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Synthesis of the rhenium allyl chloride complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl$ and reactions to give hydrido, phenyl and alkyl derivatives

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Abstract

The rhenium η^3-allyl chloro complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl$ (**5**) has been synthesized from the photolysis of $Cp^*Re(CO)_3$ and allyl chloride, or from the reaction of the cationic complex $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2]^+$ with PhIO and Me_4NCl. Complex **5** is readily converted to the η^3-allyl hydrido complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)H$ by reaction with $LiBEt_3H$, and to the phenyl or alkyl derivatives $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Ph$ or $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)R$ by treatment with LiPh or Grignard reagents.

Keywords: Rhenium; Allyl; Synthesis; Cyclopentadienyl; Hydride; Chloride

1. Introduction

The rhenium η^3-allyl hydrido complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)H$ (**7**) was first reported by our group in 1989 [1,2]. It was discovered to result in a low yield from the photolysis of $Cp^*Re(CO)_3$ and propene, and was considered to be formed from photochemical C–H activation of the propene complex $Cp^*Re(C_3H_6)(CO)_2$. The allyl hydrido complex **7** is of considerable interest in view of its stability, and because both *exo* and *endo* isomers could be separated, isolated, and crystallized, and their X-ray structures were determined [1]. In order to investigate the chemistry of **7**, a more efficient method of synthesis of this complex needs to be developed. One attractive possibility would be to prepare **7** from the chloride $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl$ or the corresponding bromide. The latter was reported to result from the reaction of **7** with $CHBr_3$ and was shown to reform the hydrido complex **7** when reacted with $LiBEt_3H$ [2], but as far as we can determine $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl$ has not been previously synthesized. In this paper, we report both photochemical and thermal syntheses of $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl$ (**5**), and show that it can be used as a precursor for the synthesis of **7**. The syntheses and characterization of the phenyl and alkyl derivatives $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)R$ (**9–12**), and the hydride derivative $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)H$ (**7**), through the reactions of **5** with C_6H_5Li, RMgX (X = Cl, $R = C_4H_9$; X = Br, $R = CH_3$, C_2H_5, C_3H_5), or $LiBEt_3H$ are detailed.

2. Experimental section

2.1. General procedures

All reactions were carried out under dry nitrogen in Schlenk apparatus. Solvents were purified by standard methods and were freshly distilled under dry nitrogen. All reagents were obtained from Aldrich except where mentioned. The reagents RMgX (X = Cl, Br; $R = CH_3$, C_2H_5, C_3H_5 and $n\text{-}C_4H_9$) were synthesized by using standard methods [3]. UV irradiation was carried out by using a water-jacketed 200 W Hanovia Model 654A-0360 high pressure mercury vapour lamp. FTIR spectra were recorded on a Bomem Michelson-120 instrument. The ^1H and ^{13}C NMR spectra were recorded by Mrs. M.M. Tracey of the SFU NMR service by using a Bruker WM-400 instrument operating at 400.13 and 100.6 MHz respectively. Mass spectra were obtained by Mr. G. Owen on a Hewlett–Packard Model-5985 GC-MS instrument. Masses are quoted for ^{187}Re and ^{35}Cl

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isotopes where present. Correct isotopic distribution patterns were observed for all parent peaks. Microanalyses were performed by Mr. M.K. Yang of the SFU Microanalytical Laboratory. $Cp^*Re(CO)_3$ and $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ (**1**) were synthesized as described previously [4].

2.2. Reaction of $Cp^*Re(CO)_3$ with allyl bromide

$Cp^*Re(CO)_3$ (16.3 mg, 0.04 mmol) was dissolved in 10 ml of hexane at 0 °C and 0.01 ml (14.0 mg, 0.12 mmol) of allyl bromide was added. This solution was irradiated for 10 min and a precipitate formed, which was shown by spectroscopy (below) to be a mixture of the *cis* and *trans* isomers of $Cp^*Re(CO)_2Br_2$ (**2**). The IR of the solution showed ν(CO) absorptions for only unreacted $Cp^*Re(CO)_3$. Irradiating for a further 1 h formed more precipitate. $Cp^*Re(CO)_3$ was recovered from the solution and the precipitate was recrystallized from CH_2Cl_2/ether to give pure **2** as a brown solid (mixture of *cis* and *trans* isomers) [5]. EIMS (*m/z*): 538 (M^+), 510 ($M^+ - CO$), 482 ($M^+ - 2CO$), 400 ($M^+ - 2CO - HBr$, base). IR (CH_2Cl_2, cm^{-1}): *cis* isomer, $\nu_{CO} = 2035$, 1960; *trans* isomer, $\nu_{CO} = 2049$, 1981. ^1H NMR (δ, $CDCl_3$): *cis* isomer, 2.07 (15H, s, Cp^*); *trans* isomer, 2.01 (15H, s, Cp^*).

