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Preliminary communication

Generation of the dichloromethane complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+\ BF_4^-$, and its conversion to the oxidative addition product $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Cl)(CH_2Cl)]^+\ BF_4^-$

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Abstract

Reaction of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CH_3)$ and $HBF_4 \cdot OEt_2$ in CH_2Cl_2 at −78 °C gives the dichloromethane complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+$ BF_4^-, which undergoes the title transformation at −35 °C. The $ReClCH_2Cl$ carbon is attacked by halide nucleophiles (X^-) to give XCH_2Cl and the chloride complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Cl)$, and exhibits a ^{13}C NMR resonance that is coupled to phosphorus (d, $^3J(CP)$ 5.0 Hz) and geminal hydrogens (t, $^1J(CH)$ 186 Hz).

The oxidative addition of an alkyl halide to a coordinatively unsaturated metal complex is a key step in a variety of important transformations (e.g., Monsanto methanol to acetic acid process [1], carbon–carbon bond-forming cross-coupling reactions [2]). Although several mechanisms have been documented [3], competing or prior alkyl halide coordination remains a possibility in nearly all cases. Alkyl halide complexes have recently been synthesized [4–6], but none have yet been found to directly lead to oxidative addition products. However, Crabtree has made the important observation that addition of an H_2 acceptor reagent to the Ir^{III} methyl iodide complex $[(Ph_3P)_2Ir(H)_2(ICH_3)_2]^+$ gives a dimer of Ir^{III} oxidative addition product $[(Ph_3P)_2Ir(CH_3)(I)]^+$ [4b]. In this communication, we report the generation of dichloromethane complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+$ BF_4^- (**1**), and its facile conversion to oxidative addition product $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Cl)(CH_2Cl)]^+$ BF_4^- (**2**).

Pentamethylcyclopentadienyl methyl complex [7] $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CH_3)$ and $HBF_4 \cdot OEt_2$ (1.01 equiv.) were combined in CH_2Cl_2 or CD_2Cl_2 at −78 °C (Scheme 1). NMR spectra (^1H, ^{13}C, $^{31}P\{^1H\}$, ^{19}F) were immediately recorded at −85 °C, and showed the clean formation of a new complex **1** [8*]. An

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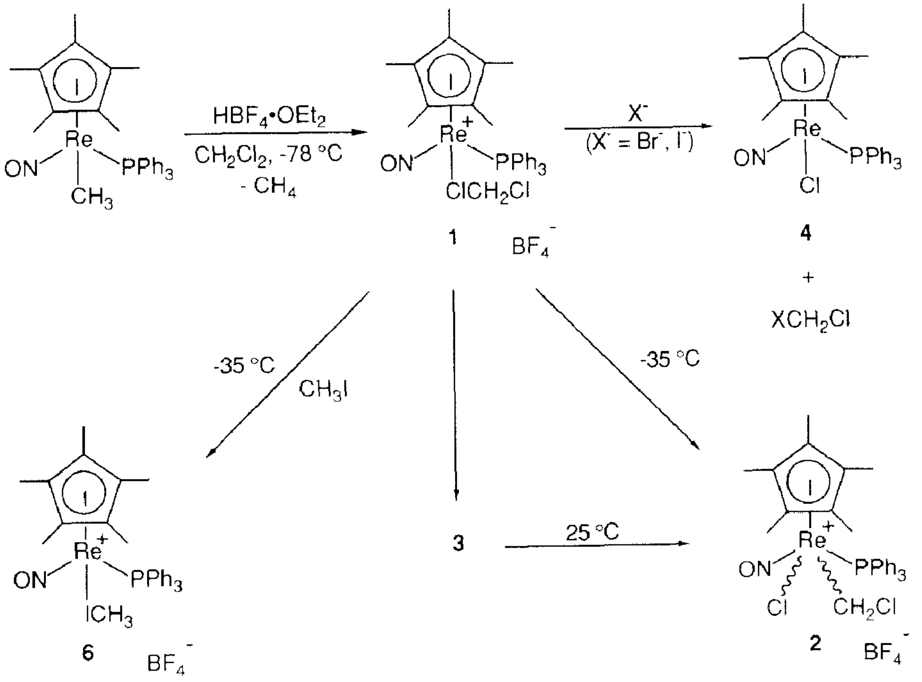
* Reference number with asterisk indicates a note in the list of references.



Scheme 1. Generation and reactions of dichloromethane complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+$ BF_4^- (**1**).

analogous reaction of cyclopentadienyl methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$-$(CH_3)$ has been shown to give dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$-$(ClCH_2Cl)]^+$ BF_4^- [9]. On the basis of spectral similarities, and particularly the dichloromethane carbon ^{13}C NMR chemical shift (22 ppm downfield from free CH_2Cl_2; Fig. 1) and coupling constants, **1** was formulated as the Re^I pentamethylcyclopentadienyl dichloromethane complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+$ BF_4^-.

