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Preliminary communication

STEREOSPECIFIC AND CHEMOSPECIFIC INTERCONVERSIONS OF THE RHENIUM ALKYLIDENE $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHC_6H_5)]^+PF_6^-$ AND THE ALKYLRHENIUM $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH(OCH_3)C_6H_5)$

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Summary

Addition of methoxide to either geometric isomer of the benzylidene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHC_6H_5)]^+PF_6^-$ (**1t**, **1k**) affords $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH(OCH_3)C_6H_5)$ (**2t**, **2k**) in which a new chiral center has been generated stereospecifically or with high stereoselectivity. Reaction of **2t** and **2k** with $Ph_3C^+PF_6^-$ results in the chemospecific abstraction of a methoxy group and the stereospecific regeneration of **1t** and **1k**, respectively.

The asymmetric synthesis of organic molecules utilizing chiral organometallic reagents or catalysts is a research area of considerable current interest [1]. Surprisingly, there has been little systematic attention directed at reactions of chiral pseudotetrahedral organometallic complexes in which new ligand-based chiral centers are generated. We have recently reported the synthesis of the benzylidene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHC_6H_5)]^+PF_6^-$, which can be prepared as either of two geometric isomers, **1k** (kinetic) or **1t** (thermodynamic) [2]. In this communication, we describe the stereochemistry of the reactions of **1k** and **1t** with $NaOCH_3$, and stereospecific and chemospecific [3] reactions of the resulting rhenium alkyls with $Ph_3C^+PF_6^-$.

A recent X-ray crystal structure determination of **1t** [4], and extended Hückel MO calculations [5], indicate **1k** and **1t** to have structures I and II, respectively (Newman projections down benzylidene—rhenium bond). Benzylidene **1t** was generated in CH_2Cl_2 as previously described [2], and treated with $NaOCH_3/CH_3OH$ at 20°C. After 20 min, solvent removal followed by residue recrystallization from CH_2Cl_2/hexane afforded the α-methoxybenzyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH(OCH_3)C_6H_5)$ (**2t**) in 74% yield (eq. 1). Since a second chiral center is generated in this reaction, two diastereomeric products are possible. However, NMR data indicate a stereospecific reaction to

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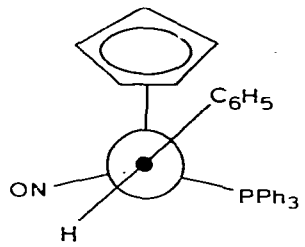
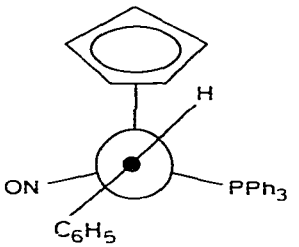
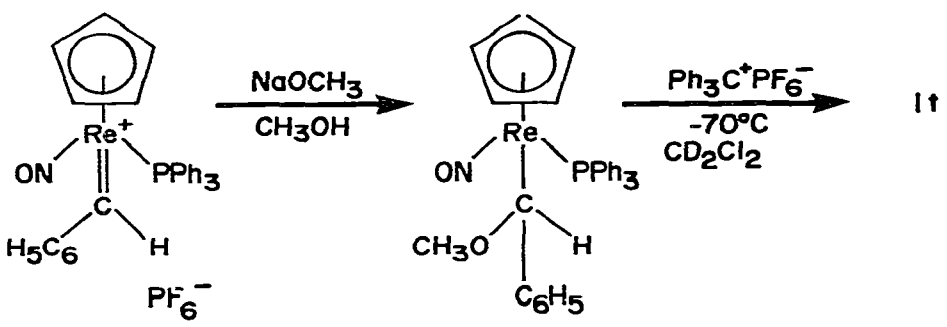


(I)