2.3. Preparation of $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl$ (5)

2.3.1. Method I

$Cp^*Re(CO)_3$ (44.8 mg, 0.11 mmol) was dissolved in benzene (20 ml) in a quartz tube, and 3 ml of allyl chloride was transferred into this solution by syringe. The solution was cooled to 10–15 °C by cold water bath, then irradiated under UV light at this temperature for 2 h. A dark red solution was produced. The IR spectrum showed this to be a mixture of **3**, **5** and unreacted $Cp^*Re(CO)_3$. Solvent was pumped off under vacuum. The residue was dissolved in CH_2Cl_2, and then transferred to a neutral alumina column. Eluting with hexane gave recovered $Cp^*Re(CO)_3$; eluting with hexane/ether/CH_2Cl_2 in a 1:1:1 ratio gave $Cp^*_2Re_2(CO)_5$ (**3**). Finally, eluting with ether gave **5**. The crude product **5** was purified again by chromatography with CH_2Cl_2/ether, then dissolved in hexane and cooled to −78 °C overnight. Pure **5** was obtained as yellow crystals (13.0 mg, 0.03 mmol, 27%), m.p. 144–145 °C. IR (cm^{-1}, hex): $\nu_{CO} = 1960$ (s). EIMS (*m/z*): 426 (M^+), 398 ($M^+ - CO$), 356 ($M^+ - CO - C_3H_6$, base), 354 ($M^+ - CO - C_3H_8$). ^1H NMR (δ, C_6D_6): 4.78 (1H, m, H_c), 3.21 (1H, dd, $J_{s'c} = 6.0$ Hz, $J_{ss'} = 3.1$ Hz, $H_{s'}$), 2.80 (1H, ddd, $J_{sc} = 6.0$ Hz, $J_{ss'} = 3.1$ Hz, $J_{as} = 0.8$ Hz, H_s), 1.76 (1H, d, $J_{ac} = 9.1$ Hz, H_a), 1.46 (15H, s, C_5Me_5), 0.85 (1H, d, $J_{a'c} = 6.9$ Hz, $H_{a'}$). Anal. Found: C, 39.72; H, 4.89. $C_{14}H_{20}ClORe$ Calc.: C, 39.47; H, 4.73%. Complex **3** was obtained by crystallization of a hexane solution at −78 °C, and was identified by a comparison of its IR, ^1H NMR, and mass spectra with literature values [6].

2.3.2. Method II

$Cp^*Re(CO)_3$ (800 mg, 1.97 mmol) was dissolved in pure allyl chloride (20 ml, 0.25 mmol) in a quartz tube. At 0 °C, the solution was irradiated under UV light for 2 h, and a dark red solution and some precipitate were obtained. Volatiles were pumped into a clean trap cooled in liquid nitrogen to recover the unreacted allyl chloride. The residue was extracted with ether. The soluble fraction was evaporated to dryness, redissolved in CH_2Cl_2 and transferred to a neutral alumina column. Eluting with hexane gave unreacted $Cp^*Re(CO)_3$, eluting with ether gave complex **5** (203.0 mg, 0.48 mmol, 24%) as the first fraction, and a very small amount of $Cp^*Re(\eta^2\text{-}C_3H_5Cl)(CO)_2$ (**13**) as the second fraction. Complex **13** was isolated in only a trace amount. IR (C_6D_6, cm^{-1}): ν_{CO} 1950, 1875. EIMS (*m/z*): 454 (M^+), 419 ($M^+ - Cl$), 398 ($M^+ - 2CO$), 356 ($M^+ - 2CO - C_3H_6$, base). The ^1H NMR and microanalysis were not obtained because of insufficient sample. The material that precipitated was $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2]Cl$ (**4**) and this was the insoluble residue after the ether extraction. It was recrystallized from CH_2Cl_2/ether as a mixture of *endo* and *exo* isomers (*endo*/*exo* = 3:1 in $CDCl_3$ from the integration of the ^1H NMR spectrum) in ca. 20% yield. IR (CH_2Cl_2, cm^{-1}): $\nu_{CO} = 2052$, 2000. FABMS (*m/z*): 419 (M^+), 389 ($M^+ - CO$), 359 ($M^+ - 2CO - 4H$). ^1H NMR (δ, $CDCl_3$) (a) *endo* isomer: 4.81 (1H, m, H_c), 3.90 (2H, d, $J_{sc} = 6.0$ Hz, H_s), 2.23 (15H, s, C_5Me_5), 1.97 (2H, d, $J_{ac} = 9.0$ Hz, H_a); (b) *exo* isomer: 4.3 (1H, m, H_c), 3.49 (2H, d, $J_{sc} = 6.0$ Hz, H_s), 2.50 (2H, d, $J_{ac} = 10$ Hz, H_a), 2.23 (15H, s, C_5Me_5).

2.3.3. Method III

$[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ (**1**, 50.6 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (5 ml) at room temperature, and PhIO (44.0 mg, 0.2 mmol) and Me_4NCl (33.0 mg, 0.3 mmol) were added to the solution. This mixture was stirred for 1 h to give a dark brown solution. At this time, the IR showed only one ν(CO) band at 1948 cm^{-1} (in CH_2Cl_2) indicating complex **5**. The solution was pumped to dryness, and the residue was extracted with hexane (0.5 ml × 5). Solvent was pumped off, and the residue was dissolved in CH_2Cl_2, then transferred to a neutral alumina column. Eluting with hexane removed organic impurities, eluting with ether gave complex **5** (39.2 mg, 0.092 mmol, 92%) as a yellow solid after recrystallization from hexane at −78 °C.

2.4. Reaction of $Cp^*Re(CO)_3$ with 2-methyl-3-chloropropene

$Cp^*Re(CO)_3$ (100.0 mg, 0.25 mmol) was dissolved in pure 2-methyl-3-chloropropene (methallyl chloride,

20 ml, 202 mmol) in a quartz tube. At 0 °C, the solution was irradiated under UV light for 2 h and a dark red solution was obtained. Excess of methallyl chloride was pumped off, and the residue was chromatographed on a neutral alumina column. Eluting with hexane gave the first fraction which was unreacted $Cp^*Re(CO)_3$. Eluting with ether gave $Cp^*Re(\eta^3\text{-}C_3H_4Me)(CO)Cl$ (**6**). This crude product was recrystallized from hexane at −78 °C to give **6** (30.0 mg, 0.068 mmol, 27%), m.p. 145–146 °C. IR (cm^{-1}, hex): ν_{CO} = 1954 (s). EIMS (*m/z*): 440 (M^+), 412 ($M^+ - CO$), 356 ($M^+ - CO - C_4H_8$, base), 354 ($M^+ - CO - C_4H_{10}$). ^1H NMR (δ, C_6D_6): 3.20 (1H, d, $J_{ss'}$ = 5.0 Hz, H_s), 2.90 (3H, s, CH_3), 2.65 (1H, d, $J_{ss'}$ = 5.0 Hz, $H_{s'}$), 2.00 (1H, s, $H_{a'}$), 1.48 (15H, s, C_5Me_5), 1.04 (1H, s, H_a). Anal. Found: C, 41.20; H, 4.96. $C_{15}H_{22}ClORe$ Calc.: C, 40.95; H, 5.04%.