The structure of **1** was further supported by reactions with halides salts $[Ph_3P{=}N{=}PPh_3]^+$ Br^- and $Ph_3P^+CH_3$ I^- (1.2–1.4 equiv, −78 °C). Subsequently isolated were mixtures of halide complexes (96–97%) of which chloride complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Cl)$ (**4**, Scheme 1) was the major component (92–95%) [10*]. Analysis of the second reaction by GLC and GLC/MS indicated the formation of ICH_2Cl (88%). Dichloromethane is normally inert towards halide ions. Hence, the dichloromethane ligand is significantly activated towards nucleophilic attack, providing a new type of easily generated chloromethylating agent.

Cyclopentadienyl dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$-$(ClCH_2Cl)]^+$ BF_4^- undergoes first-order decomposition at −25 to −10 °C to bridging chloride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+$ BF_4^- (k_{obs} $3.5 \pm 0.2 \times 10^{-4}$ s^{-1}, −10.1 °C) [9]. However, **1** is less stable thermally. A sample of **1** (−78 °C) was inserted into a −35 °C NMR probe. NMR spectra showed **1**, and two new species (**2** [11*], **3** [12*], in 61–64%, 7–12%, and 24–32% yields, respectively. Complex **1** then underwent first-order decomposition (k_{obs} $5.0 \pm 0.2 \times 10^{-4}$ s^{-1}) to **2** (k_{obs} (appearance) $5.0 \pm 0.2 \times 10^{-4}$ s^{-1}). The concentration of **3** did not change. The sample was warmed to room temperature, whereupon **3** underwent first-order

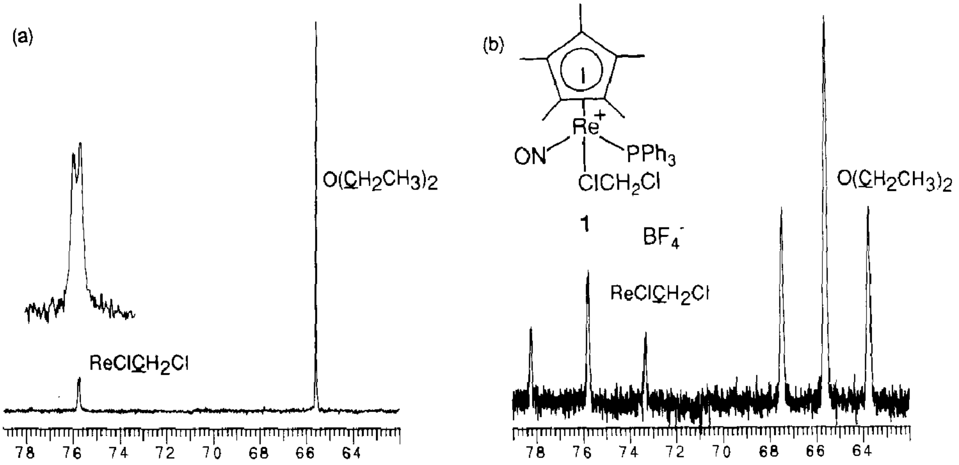


Fig. 1. (a) $^{13}C\{^1H\}$ NMR spectrum of dichloromethane complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+$ BF_4^- (**1**) with inset showing $^3J(CP)$ 5.0 Hz. (b) ^{13}C NMR spectrum of **1** showing $^1J(CH)$ 186.0 Hz. All spectra are at −85 °C.

decomposition (k_{obs} $5.1 \pm 0.2 \times 10^{-4}$ s^{-1}, 25 °C) to **2**. Hence, **2** is formed by two pathways.

Analogous preparative reactions gave **2** as a gold-yellow, spectroscopically pure powder (60–70%), which was characterized by IR and ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectroscopy [11*]. Complex **2** was assigned as the five-coordinate Re^{III} oxidative addition product $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Cl)(CH_2Cl)]^+$ BF_4^- based upon the following properties: (1) the upfield ^1H NMR chemical shifts of the CH_2 protons relative to those of CH_2Cl_2, (2) the upfield ^{13}C NMR chemical shift of the CH_2 carbon relative to that of CH_2Cl_2 and **1**, and its sizeable phosphorus coupling, (3) a mass spectral parent ion for the cation (FAB), and (4) an IR $\nu(N{\equiv}O)$ that is much greater than normal for cationic complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(L)]^+$ [7]. A similar IR $\nu(N{\equiv}O)$ trend is seen with analogous cyclopentadienyl complexes [9b].

We presently interpret the formation of dichloromethane complex **1** as proceeding via the coordinatively unsaturated fragment $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)]^+$ BF_4^- (**5**) [9b]. Hence, dichloromethane coordination to **5** is faster than oxidative addition. It is attractive to propose that oxidative addition occurs directly from **1**, analogously to pre-coordination in arene C-H oxidative addition [13]. However, our results are equally consistent with prior dichloromethane dissociation from **1** to give **5**, followed by an oxidative addition pathway not involving **1** [3]. Importantly, **1** and CH_3I (10 equiv.) react within 5 min at −35 °C to give methyl iodide complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ICH_3)]^+$ BF_4^- (**6**) [14]. This suggests that the dichloromethane ligand of **1** readily dissociates. Finally, pentamethylcyclopentadienyl ligands are more electron releasing than cyclopentadienyl ligands, and hence should facilitate the oxidation of Re^I to Re^{III}. This rationalizes the greater thermal stability (and alternative decomposition mode) of the cyclopentadienyl analogue of **1**. We further suggest that the electron withdrawing spectator chloride in **1** promotes oxidative addition, as methyl iodide complex **6** decomposes chiefly by other pathways.

