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Reaction of $C_5Me_5(CO)_2Re(HC\equiv CCH_3)$ with $Ph_3C^+PF_6^-$ produces the η^3-allyl complex $C_5Me_5(CO)_2Re[\eta^3\text{-}Ph_2CC(Ph)CHCH_3]^+PF_6^-$

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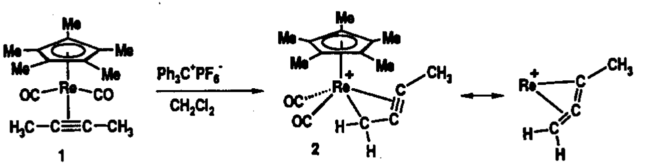
Abstract

The reaction of $C_5Me_5(CO)_2Re(HC\equiv CCH_3)$ (3) with $Ph_3C^+PF_6^-$ led to an unusual rearrangement and the formation of the π-allyl complex $C_5Me_5(CO)_2Re[\eta^3\text{-}Ph_2CC(Ph)CHCH_3]^+PF_6^-$ (4). This transformation involves addition of trityl to the η^3-allyl system, a migration resulting in attachment of methyl and hydrogen to the same carbon, and a phenyl migration.

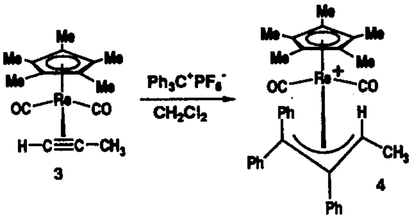
1. Introduction

We recently developed a new synthesis of η^3-propargyl complexes by hydride abstraction from rhenium alkyne complexes [1]. Reaction of the 2-butyne complex $C_5Me_5(CO)_2Re(CH_3C\equiv CCH_3)$ (1) with $(C_6H_5)_3C^+PF_6^-$ led to the clean formation of the η^3-propargyl complex $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C\equiv CCH_3)^+PF_6^-$ (2) in 87% yield. Here we report that attempted extension of this synthetic method to terminal alkyne complex failed to produce an η^3-propargyl complex. Instead, reaction of $C_5Me_5(CO)_2Re(HC\equiv CCH_3)$ (3) with $Ph_3C^+PF_6^-$ led to the unexpected formation of an η^3-allyl complex incorporating the elements of the Ph_3C^+ cation.



The reaction of $C_5Me_5(CO)_2Re(THF)$ [2] with a five-fold excess of propyne in THF at room temperature for 12 h gave a 75% yield of $C_5Me_5(CO)_2Re(HC\equiv CCH_3)$ (3) which was isolated as a yellow solid.

Attempted hydride abstraction from rhenium propyne complex 3 failed to produce the expected η^3-propargyl complex $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C\equiv CH)^+PF_6^-$. When the reaction of rhenium propyne complex $C_5Me_5(CO)_2Re(HC\equiv CCH_3)$ (3) with $Ph_3C^+PF_6^-$ in CD_2Cl_2 was followed by ^1H NMR, clean transformation to a single new product was observed. The observation of a quartet ($J = 5.7$ Hz) at δ 4.20 suggested that the acetylenic proton had migrated to the carbon bearing the methyl group.



In a preparative reaction, a mixture of 3 and $Ph_3C^+PF_6^-$ in CH_2Cl_2 was stirred for 2 h at room temperature. The color of the solution turned from yellow to dark brown. The solution was concentrated and Et_2O was added to give a pale brown precipitate of $C_5Me_5(CO)_2Re[\eta^3\text{-}Ph_2CC(Ph)CHCH_3]^+PF_6^-$ (4). The formation of this η^3-allyl complex requires addition of the CPh_3 group to the complexed propyne, a phenyl migration, and a migration resulting in attachment of the methyl and hydrogen to the same carbon.