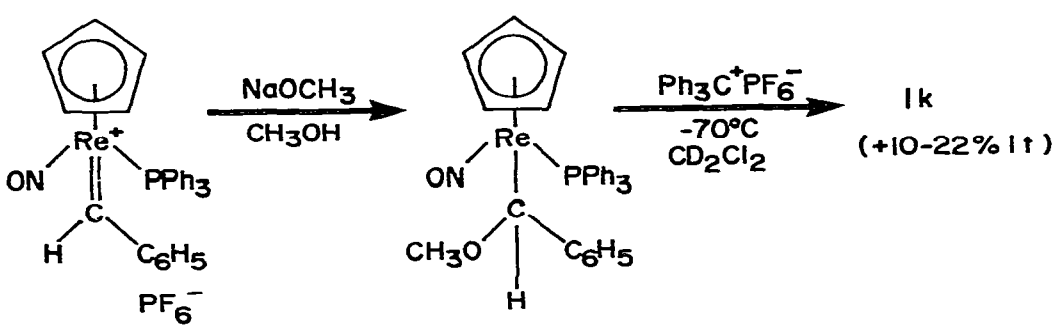


(II)

have taken place yielding diastereomerically pure **2t**: m.p. 169—172°C (dec.); ^{1}H NMR (δ, $CDCl_3$): 7.58–6.90 (m, 20H), 5.97 (d, 1H, $J(^{31}P—^1H)$ 5 Hz), 4.66 (s, 5H), 2.55 (s, 3H). IR (cm^{-1}, CH_2Cl_2): ν(NO) 1630; Anal.: Found: C, 55.81, H, 4.47; N, 2.34; P, 4.61. $C_{31}H_{29}NO_2PRe$ calcd.: C, 56.01; H, 4.40; N, 2.11; P, 4.66%.



(1)

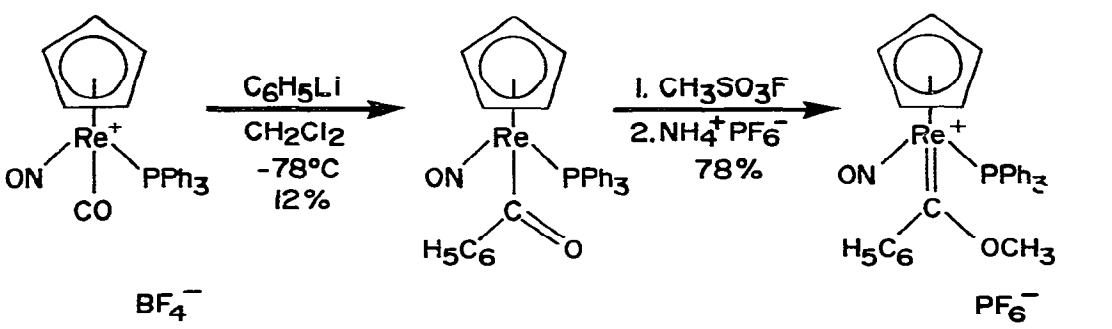


(2)

The less stable benzylidene geometric isomer **1k** was generated in situ as previously described, and treated with $NaOCH_3/CH_3OH$ at –78°C. After warming to room temperature, α-methoxybenzyl complex (η-C_5H_5)Re(NO)(PPh_3)-($CH(OCH_3)C_6H_5$) was again isolated, but now as a 90/10 mixture of diastereoisomers in which the carbon configuration in the predominant one (**2k**)

was opposite to that of 2t (eq. 2)[‡]. To test for possible fractionation of the diastereoisomers during workup [6], a crude reaction mixture was examined by ^{1}H NMR. Integration of the methine resonances indicated a 78/22 ratio of 2k to 2t. Data on 2k: ^{1}H NMR (δ, $CDCl_3$): 7.88—6.82 (m, 20H), 5.75 (d, 1H, $J(^{31}P—^1H)$ 2.5 Hz), 4.89 (s, 5H), 2.67 (s, 3H): Anal (90/10 2k/2t mixture): Found: C, 55.93; H, 4.51. Calcd.: see 2t.