Several dichloromethane oxidative addition products have been previously reported [15]. Our data suggest that these may form via similar coordination/oxidative addition sequences. Additional properties of dichloromethane complexes will be described in the near future [9b].

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8 Data on **1** (CD_2Cl_2 or CH_2Cl_2, −85 °C): ^{1}H NMR (δ) 1.68 (s, 5Me); $^{13}C\{^1H\}$ NMR (ppm) 102.58 (s, *C*$_5$Me$_5$), 75.76 (d, ^3J(CP) 5.0 Hz, CH$_2$), 9.37 (s, C$_5$*Me*$_5$); $^{31}P\{^1H\}$ NMR (ppm) 16.3 (s); ^{19}F NMR (δ) −152.68 (s).

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10 Authentic samples of halide complexes (η^5-C_5Me_5)Re(NO)(PPh$_3$)(X) were prepared in high yields by reactions of (η^5-C_5Me_5)Re(NO)(PPh$_3$)(CH$_3$) and HCl (CH_2Cl_2), HBr (C_6H_6), and HI (C_6H_6), respectively. These were characterized by microanalyses (C,H), and IR (cm^{-1}, KBr: ν(N≡O) 1635, 1642, 1644), ^{1}H NMR (δ, CDCl$_3$: C$_5$Me$_5$ (s) 1.63, 1.66, 1.73), $^{13}C\{^1H\}$ NMR (ppm, CDCl$_3$: *C*$_5$Me$_5$ (d, J(CP) 1.8–2.0 Hz) 100.36, 100.14, 99.78; C$_5$*Me*$_5$ (s) 9.75, 10.02, 10.65), and $^{31}P\{^1H\}$ NMR (ppm, CDCl$_3$: 18.2, 16.8, 14.8 (s)) spectroscopy.

11 Data on **2**: ^{1}H NMR (δ, CDCl$_3$) 7.75–7.36 (m, 15H), 4.58 (dd, J(HH) 7.1 Hz, J(HP) 3.1 Hz, C*H*H′), 4.22 (dd, J(HH) 7.2 Hz, J(HP) 3.0 Hz, CH*H*′), 1.93 (s, 5Me); $^{13}C\{^1H\}$ NMR (ppm, CDCl$_3$) 135.10 (d, J(CP) 9.0 Hz), 133.49 (s), 132.9 (d, J(CP) 52.5 Hz), 129.07 (d, J(CP) 11.0 Hz), 115.91 (s, *C*$_5$Me$_5$), 47.68 (d, J(CP) 15.5 Hz, CH$_2$), 10.22 (s, C$_5$*Me*$_5$); $^{31}P\{^1H\}$ NMR (ppm, CDCl$_3$) 10.1 (s); IR (cm^{-1}, KBr) ν(NO) 1739, ν(BF) 1084, 1055; mass spectrum ((+)-FAB, 7 kV, Ar, 3-nitrobenzyl alcohol; m/Z (relative intensity), ^{187}Re, ^{35}Cl) 698 (M^+, 26%), 649 ($M^+ - CH_2Cl$, 84%), 436 ($M^+ - PPh_3$, 59%), 262 (Ph_3P^+, 63%), 154 (100%). Compound **2** forms as one geometric isomer, and decomposes over the course of 24 h in CH_2Cl_2; analytically pure samples have not been obtained: Found: C, 45.06; H, 4.11; Cl, 7.89. $C_{29}H_{32}BCl_2F_4NOPRe$ calcd.: C, 44.34; H, 4.11; Cl, 9.03%.

12 Data on **3** (CD_2Cl_2, −85 °C): ^{1}H NMR (δ) 1.60 (s, 5Me); $^{13}C\{^1H\}$ NMR (ppm) 101.35 (s, *C*$_5$Me$_5$), 9.74 (s, C$_5$*Me*$_5$); $^{31}P\{^1H\}$ NMR (ppm) 22.2 (s); ^{19}F NMR (δ) −152.16 (s). We have not been able to identify a fourth ligand in **3**. No NMR evidence is observed for ether or BF_4^- coordination, and an identical species forms under argon. Addition of $[Ph_3P{=}N{=}PPh_3]^+$ I^- immediately gives iodide complex (η^5-C_5Me_5)Re(NO)(PPh$_3$)(I). We are reluctant to formulate **3** as the unencumbered Lewis acid $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)]^+$ BF_4^- (**5**).

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14 Data on **6**: ^{1}H NMR (δ, CD_2Cl_2) 7.54–7.26 (m, 15H), 2.44 (s, ICH$_3$), 1.85 (s, 5Me); $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2) 15.8 (s); IR (cm^{-1}, nujol) ν(N≡O) 1681. Ether precipitates **6** (72%) as a tan powder of ca. 90% purity; decomposition occurs over several hours in chlorinated solvents.

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