2.5. $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)H$ (7)

To a solution of complex **5** (15.0 mg, 0.035 mmol) in 2 ml of freshly distilled ether was added by syringe 0.2 ml of $LiBEt_3H$ in ether solution (1 M). This solution was stirred at 0 °C for 3 h. By this time, the IR showed that the ν(CO) band for complex **5** had disappeared, and a new ν(CO) band appeared at 1900 cm^{-1} which is assigned to the *endo* isomer of complex **7**. Solvent was pumped off, and the residue was extracted with hexane, then chromatographed on a neutral alumina column. Eluting with ether/hexane (1:1) gave crude **7**. Chromatography was repeated with pure hexane, and the pure product was obtained as a white solid after removing the solvent. This is assigned as the *endo* isomer from the IR spectrum. The residue on the column (after elution with hexane) was eluted again with ether to give a very small amount of the *exo* isomer. Total yield (*endo* and *exo*) 12.0 mg, 88%. IR (cm^{-1}, hexane): ν_{CO} = 1914 (*endo* isomer), 1906 (*exo* isomer). ^1H NMR (δ, CD_2Cl_2) for the *endo* isomer: 3.78 (1H, m, H_c), 3.10 (1H, m, H_s), 2.47 (1H, m, H_s), 2.01 (15H, s, Cp*), 0.67 (1H, d, J_{ac} = 9.6 Hz, H_a), 0.24 (1H, d, J_{ac} = 9.0 Hz, H_a), −12.15 (1H, s, Re–H). ^1H NMR (δ, CD_2Cl_2) for the *exo* isomer: 2.56 (1H, m, H_c), 2.40 (1H, m, H_s), 2.15 (1H, m, H_s), 1.98 (15H, s, Cp*), 1.54 (1H, d, J_{ac} = 9.0 Hz, H_a), 1.33 (1H, d, J_{ac} = 9.6 Hz, H_a), −9.75 (1H, s, Re–H).

2.6. $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(C_6H_5)$ (8)

A solution of complex **5** (30.0 mg, 0.07 mmol) in 14 ml of ether was added to 0.1 ml of C_6H_5Li (1.95 M in THF/ether) at −20 °C. When the solution was stirred for 1 h, the colour changed from yellow to colourless and some white solid formed. Two drops of water were added to this solution to destroy excess C_6H_5Li. The solution was filtered through Celite. Solvent was pumped off, and the residue was dissolved in a small amount of benzene, and transferred to a neutral alumina column. Eluting with hexane gave crude **8**, which was recrystallized from hexane at −78 °C to give the pure product as white planar crystals (25.0 mg, 0.053 mmol, 76%), m.p. 101–102 °C. IR (cm^{-1}, hexane): ν_{CO} = 1919 (s). EIMS (*m/z*): 468 (M^+), 466 ($M^+ - 2H$), 440 ($M^+ - CO$, base), 438 ($M^+ - CO - 2H$), 425 ($M^+ - C_3H_6 - H$), 423 ($M^+ - C_3H_8 - H$). ^1H NMR (δ, C_6D_6): 7.86–7.14 (5H, m, Re–C_6H_5), 4.42 (1H, m, H_c), 2.90, 2.48 (2H, dd, J_{sc} = 5.6 Hz, $J_{ss'}$ = 3.2 Hz, $H_{s'}$, H_s), 1.61 (1H, d, J_{ac} = 8.0 Hz, H_a), 1.43 (15H, s, C_5Me_5), 0.58 (1H, d, $J_{a'c}$ = 7.2 Hz, $H_{a'}$). Anal. Found: C, 51.38; H, 5.42. $C_{20}H_{25}ORe$ Calc.: C, 51.37; H, 5.39%.

2.7. $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(CH_3)$ (9)

To a solution of **5** (40.0 mg, 0.09 mmol) in 5 ml of ether was added by syringe 0.4 ml of CH_3MgBr in ether solution (1 M, 0.4 mmol). This solution was stirred for 2 h at 0 °C, the solution changed colour from yellow to colourless, and a white solid formed which is the salt MgClBr. Excess of CH_3MgBr was destroyed by adding three drops of water, then 5 ml of hexane was added to the solution to extract the product. The solution was transferred to another Schlenk tube, and the solvent was pumped off. The residue was extracted with hexane, and purified by chromatography (neutral alumina column). Eluting with hexane gave complex **9** which was recrystallized from hexane at −78 °C as a white solid (21.0 mg, 0.052 mmol, 58%), m.p. 114–115 °C. IR (cm^{-1}, hexane): ν_{CO} = 1917 (s). EIMS (*m/z*): 406 (M^+), 404 ($M^+ - 2H$), 392 ($M^+ - CH_2$), 390 ($M^+ - CH_4$), 376 ($M^+ - CO - 2H$), 374 ($M^+ - CO - 4H$, base), 362 ($M^+ - CO - CH_4$), 360 ($M^+ - CO - CH_4 - 2H$), 358 ($M^+ - CO - CH_4 - 4H$), 348 ($M^+ - C_3H_6 - CH_4$), 346 ($M^+ - C_3H_6 - CH_4 - 2H$). ^1H NMR (δ, C_6D_6): 3.96 (1H, m, H_c), 2.59, 2.10 (2H, dd, J_{sc} = 5.4 Hz, $J_{ss'}$ = 3.1 Hz, $H_{s'}$, H_s), 1.51 (15H, s, C_5Me_5), 1.04 (1H, d, J_{ac} = 9.0 Hz, H_a), 0.40 (1H, d, $J_{a'c}$ = 7.5 Hz, $H_{a'}$), 0.20 (3H, s, Re–CH_3). Anal. Found: C, 44.66; H, 5.71. $C_{15}H_{23}ORe$ Calc.: C, 44.42; H, 5.72%.