Previously, $Ph_3C^+PF_6^-$ has been observed to abstract both α-hydrides and α-methoxides from alkylmetal compounds. For example, Cutler has reported [7] that $(\eta\text{-}C_5H_5)Fe(CO)(L)(CH_2OCH_3)$ and $Ph_3C^+PF_6^-$ react to form $[(\eta\text{-}C_5H_5)Fe(CO)(L)(CHOCH_3)]^+PF_6^-$ (L = CO, PPh_3), whereas Brookhart has noted [8] that $(\eta\text{-}C_5H_5)Fe(CO)(L)(CH(OCH_3)C_6H_5)$ and $Ph_3C^+PF_6^-$ yield benzylidene $[(\eta\text{-}C_5H_5)Fe(CO)(L)(CHC_6H_5)]^+PF_6^-$ (L = CO, PPh_3). Hence it was of interest to examine the reaction of $Ph_3C^+PF_6^-$ with 2t and 2k. Before proceeding, an authentic sample of the hydride abstraction product $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3)C_6H_5)]^+PF_6^-$ (5) was prepared as shown in eq. 3. By treatment of cation 3 with C_6H_5Li, orange benzoyl complex 4 could be obtained in low yield after column chromatography. (IR (cm^{-1}, CH_2Cl_2): ν(NO) 1655, ν(C=O) 1515). Subsequent reaction of 4 with CH_3SO_3F ($CDCl_3$, 20°C) followed by addition of excess $NH_4^+PF_6^-$ in acetone, solvent evaporation and residue extraction with $CHCl_3$, and CH_2Cl_2/hexane recrystallization, yielded 5 (78%) as orange prisms. Data: m.p. 212—216°C (dec.); ^{1}H NMR (δ, $CDCl_3$): 7.51—7.25 (m, 20H), 5.80 (s, 5H), 3.93 (s, 3H); IR (cm^{-1}, CH_2Cl_2): ν(NO) 1720; Anal.: Found: C, 45.89; H, 3.62; N, 1.79; P, 7.47. $C_{31}H_{28}F_6NO_2P_2Re$ calcd.: C, 46.02; H, 3.49; N, 1.73; P, 7.66%.



3 4 5 (3)

When 2t in CD_2Cl_2 was treated with 1.5 equiv of $Ph_3C^+PF_6^-$ at −70°C in a ^{1}H NMR monitored reaction, 1t formed exclusively (eq. 1). No 5 could be detected. When a 90/10 2k/2t mixture was similarly treated with $Ph_3C^+PF_6^-$ at −70°C (eq. 2), a 90/10 1k/1t mixture formed. Both of these reactions were complete within 3 minutes at −70°C.

[‡]In this paper, we begin the convention of depicting the alkyl or aryl group "*syn*" to the NO ligand in the "thermodynamic" alkylidenes in two dimensional representations of the type in eq. 1 and 2. Conversely, the hydrogen will be drawn as "*syn*" to the NO ligand for the "kinetic" alkylidenes (1k in eq. 2). The terms "*cis*" and "*trans*" are clearly inadequate for describing this type of geometric isomerism. By IUPAC systematic nomenclature, projections I (1k) and II (1t) can be unambiguously designated as synclinical and anticlinical, respectively: Pure Appl. Chem., 45 (1976) 11; see section E-5.6., p. 24.

From the preceding data, the following conclusions may be drawn: (1) Methoxide stereospecifically attacks only one face of the benzylidene ligand in **1t** (refer to Newman projection II). (2) Methoxide abstraction occurs chemospecifically [3] and stereospecifically when **2k** and **2t** are treated with $Ph_3C^+PF_6^-$; importantly, mixtures of **2k** and **2t** generate identical ratios of **1k** and **1t**. (3) Methoxide attack upon **1k** occurs preferentially on one face of the benzylidene ligand to yield **2k**. Of relevance to this last point, the possibility that partial isomerization of **1k** to **1t** might occur competitively with methoxide attack was considered. However, when a CD_2Cl_2 solution of **1k** was treated with $NaOCD_3/CD_3OD$ at −70°C, ^1H NMR monitoring showed the reaction to be complete within 3 minutes; a **2k**-d_3/**2t**-d_3 mixture (85/15) formed.

Several direct comparisons are available which indicate metal=$C(OCH_3)C_6H_5$ complexes to be more stable than metal=CHC_6H_5 complexes [10]. Hence we believe the chemospecific abstraction by $Ph_3C^+PF_6^-$ of methoxide over hydride from **2t** and **2k** to be a kinetic phenomenon. In contrast to Cutler's observations with (η-C_5H_5)Fe(CO)(L)(CH_2OCH_3) (vide supra), we find that (η-C_5H_5)Re(NO)(PPh_3)(CH_2OCH_3) also undergoes predominant (95/5) methoxide abstraction when treated with $Ph_3C^+PF_6^-$ in CD_2Cl_2 at −70°C [12].

In summary, (η-C_5H_5)Re(NO)(PPh_3)-alkyl and -alkylidene complexes are becoming increasingly recognized as capable of a wide variety of stereospecific and/or highly stereoselective transformations [2]. Additional examples, methods for the optical resolution of (η-C_5H_5)Re(NO)(PPh_3)X compounds, and means for effecting rhenium—carbon bond cleavage will be the subject of future reports from this laboratory.

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