Since the structure of this rearrangement product could not be ascertained by spectroscopy, we undertook a single crystal X-ray diffraction study. Bright yellow single crystals of 4 were obtained by dissolution in acetone and layering with Et_2O at room temperature. In the solid-state structure of $C_5Me_5(CO)_2Re[\eta^3\text{-}Ph_2CC(Ph)CHCH_3]^+PF_6^-$ (4), the allyl unit is *endo* relative to the Cp* ligand and the methyl group is *syn* to the Ph group on the central carbon of the allyl ligand (Fig. 1, Tables 1 and 2). The Re carbon distance to the diphenyl-substituted allyl carbon 2.413(12) Å is

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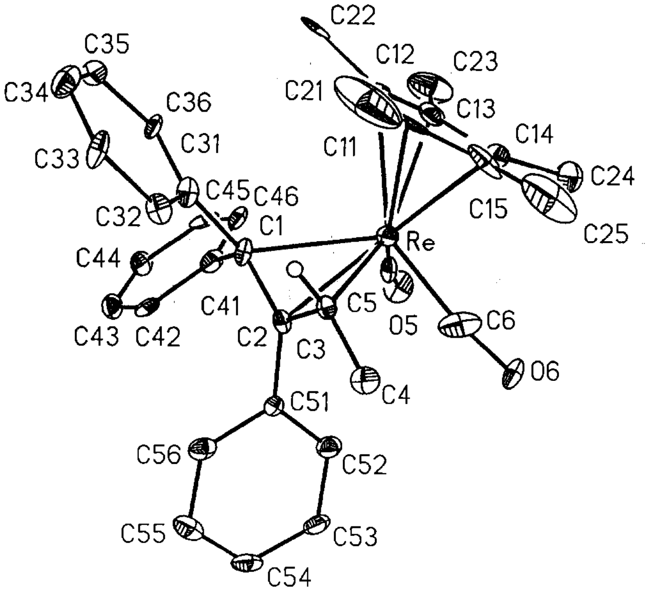


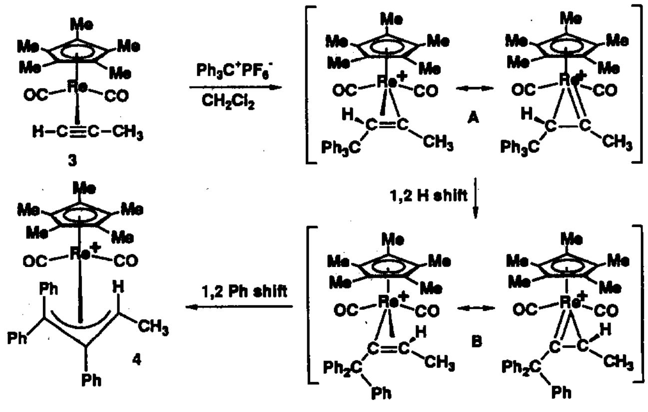
Fig. 1. Structure of $C_5Me_5(CO)_2Re[\eta^3\text{-}Ph_2CC(Ph)CHCH_3]^+ PF_6^-$ (4).

somewhat longer than the distances to the two other allyl carbons 2.275(11) Å and 2.254(12) Å.

A plausible mechanism for the formation of η^3-allyl complex **4** is shown in Scheme 1. The first step involves electrophilic addition of Ph_3C^+ to the less crowded terminus of the complexed propyne of **3** to give the η^2-vinyl intermediate **A**. (The failure of Ph_3C^+ to attack complexed 2-butyne of **1** may be due to steric effects.) The regiochemistry of this addition places the electron-donating methyl substituent on the more electron-deficient carbon of the η^2-vinyl ligand. Many well characterized η^2-vinyl complexes have been reported [3]. Green [4] has reported that protonation of the bis-alkyne complex $C_5H_5(Br)Mo(CH_3C{\equiv}CCH_3)_2$ produces the η^2-vinyl complex $C_5H_5(Br)Mo[\eta^2\text{-}C(CH_3){=}$

TABLE 2. Crystallographic data for $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_3CHC(Ph)CPh_2]^+ PF_6^-$ (4)

Formula	$C_{34}H_{34}F_6O_2PRe$
Formula weight	805.8
a, Å	9.411(2)
b, Å	14.964(3)
c, Å	21.622(4)
V, Å^3	3044(1)
Z	4
Space group	$P2_12_12_1$
T, °C	22
λ, Å	0.71073 (Mo Kα)
ρ_{calcd}, g cm^{-3}	1.758
μ, mm^{-1}	4.162
scan mode	ω
2θ limits (deg)	3.5–50.0
No. independent data [$\lvert F\rvert > 3\sigma(F)$]	3505
No. parameters refined	398
$R_1(F)$	4.98
$R_2(F)$	6.45



Scheme 1.

