 (t, $^2J_{PC}$ = 4.9 Hz, m-Ph), 130.94 (p-Ph), 139.05 (m, ipso-Ph), 134.00 (t, $^3J_{PC}$ = 4.9 Hz, o-Ph), 349.94 (t, $^2J_{PC}$ = 15.2 Hz, Ru=C=). ^{31}P NMR (CD$_3$CN, 162 MHz, referred to 85% H$_3$PO$_4$): δ –143.90 (sep, $^1J_{PF}$ = 706.2 Hz, PF$_6$), 49.37 (PPh$_3$). Anal. Calcd for C$_{48}$H$_{47}$F$_6$P$_3$Ru·C$_4$H$_{10}$O: C, 62.08; H, 5.71. Found: C, 62.00; H, 5.67.

(η^5-C$_5$Me$_5$)(PPh$_3$)$_2$Ru(C≡CSiMe$_3$) (5). To a suspension of **2** (453 mg, 0.5 mmol) in THF (25 mL) was added *t*-BuLi (1.0 M in pentane, 1.8 mL, 1.8 mmol) at –78 °C. The solution was stirred for 3 h. To the resulting yellow orange clear solution was added ClSiMe$_3$ (0.8 mL, 6.3 mmol) at –78 °C. The mixture was stirred for 1 h and then warmed to room temperature followed by stirring for 0.5 h. After the solvent had been removed *in vacuo*, the residue was chromatographed on basic alumina (the Brockman scale *ca.* III) using CH$_2$Cl$_2$–hexane (1:1, v/v) as an eluent. The yellow first fraction was collected and evaporated to give **3** as a yellow solid. An analytically pure sample was obtained by recrystallization from benzene–hexane. Yellow crystals formed. Yield: 354 mg (86%). Mp: 175 °C (dec). IR (KBr): 1992 cm^{-1} ($\nu_{C≡C}$). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 0.18 (s, 9H, SiMe$_3$), 1.15 (s, 15H, C$_5$Me$_5$), 7.02–7.60 (m, 30H, Ph). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 2.24 (SiMe$_3$), 9.66 (C$_5$*Me*$_5$), 93.72 (*C*$_5$Me$_5$), 116.29 (≡CSi), 126.96 (t, $^2J_{PC}$ = 4.4 Hz, o-Ph), 128.44 (m-Ph), 135.15 (bs, p-Ph), 137.93 (m, ipso-Ph), 153.94 (t, $^2J_{PC}$ = 22.7 Hz, RuC≡). ^{31}P NMR (C$_6$D$_6$, 162 MHz, referred to 85% H$_3$PO$_4$): δ 51.75. Anal. Calcd for C$_{51}$H$_{54}$SiP$_2$Ru·C$_6$H$_6$: C, 73.13; H, 6.46. Found: C, 72.83; H, 6.60.

(η^5-C$_5$Me$_5$)(PPh$_3$)$_2$Ru(C≡CMe) (6). Complex **6** was prepared from **2** (181.3 mg, 0.2 mmol), *t*-BuLi (1.5 M in pentane, 0.5 mL, 0.75 mmol), and MeI (0.5 mL, 8.0 mmol) according to the procedure similar to that for **5**. An analytically pure sample was obtained by recrystallization from benzene–methanol. A yellow powder formed. Yield: 60 mg (39%). Mp: 140 °C (dec). IR (KBr): 2097 cm^{-1} ($\nu_{C≡C}$). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 1.43 (s, 15H, C$_5$Me$_5$), 2.67 (s, 3H, ≡CMe), 7.03 (bs, 18H, Ph), 7.93 (bs, 12H, Ph). ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ 8.53 (≡C*Me*), 9.91 (C$_5$*Me*$_5$), 93.02 (*C*$_5$Me$_5$), 101.05 (t, $^2J_{PC}$ = 25.1 Hz, RuC≡), 102.92 (≡*C*Me), 126.96 (t, $^2J_{PC}$ = 4.3 Hz, o-Ph), 128.11 (bs, m-Ph), 135.18 (p-Ph), 138.56 (t, $^2J_{PC}$ = 18.5 Hz, ipso-Ph). ^{31}P NMR (C$_6$D$_6$, 162 MHz, referred to 85% H$_3$PO$_4$): δ 52.48. Anal. Calcd for C$_{49}$H$_{48}$P$_2$Ru: C, 73.57; H, 6.05. Found: C, 73.33; H, 6.05.

Structure Determination for 2 and 5. Oscillation and nonscreen Weisenberg photographs were recorded on the

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(15) The cyclopentadienyl analog of **2**, [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$Ru=C=CH$_2$]PF$_6$ could be doubly (or triply) deprotonated with *t*-BuLi to generate the corresponding lithioacetylide complex, which was trapped with Me$_3$SiCl or MeI. However, the product obtained was an inseparable mixture of (η^5-C$_5$H$_5$)(PPh$_3$)$_2$RuC≡CR (in a low ~11% yield by ^{1}H NMR) and (η^5-C$_5$H$_4$R)(PPh$_3$)$_2$RuC≡CR (in 60–67% yield by ^{1}H NMR) (R = SiMe$_3$ or Me).

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imaging plates of a Mac Science DIP3000 diffractometer with graphite-monochromated Mo Kα radiation and an 18-kW rotating anode generator. Data reduction and determination of cell parameters were made by the MAC DENZO program system.[17] The structures were solved by direct methods (SIR)[18] in CRYSTAN-GM (software package for structure determination) and refined by full-matrix least-squares procedures. Anisotropic refinements for non-hydrogen atoms were carried out. All the hydrogen atoms, partially located from difference Fourier maps, were isotropically refined.

Supporting Information Available: Tables of X-ray parameters, positional and thermal parameters, and bond distances and angles and ORTEP diagrams (59 pages). Ordering information is given on any current masthead page.

OM9608824

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Additions and Corrections

1996, Volume 15

Jinfeng Ni,* Yuhua Qiu, Tamara M. Cox, Cynthia A. Jones, Chala Berry, Laura Melon, and Simon Bott*: Carbon Dioxide Chemistry: Characterization of the Carbon Dioxide Reaction Product of a Dinuclear Titanium Complex

Page 4669. Contrary to what was stated, the molecular structure of the complex $[CpTi(\mu\text{-}H)]_2(C_{10}H_8)$ has been solved and the Ti−Ti separation is 2.989 Å (Troyanov, S. I.; Antropiusova, H.; Mach, K. *J. Organomet. Chem.* **1992**, *427*, 49).