2.8. $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(CH_2CH_3)$ (10)

To a solution of complex **5** (30.0 mg, 0.07 mmol) in 5 ml of ether was added CH_3CH_2MgBr in ether dropwise by syringe (0.5 ml, 2.55 M). This solution was stirred at 0 °C for 3 h. A white solid was produced and the solution changed colour from yellow to colourless. By using the same purification method as was used for complex **9**, **10** was obtained as a white solid (19.0 mg, 0.045 mmol, 65%), m.p. 103–104 °C. IR (cm^{-1}, hexane): ν_{CO} = 1912 (s). EIMS (*m/z*): 420 (M^+), 418 ($M^+ - 2H$), 416 ($M^+ - 4H$), 390 ($M^+ - CO - 2H$), 389 ($M^+ - CO - 3H$), 388 ($M^+ - CO - 4H$), 387 ($M^+ -$

$C_2H_6 - 3H$), 386 ($M^+ - C_2H_6 - 4H$), 376 ($M^+ - C_3H_6 - 2H$), 374 ($M^+ - C_3H_6 - 4H$), 362 ($M^+ - CO - C_2H_6$), 361 ($M^+ - CO - C_2H_6 - H$), 360 ($M^+ - CO - C_2H_6 - 2H$), 359 ($M^+ - CO - C_2H_6 - 3H$, base), 348 ($M^+ - C_2H_6 - C_3H_6$), 346 ($M^+ - C_2H_6 - C_3H_6 - 2H$). ^1H NMR (δ, C_6D_6): 4.16 (1H, m, H_c), 2.60, 2.17 (2H, dd, $J_{sc} = 5.4$ Hz, $J_{ss'} = 3.2$ Hz, $H_{s'}$, H_s), 1.53 (3H, t, $J = 7.7$ Hz, CH_3), 1.48 (15H, s, C_5Me_5), 1.05 (1H, d, $J_{ac} = 7.7$ Hz, H_a), 0.91 (2H, m, Re–CH_2), 0.51 (1H, d, $J_{a'c} = 7.7$ Hz, $H_{a'}$). $^{13}C\{^1H\}$ NMR (δ, C_6D_6): 95.1 (s, C_5Me_5), 77.0 (s, C_3H_5), 30.3 (s, C_3H_5), 28.3 (s, C_3H_5), 27.1 (s, CH_3), 17.5 (s, Re–CH_2), 9.6 (s, $C_5\{CH_3\}_5$). Anal. Found: C, 45.50; H, 6.08. $C_{16}H_{25}ORe$ Calc.: C, 45.80; H, 6.01%.

2.9. $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(\eta^1\text{-}C_3H_5)$ (11)

To a solution of complex **5** (30.0 mg, 0.07 mmol) in 5 ml of ether was added (η^1-C_3H_5)MgBr by syringe (1 ml, 2.3 M in ether). This solution was stirred at 0 °C for 5 h. A colourless solution and white solid were produced. By using the same purification method as was used for complex **9**, **11** was obtained as a white solid (17.0 mg, 0.039 mmol, 56%). IR (cm^{-1}, hex): $\nu_{CO} = 1914$ (s). EIMS (m/z): 432 (M^+), 430 ($M^+ - 2H$), 402 ($M^+ - CO - 2H$), 400 ($M^+ - CO - 4H$) or ($M^+ - C_2H_6 - 2H$, base), 398 ($M^+ - C_2H_6 - 4H$), 385 ($M^+ - CO - CH_4 - 3H$), 374 ($M^+ - CO - C_2H_6$), 360 ($M^+ - C_3H_6 - CO - 2H$). ^1H NMR (δ, C_6D_6): 6.02 (1H, m, =CH–), 5.17 (2H, m, $=CH_2$), 4.11 (1H, m, H_c), 2.53, 2.29 (2H, dd, $J_{sc} = 5.3$ Hz, $J_{ss'} = 3.4$ Hz, $H_{s'}$, H_s), 2.30 (1H, m, Re–CH_2–), 2.20 (1H, m, Re–CH_2), 1.47 (15H, s, C_5Me_5), 1.09 (1H, d, $J_{ac} = 9.1$ Hz, H_a), 0.57 (1H, d, $J_{a'c} = 6.4$ Hz, $H_{a'}$).