TABLE 1. Selected bond lengths (Å) and angles (°) for 4

Re–Cp	1.968	C(1)–C(2)	1.453(16)	C(5)–O(5)	1.150(14)		
Re–C(1)	2.413(12)	C(2)–C(3)	1.441(15)	Re–C(6)	1.901(15)		
Re–C(2)	2.275(11)	C(1)–C(31)	1.534(17)	C(6)–O(6)	1.179(18)		
Re–C(3)	2.254(12)	C(1)–C(41)	1.526(17)				
		C(2)–C(51)	1.482(16)				
		C(3)–C(4)	1.476(17)				
		Re–C(5)	1.940(11)				
Cp–Re–C(1)	122.6	C(5)–Re–C(3)	125.3(4)	C(1)–C(2)–C(3)	117.4(10)	Re–C(2)–C(51)	126.2(8)
Cp–Re–C(2)	145.0	C(6)–Re–C(1)	123.4(5)	C(2)–C(1)–C(31)	120.0(10)	Re–C(2)–C(1)	77.2(7)
Cp–Re–C(3)	117.8	C(6)–Re–C(2)	89.4(5)	C(2)–C(1)–C(41)	120.1(10)	Re–C(2)–C(3)	70.7(6)
Cp–Re–C(5)	116.9	C(6)–Re–C(3)	78.9(5)	Re–C(1)–C(31)	117.1(8)	Re–C(3)–C(2)	72.2(7)
Cp–Re–C(6)	111.9	Re–C(5)–O(5)	171.7(9)	Re–C(1)–C(41)	118.5(8)	Re–C(3)–C(4)	126.9(8)
C(5)–Re–C(6)	82.2(6)	Re–C(6)–O(6)	171.7(12)	Re–C(1)–C(2)	66.8(6)	C(2)–C(3)–C(4)	122.9(10)
C(5)–Re–C(1)	86.3(4)	C(1)–Re–C(2)	36.0(4)	C(31)–C(1)–C(41)	109.2(9)	C(2)–Re–C(3)	37.1(4)
C(5)–Re–C(2)	92.5(4)	C(1)–Re–C(3)	63.9(4)	C(1)–C(2)–C(51)	123.7(10)		

$CHCH_3)(CH_3C{\equiv}CCH_3) + BF_4^-$. The second step in the mechanism is a 1,2 hydrogen shift to produce the isomeric η^2-vinyl intermediate **B**. While there are no reported 1,2 hydrogen shifts for η^2-vinyl complexes, 1,2 hydride shifts to the electron-deficient centers are well known. For example, the rearrangement of electrophilic carbene complexes to alkene complexes involves a 1,2 hydrogen shift to the electron-deficient carbene carbon [5]. (For an example of carbon migration to a carbene carbon of a metal carbene complex see ref. 5(d).) The third step in the mechanism is a 1,2 phenyl shift from the trityl carbon to the electron-deficient carbon of the η^2-vinyl intermediate **B** to produce the η^3-vinyl product **4**. Again, carbon migrations in η^2-vinyl complexes have not been reported, but phenyl migrations to electron-deficient carbon centers are very common in organic chemistry.

The η^2-vinyl intermediate **B** might also be accessed by Ph_3C^+ attack at the more substituted alkyne carbon of **3** followed by methyl migaration. However, the regiochemistry of the initial addition seems unlikely for the reasons outlined above. Another possible mechanism would involve initial rearrangement of the alkyne complex to a vinylidene complex $Re{=}C{=}CHCH_3$ followed by Ph_3C^+ attack at the α-vinylidene carbon to generate η^2-vinyl intermediate **B**. This mechanism is highly unlikely since electrophiles are known to attack the β-vinylidene carbon to produce carbyne complexes [6].