2.10. $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(n\text{-}C_4H_9)$ (12)

Complex **5** (23.6 mg, 0.06 mmol) was dissolved in 5 ml of freshly distilled ether, and n-C_4H_9MgCl in ether solution (0.2 ml, 1.9 M) was added to it by syringe. This mixture was stirred at 0 °C for 1 h. A colourless solution and white solid were obtained. By using the same purification method as was used for complex **9**, **12** was obtained as a white solid (18.4 mg, 0.04 mmol, 75%). IR (cm^{-1}, hex): $\nu_{CO} = 1910$. EIMS (m/z): 448 (M^+), 446 ($M^+ - 2H$), 416 ($M^+ - C_2H_6 - 2H$), 414 ($M^+ - C_2H_6 - 4H$), 404 ($M^+ - C_3H_8$), 402 ($M^+ - C_3H_8 - 2H$), 389 ($M^+ - C_4H_{10} - H$), 376 ($M^+ - CO - C_3H_8$), 374 ($M^+ - CO - C_3H_8 - 2H$, base), 361 ($M^+ - CO - C_4H_{10} - H$), 359 ($M^+ - CO - C_4H_{10} - 3H$), 348 ($M^+ - C_3H_6 - C_4H_{10}$), 346 ($M^+ - C_3H_6 - C_4H_{10} - 2H$). ^1H NMR (δ, C_6D_6): 4.18 (1H, m, H_c), 2.59, 2.17 (2H, dd, $J_{sc} = 5.4$ Hz, $J_{ss'} = 3.3$ Hz, $H_{s'}$, H_s), 1.50 (15H, s, C_5Me_5), 1.50–0.8 (m, Re–C_4H_9), 1.38 (1H, d, $J_{ac} = 5.5$ Hz, H_a), 0.50 (1H, d, $J_{a'c} = 7.1$ Hz, $H_{a'}$).

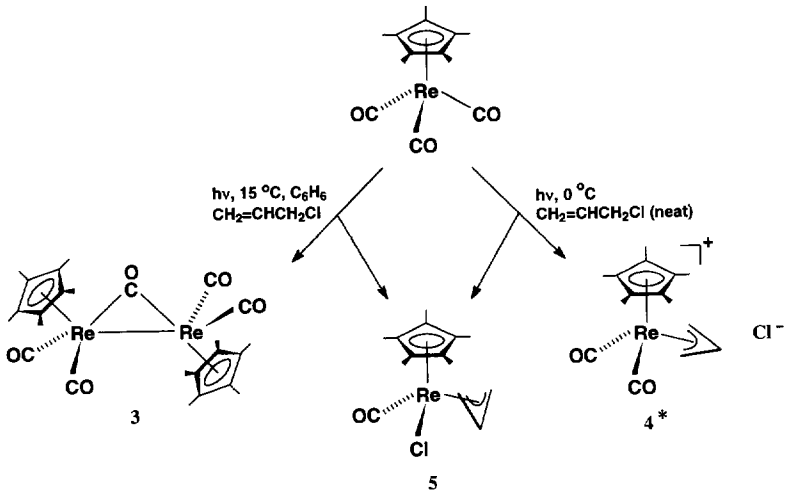
2.11. $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)I$ (14)

Complex **14** was obtained by using the same procedure used for synthesis of **9**, but **5** was treated with CH_3MgI instead of CH_3MgBr at room temperature in ether solution for 5 h. The pure product was obtained by crystallization from ether as yellow crystals after chromatography on a neutral alumina column (eluting with ether). IR (cm^{-1}, ether): $\nu_{CO} = 1948$ (s). EIMS (m/z): 518 (M^+), 516 ($M^+ - 2H$), 490 ($M^+ - CO$), 488 ($M^+ - 2H - CO$), 448 ($M^+ - CO - C_3H_6$, base), 446 ($M^+ - CO - C_3H_6 - 2H$). ^1H NMR (δ, C_6D_6): 4.48 (1H, m, H_c), 3.87 (1H, dd, $J_{s'c} = 6.0$ Hz, $J_{ss'} = 3.1$ Hz, $H_{s'}$), 2.76 (1H, ddd, $J_{sc} = 6.0$ Hz, $J_{ss'} = 3.1$ Hz, $J_{sa} = 0.6$ Hz, H_s), 1.55 (15H, s, C_5Me_5), 1.42 (1H, d, $J_{ac} = 9.2$ Hz, H_a), 0.56 (1H, d, $J_{a'c} = 7.5$ Hz, $H_{a'}$).

3. Results

The photolysis of $Cp^*Re(CO)_3$ with $CH_2=CHCH_2Br$ in hexane did not give the target product $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Br$. Instead, both *cis* (**2a**) and *trans* (**2b**) isomers of $Cp^*Re(CO)_2Br_2$ (**2**) resulted. The ^1H NMR of **2a** gave a singlet at δ 2.07 for Cp^*, while the Cp^* signal for **2b** occurred at δ 2.01. The IR spectra for the mixture of **2a** and **2b** in CH_2Cl_2 showed four strong ν(CO) bands, assigned as 2035, 1960 cm^{-1} for **2a** and 2049, 1981 cm^{-1} for **2b**. These assignments are in agreement with data reported in the literature [5].

Irradiation of $Cp^*Re(CO)_3$ with $CH_2=CHCH_2Cl$ in benzene at 10–15 °C afforded two products identified as $Cp^*_2Re_2(CO)_5$ (**3**) and $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl$ (**5**), while irradiation of $Cp^*Re(CO)_3$ in pure $CH_2=CHCH_2Cl$ resulted in production of $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2][Cl]$ (**4**) and **5** (Scheme 1). Characterization of **3** gave data in agreement with the literature [6–8]. Complex **4** (total ca. 5%) was produced as a mixture of both the *endo* and *exo* isomers. Except that the counter anion is Cl^-, the cation of **4** is exactly the same as that of previously prepared $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ (**1**) [4,9]. Complex **5** was also (and in best yield) synthesized by treating **1** or **4** with PhIO in the presence of Me_4NCl in CH_2Cl_2 (Scheme 2). Although in this case the starting material for the synthesis of **5** is a mixture of the *exo* and *endo* isomers of the cation, the ^1H NMR NOE experiments on the product indicated that **5** was obtained as the pure *endo* isomer only. Saturation of Cp^* at δ 1.46 induced enhancements for both H_a signals at δ 1.76 and δ 0.85, which indicated proximity of Cp^* protons with the two H_a protons as expected for the *endo* structure but not for *exo*. Saturation of H_c at δ 4.78 gave expected enhancements for both H_s protons at δ 3.21 and δ 2.80, which confirmed the assignments of H_c and H_s, but there was no enhancement of the H_a protons or the



Scheme 1. UV irradiation of $Cp^*Re(CO)_3$ with allyl chloride. * Complex **4** is a mixture of *exo* and *endo* isomers.

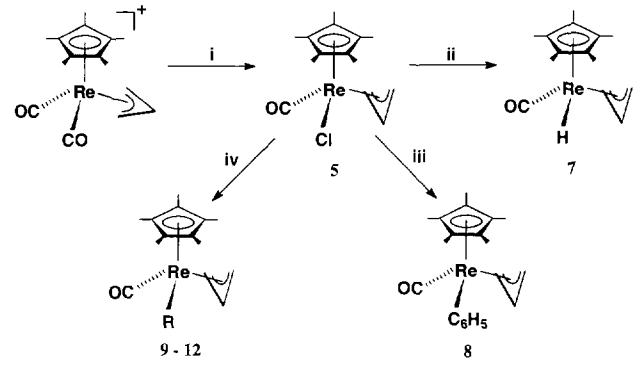
Cp^* resonance (which is as expected for an *endo* structure).

When allyl chloride was replaced by $CH_2=C(Me)CH_2Cl$, the irradiation of $Cp^*Re(CO)_3$ with pure $CH_2=C(Me)CH_2Cl$ gave the methallyl complex $Cp^*Re(\eta^3\text{-}C_4H_7)(CO)(Cl)$ (**6**), and no other product was isolated from this reaction. The ^1H NMR spectrum of **6** in C_6D_6 clearly exhibited all the resonances for the methallyl protons. Only one isomer was observed. This is assigned as the *endo* isomer by the similarity of the methylene proton resonances to those of **5**, which, as just described, was identified to be the *endo* isomer by NOE experiments.

Complex **5** reacted with $LiBEt_3H$ in freshly distilled ether at 0 °C to give the hydrido complex **7** (Scheme 2). Although complex **7** was reported [2] to react with $CHBr_3$ to give the bromide $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Br$, it is stable in CD_2Cl_2 and the ^1H NMR spectrum was recorded in this solvent. For the *endo* isomer, the Cp^* resonance occurred at δ 2.01, and the Re–H signal appeared at δ −12.2. For the *exo* isomer, the Cp^* resonance occurred at δ 1.98, and the Re–H signal occurred at δ −9.75. The chemical shifts of the allyl protons for both the *endo* and the *exo* isomers are given in the experimental section.

Complex **5** reacted with C_6H_5Li in dry ether at 0 °C to produce the phenyl complex **8**. The IR spectrum showed a strong ν(CO) absorption at 1919 cm^{-1} in hexane, which is much lower than that of complex **5** (1960 cm^{-1} in hexane), indicating more electron donation to the metal centre from C_6H_5 than Cl. The ^1H NMR spectrum of **8** in C_6D_6 showed two sets of multiplets at δ 7.86 and δ 7.14 for the five protons of the coordinated phenyl group. The allyl ligand gave resonances at δ 4.42 for H_c (multiplet), δ 2.90 and δ 2.48 for H_s (doublet of doublets), and δ 1.61, δ 0.58 for H_a (doublet). The Cp^* showed a singlet at δ 1.43. Saturation at δ 1.43 for Cp^* caused an NOE enhancement of the H_a resonances at δ 0.58 and δ 1.61, which indicated an *endo* structure for the η^3-allyl ligand in complex **8**, and in agreement no enhancement was observed for H_c when Cp^* was saturated. Saturation at δ 4.42 for H_c induced an enhancement for both H_s signals, and decoupled H_s from a doublet of doublets to a doublet, but no enhancement of the Cp^* resonance was observed. All the evidence from the ^1H NMR NOE experiment supports an *endo* structure for complex **8**.

Complex **5** reacted with an excess of RMgBr or RMgCl at 0 °C in freshly distilled ether to produce the rhenium η^3-allyl alkyl complexes **9–12** (R = Me (**9**), Et (**10**), $CH_2CH=CH_2$ (**11**), and *n*-Bu (**12**)). When **5** was treated with CH_3MgI at room temperature for 1 h in ether, the IR spectrum showed the production of ν(CO) absorptions for complex **9** and those of remaining **5**. However, when the reaction was continued for 5 h in an attempt to complete the conversion of **5** to **9**, no **9** was obtained. Instead, the product was the iodide complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)I$ (**14**). It appears that under these



Scheme 2. Synthesis and reactions of $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl$ (**5**). Conditions: (i) $PhIO/Me_4NCl/CH_2Cl_2$; (ii) $LiBEt_3H$/ether; (iii) C_6H_5Li/ether; (iv) RMgBr/ether, R = CH_3 (**9**), C_2H_5 (**10**), C_3H_5 (**11**), *n*-C_4H_9 (**12**).

conditions, the coordinated methyl group was easily substituted by iodide to give **14**. Rhenium η^3-allyl alkyl complexes do not appear to have been previously synthesized.

The spectroscopic data for complexes **8–12** are described in the experimental section. The EIMS spectra of **9–12** showed clear parent peaks. For complexes **9**, **10** and **12**, the intensity for the fragment $[M^+ - 2H]$ was much stronger than that of M^+. This may indicate that the C–H bond of the coordinated alkyl group is easily broken during mass spectroscopy. We have not previously found this strong $[M^+ - 2H]$ fragment in the MS of any of the other rhenium complexes prepared in this study [4,10]. Both CO and RH fragments are found to be lost very easily from the molecules, and lead to strong intensities for the fragments $[M^+ - RH]$ or $[M^+ - CO]$ which are the observed base peaks for compounds **9–12**.