2. Experimental details

2.1. General

^1H NMR spectra were obtained on a Bruker WP200 spectrometer. $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AM500 spectrometer (126 MHz). Infrared spectra were measured on a Mattson Polaris (FT) spectrometer. Mass spectra were determined on a KRATOS MS-80.

Diethyl ether, $[(CH_3)_2CH]_2O$, hexane, and THF were distilled from purple solutions of sodium and benzophenone immediately prior to use. Dichloromethane and CD_2Cl_2 were dried over P_2O_5 or CaH_2 and distilled prior to use. Air-sensitive materials were manipulated in an inert atmosphere glovebox or by standard Schlenk techniques.

2.2. $C_5Me_5(CO)_2Re(HC{\equiv}CCH_3)$ (3)

Excess propyne (1.6 mmol) was vacuum transferred into a THF solution of $C_5Me_5(CO)_2Re(THF)$ [2] (145 mg, 0.322 mmol), and the reaction mixture was stirred at room temperature for 12 h in a closed system. Solvent and excess propyne were evaporated, and the residue was chromatographed (silica gel, 3 : 1 hexane : Et_2O) to give $C_5Me_5(CO)_2Re(HC{\equiv}CCH_3)$ (**3**) (101 mg, 75%) as a yellow solid. ^1H NMR (CD_2Cl_2, 200 MHz): δ 4.8 (q, $J = 1.7$ Hz, $HC{\equiv}C$), 2.54 (d, $J = 1.7$ Hz, ${\equiv}CCH_3$), 1.96 (s, C_5Me_5). ^{13}C NMR (CD_2Cl_2, 126 MHz): δ 209.4 (s, CO), 198.7 (s, CO), 99.8 (s, C_5Me$_5$), 82.6 (s, $HC{\equiv}C$), 59.9 (d, $J = 157.3$ Hz, $HC{\equiv}C$), 10.9 (q, $J = 128.6$, ${\equiv}CCH_3$), 10.5 (q, $J = 127.7$ Hz, C$_5Me_5$). IR (Et_2O): 1954 (s), 1873 (s) cm^{-1}. HRMS: Found: 418.0940. $C_{15}H_{19}O_2Re$ calcd.: 418.0944.

2.3. $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_3CHC(Ph)CPh_2]^+PF_6^-$ (4)

A mixture of $C_5Me_5(CO)_2Re(HC{\equiv}CCH_3)$ (**3**) (30 mg, 0.0718 mmol) and $Ph_3C^+PF_6^-$ (28 mg, 0.0718 mmol) was stirred in 10 ml of CH_2Cl_2 at room temperature for 2 h. The color of the solution turned from yellow to dark brown. The solution was concentrated and Et_2O was added to give a pale brown precipitate. The precipitate was filtered and washed with Et_2O to give $C_5Me_5(CO)_2Re[\eta^3\text{-}Ph_2CC(Ph)CHCH_3]^+PF_6^-$ (**4**) (35 mg, 61%) as a pale brown solid. ^1H NMR (acetone-d_6, 200 MHz): δ 7.7–6.8 (m, Ph), 4.20 (q, $J = 5.7$ Hz, CH), 2.15 (d, $J = 5.7$ Hz, CHCH_3), 2.05 (s, C_5Me_5). ^{13}C NMR (acetone-d_6, 126 MHz): δ 197.5 (s, CO), 194.5 (s, CO), 145.1 (s, *ipso*), 135–127 (phenyl carbons), 108.0 (s, CH_3CHCPh), 106.8 (s, C_5Me$_5$), 86.1 (s, CPh$_2$), 59.8 (d, $J = 159.7$ Hz, CHCH$_3$), 18.0 (q, $J = 129.1$ Hz, CHCH$_3$), 9.5 (q, $J = 130.1$ Hz, C$_5Me_5$). IR (CH_2Cl_2): 2036 (s), 1984 (m) cm^{-1}. Anal. Found: C, 49.60; H, 4.35. $C_{34}H_{34}O_2RePF_6$ calcd: C, 50.68; H, 4.25%.