The ^{1}H NMR spectra of complexes **5**, **6** and **14** showed only the *endo* isomer to be present in each case. The two *syn* protons from two different carbon termini in each complex gave different coupling patterns, since the allyl is bonded to a chiral metal centre and the two carbon atoms from the different allyl termini have a different chemical environment. In complex **5**, one *syn* proton (s′) showed a doublet of doublets with the coupling $J_{s'c} = 6.0$ Hz, $J_{ss'} = 3.1$ Hz. (The W pattern long range coupling of the two *syn* protons was observed for all the neutral rhenium η^3-allyl complexes, as it was in the cationic rhenium allyl compounds [4,10,11].) The other *syn* proton (s) showed a doublet of doublets of doublets pattern. The extra coupling of 0.77 Hz for this *syn* proton could not be ignored. The *syn* protons in complex **14** have the same coupling pattern as in **5**, one is a doublet of doublets with a separation of $J_{s'c} = 6.0$ Hz and $J_{ss'} = 3.1$ Hz, the other is a doublet of doublets of doublets, with an extra coupling of 0.6 Hz. We propose that this extra coupling is the coupling of the *syn* and *anti* protons from the same carbon terminus, which is not generally resolved.

In complex **6**, since the central proton was replaced by the methyl group, the coupling to the central allyl proton disappeared. The *syn* protons in this case showed only a doublet coupled to the other *syn* proton with $J_{ss'} = 4.7$ Hz, and the *anti* protons gave a simple singlet.

The NOE experiment for **8** indicated that the allyl group in this compound adopts the *endo* structure. The ^{1}H NMR spectra of complexes **9–12** showed similar allyl proton patterns to those of **8**, and the chemical shifts of the allyl protons are in the same region. The central protons H_c gave multiplet resonances at δ 4.5 to δ 4.0, the *syn* protons at δ 3.0 to δ 2.0 are doublet of doublets, and the *anti* protons appeared at higher field as a doublet. One is at δ 0.6–0.4, the other is at δ 1.7–1.0 ppm. Because the NMR characters of these allyl protons are similar compared with those of **8**, we assume that the observed isomers of complexes **9–12** are also the *endo* isomers.

We did try to individually identify the two inequivalent *syn* (and similarly the *anti*) protons where present by ^{1}H NMR experiments using NOE and ^{1}H–^{1}H correlation experiments. The NOE experiments for complexes **5** and **8** indicated that the *syn* proton at the lower field and the *anti* proton at the higher field are from the same carbon terminus. For example, saturation for the *anti* proton at δ 1.61 in complex **8** caused an enhancement for the *syn* proton at δ 2.48 instead of the one at δ 2.90. No further distinction was possible.

The ^{1}H NMR spectrum of **11** showed resonances for the η^1-allyl at δ 6.02 (multiplet, central proton), δ 5.17 (multiplet, two terminal protons), and δ 2.30 (multiplet, Re–CH_2–); the *endo* η^3-allyl gave signals at δ 4.11 (multiplet, H_c), δ 2.53, δ 2.29 (doublet of doublets, H_s), and δ 1.09, δ 0.57 (doublet, H_a). The assignments were confirmed by ^{1}H NMR decoupling experiments, and by a comparison of our data with those reported in the literature for other η^1-allyl complexes [12].

Variable temperature ^{1}H NMR experiments were conducted in toluene-d_8 for **11** in order to study the possible exchange of the η^1-allyl with η^3-allyl in **11**. There was no evidence supporting the exchange of the η^1-allyl with η^3-allyl even after complex **11** was heated to 335 K in toluene-d_8. We were also expecting the possible loss of coordinated CO from **11** at high temperature, followed by a conversion of the η^1-allyl to the η^3-allyl to give unknown $Cp^*Re(\eta^3\text{-}C_3H_5)_2$. The experiment showed instead that **11** decomposed slowly at 335 K in toluene-d_8; the IR showed that the ν(CO) absorption disappeared and the ^{1}H NMR of this solution ultimately showed no signals for the Cp^* or allyl protons.

For complexes **8–12** the possible insertion of CO to give $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(COR)$ was probed. Complex **9** was dissolved in hexane, and CO was bubbled through the solution until saturated and the solution was stirred at room temperature for 48 h. The IR spectrum showed no new ν(CO) absorption, and the ^{1}H NMR showed only pure **9**. The same experiment was conducted with complexes **8** and **11**, and again CO did not insert into the Re–R bonds ($R = C_6H_5$, CH_3, C_3H_5) under the experimental conditions employed.

4. Discussion

4.1. Photoreactions of $Cp^*Re(CO)_3$ with allyl chloride

CO substitution reactions occur under UV irradiation of carbonyl complexes, owing to dissociation of CO and formation of coordinatively unsaturated compounds [13–18]. This led us to attempt the synthesis of **5** by irradiating $Cp^*Re(CO)_3$ in the presence of allyl chloride, since the allyl chloride is a potential ligand which

could coordinate to the coordinatively unsaturated metal centre either by using the double bond or by oxidative addition.

The photoreactions of $CpRe(CO)_3$ or $Cp^*Re(CO)_3$ with allyl chloride do not appear to have been studied previously. However, those of the manganese analogue $CpMn(CO)_3$ were studied by Hill [19]. The results indicated that the dicarbonyl η^2-alkene complex $CpMn(\eta^2\text{-}C_3H_5Cl)(CO)_2$ was first formed, and further irradiation led to the conversion of the η^2-alkene to η^3-allyl to give the complex $[CpMn(\eta^3\text{-}C_3H_5)(CO)_2][Cl]$. The chloro substituted complex $CpMn(\eta^3\text{-}C_3H_5)(CO)Cl$, unfortunately, was not observed. The photoreactions of complexes $CpM(CO)_3X$ (M = Mo, W; X = Cl, Br, I) with allyl halides were also studied by the same group; again, the η^2-alkene complexes $CpM(\eta^2\text{-}C_3H_5X)(CO)_2X$ were concluded to be intermediates, but now there was formation of the η^3-allyl compounds $CpM(\eta^3\text{-}C_3H_5)(CO)X_2$ [20].

In our case, when $Cp^*Re(CO)_3$ was irradiated with allyl chloride, the experimental data suggested that the irradiation of $Cp^*Re(CO)_3$ did lead to the dissociation of one CO first to produce $[Cp^*Re(CO)_2]$ [7], followed by coordination of the allyl chloride to $[Cp^*Re(CO)_2]$ to give the intermediate $[Cp^*Re(CH_2{=}CHCH_2Cl)(CO)_2]$ (**13**). By using benzene as the solvent the binuclear carbonyl complex $Cp^*_2Re_2(CO)_5$ (**3**) was an observed by-product, as expected if the intermediate $[Cp^*Re(CO)_2]$ is formed, and reacts with further tricarbonyl. When irradiation was conducted in pure allyl chloride, a small amount of **13** could actually be isolated from the reaction. In addition to the formation of the target product **5**, the ionic complex $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2][Cl]$ (**4**), corresponding to Hill's observed manganese product, was also obtained. This is consistent with the possibility that further irradiation of **4** results in substitution of a CO ligand by chloride, while irradiation of **13** causes dissociation of a CO followed by a C–Cl bond activation, both yielding **5**. This latter reaction would be analogous to the previously observed photochemical C–H bond activation of $Cp^*Re(\eta^2\text{-}C_3H_6)(CO)_2$ giving $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)H$ [1,2].

4.2. Substitution reactions of $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl$ (5)

The desired improved synthesis of the hydrido complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)H$ (**7**) was achieved by reacting **5** with $LiBEt_3H$, which afforded **7** in 88% total isolated yield. Interestingly, this non-photochemical method of synthesis overwhelmingly resulted in the *endo* isomer. A small amount of the *exo* isomer was isolated by chromatography, but it is possible that this may arise from slow solution isomerization of the initially formed *endo* isomer. By contrast, the photochemical synthesis gave about a 2:1 excess of the *exo* isomer [1,2]. It was previously reported that the bromide $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Br$ gave $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)H$ (**7**) in about a 4:1 ratio of *endo* to *exo* when reacted with $LiBEt_3H$ [2].

The chloride **5** is also readily convertible to the phenyl (**8**) or representative alkyl complexes (**9–12**) in moderate yield by using appropriate lithium or Grignard reagents.

4.3. Endo–exo isomerization of 7

When **7** was stored for eventual use in further reactions, the *exo* isomer of **7** was kept in the pure solid state at 0–5 °C for three days, at the end of which no presence of the *endo* isomer was detected from the ^1H NMR spectrum in CD_2Cl_2. The *endo* isomer was kept under the same conditions for the same time, but its ^1H NMR in CD_2Cl_2 now showed the appearance of the *exo* isomer, with the ratio *endo/exo* ≈ 3:1 in CD_2Cl_2 at room temperature (the sample was dissolved in CD_2Cl_2 at 18–22 °C and kept at this temperature for about 2 h before the spectrum was recorded). This solution was cooled to 213 K (over 4 h) and the ^1H NMR spectrum was recorded periodically as the temperature was lowered. The chemical shift of the hydride and other protons changed as the temperature changed, but the ratio of the *endo/exo* isomers showed no obvious change.

In the previous work [1,2], **7** was obtained in a photochemical reaction, and the *exo* isomer was the one which had the higher population compared with the *endo* isomer initially. The thermal conversion of the *exo* isomer to an *exo/endo* mixture was then studied at different temperatures in C_6D_6, and it was observed that the *exo/endo* ratio fell from approximately 36 at −12 °C to approximately 0.33 at 27.5 °C. In the present work, we have observed that the pure *endo* isomer isomerizes to give an *exo/endo* mixture and that the ratio of the *exo* to the *endo* isomer in solution in CD_2Cl_2 is almost the same as the result obtained previously in benzene at a comparable temperature, starting with the pure *exo* isomer [2,21]. This suggests that the isomerization is a thermally reversible process, and the observed *endo/exo* ratio at 20 °C (*endo/exo* ≈ 3:1) in CD_2Cl_2 approximates to the equilibrium ratio at that temperature.

5. Conclusions

The reactions of $Cp^*Re(CO)_3$ with $CH_2{=}CHCH_2Br$ under UV light in hexane did not give the desired allyl complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Br$. Instead, the reaction afforded only the dibromo complex $Cp^*Re(CO)_2Br_2$. $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)Cl$ (**5**) was, however, synthesized

by both photochemical and thermal reactions. In addition to **5**, the by-products from the irradiation of $Cp^*Re(CO)_3$ with allyl chloride (in benzene or using neat allyl chloride) under UV light were also characterized. Complex **5** is a useful precursor for the synthesis of other neutral rhenium η^3-allyl compounds by substituting Cl. In particular, the reaction of **5** with $LiBEt_3H$ to give $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)H$ (**7**) is an effective method to make this hydrido complex. A study of the reactivity of the allyl hydrido complex **7** will be reported in a subsequent paper.

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