2.4. X-ray crystal structure determination of $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_3CHC(Ph)CPh_2]^+PF_6^-$ (4)

Crystals of $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_3CHC(Ph)CPh_2]^+PF_6^-$ (**4**) suitable for an X-ray diffraction study were obtained by layering of $[(CH_3)_2CH]_2O$ over a saturated acetone solution of **4**. A bright yellow plate was mounted on the tip of a thin glass fiber and X-ray data were collected. No decomposition of the crystal was observed during data collection. Four molecules of **4** crystallized in an orthorhombic unit cell with space group symmetry $P2_12_12_1$; $a = 9.431(3)$ Å, $b = 14.966(7)$ Å, $c = 21.62(1)$ Å, $V = 3044(2)$ Å^3. The rhenium position of the crystallographically independent molecule of **4** was determined by direct methods and the other non-hydrogen atom positions were readily determined from successive Fourier difference maps. All of these non-hydrogen atoms were anisotropically refined; all hydrogen atoms were fixed at idealized positions and with isotropic thermal parameters fixed at $U = 0.08$ Å^2. An empirical absorption correction was applied to the data and the final difference map disclosed no unusual features. Tables giving full crystallographic details (for **4**) are available on request from the author.

Acknowledgement

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References

1 C. P. Casey and C. S. Yi, *J. Am. Chem. Soc., 114* (1992) 6597.

2 (a) D. Sellmann and E. Kleinschmidt, *Z. Naturforsch, B: Anorg. Chem, Org. Chem., 32B* (1977) 795; (b) H. G. Alt and H. E. Engelhardt, *J. Organomet. Chem., 342* (1988) 235; (c) A. N. Nesmeyanov, N. E. Kolobova, Y. V. Makarov, B. V. Lokshin and E. B. Rusach, *Bull. Aca. Sci. USSR, 25* (1976) 612; (d) D. Sutton, F. W. B. Einstein and K. G. Tyers, *Organometallics, 4* (1985) 489; (e) C. P. Casey, H. Sakaba, P. N. Hazin and D. P. Powell, *J. Am. Chem. Soc., 113* (1991) 8165.

3 For recent examples of η^2-vinyl complexes see: (a) A. S. Gamble, P. S. White and J. L. Templeton, *Organometallics, 10* (1991) 693; (b) A. S. Gamble, K. R. Birdwhistell and J. L. Templeton, *J. Am. Chem. Soc., 112* (1990) 1818: (c) W. Clegg, M. Green, C. A. Hall, D. C. R. Hockless, N. C. Norman and C. M. Woolhouse, *J. Chem. Soc., Chem. Commun.*, (1990) 1330; (d) F. J. Feher, M. Green and R. A. Rodrigues, *J. Chem. Soc., Chem. Commun.*, (1987) 1206; (e) J. L. Davidson, *J. Chem. Soc., Dalton. Trans.*, (1987) 2715; (f) S. G. Feng, P. S. White and J. L. Templeton, *J. Am. Chem. Soc., 112* (1990) 8192.

4 G. C. Conole, M. Green, M. McPartlin, C. Reeve and C. M. Woolhouse, *J. Chem. Soc., Chem. Commun.*, (1988) 1310.

5 (a) C. P. Casey, W. H. Miles and H. Tukada, *J. Am. Chem. Soc., 107* (1985) 2924; (b) W. G. Hatton and J. A. Gladysz, *J. Am. Chem. Soc., 105* (1983) 6157; (c) M. Brookhart, J. R. Tucker and G. R. Husk, *J. Am. Chem. Soc., 105* (1983) 258; (d) For an example of carbon migration to a carbene carbon of a metal carbene complex see: R. S. Bly, R. K. Bly, M. M. Hossain, L. Leboida and M. Raja, *J. Am. Chem. Soc., 110* (1988) 7723.

6 M. I. Bruce, *Chem. Rev., 91* (1991) 197.