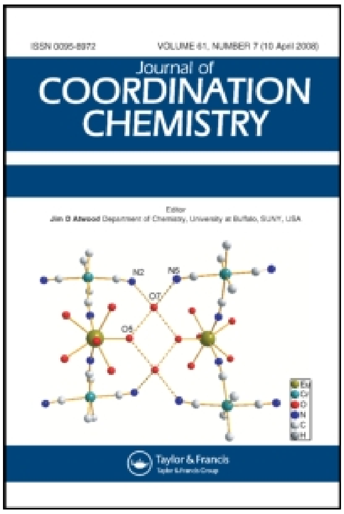

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SYNTHESES AND REACTIONS OF THE COMPLEXES (η^5-C_5Me_5)Re(CO)$_2$($C_6CL_{5-n}H_n$)Cl (n = 2,3): COMPOUNDS DERIVED FROM INITIAL C—CI ACTIVATION

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SYNTHESES AND REACTIONS OF THE COMPLEXES (η^5-C_5Me_5)Re$(CO)_2$($C_6Cl_{5-n}H_n$)Cl (n = 2, 3): COMPOUNDS DERIVED FROM INITIAL C—Cl ACTIVATION

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The UV irradiation of (η^5-C_5Me_5)Re$(CO)_3$ in the presence of 1,2,4,5-$C_6Cl_4H_2$ and 1,3,5-$C_6Cl_3H_3$ ($\lambda = 350$ nm, hexane solution) effected intramolecular C—Cl activation, generating the complexes *trans*-(η^5-C_5Me_5)Re$(CO)_2$(2,4,5-$C_6Cl_{5-n}H_n$)Cl, ((**1**), n = 2; (**2**), n = 3), respectively. Complex (**1**) dissolved in polar organic solvents produces, an equilibrium mixture with its *cis* isomer. The reaction of (**1**) with $AgBF_4$, in acetonitrile, led to formation of the cationic complex [*cis*-(η^5-C_5Me_5)Re$(CO)_2$(2,4,5-$C_6Cl_3H_2$)(MeCN)]$^+$. The tetramethylfulvene complex (η^6-$C_5Me_4CH_2$)Re$(CO)_2$(2,4,5-$C_6Cl_3H_2$) (**3**) was obtained by reacting the cationic complex with the fluorinating agent $Et_3N \cdot 3HF$.

Keywords: C—Cl activation; Tetramethylfulvene; Rhenium; Complexes

INTRODUCTION

As part of a continuing investigation on the reactions of pentamethylcyclopentadienyl rhenium carbonyl complexes, we have recently turned our attention to the insertion products of the photogenerated fragment

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$(\eta^5\text{-}C_5Me_5)Re(CO)_2$ into the C—F, C—H and C—Cl bonds of halogenated arenes [1–3]. The photochemical reaction of $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ in neat C_6F_6 afforded the fulvene complex $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(C_6F_5)$ as a result of an insertion into a C—F bond of hexafluorobenzene and concomitant insertion into a methyl C—H bond [1]. With partially fluorinated benzenes such as C_6F_5H or 1,2,4,5-$C_6F_4H_2$, under similar reaction conditions, the tricarbonyl complex yielded, instead, only C—H oxidative addition complexes *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2(C_6F_4R)H$ (R = F and H) [2]. More recently, we have found that photolysis of $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ in pentachlorobenzene furnished the tetrachlorophenyl chloro complex *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2(2,3,4,5\text{-}C_6Cl_4H)Cl$, which was isomerized to the *cis* isomer. The structure of both isomers was established by spectroscopy and X-ray crystallography [3]. As far as we know, our work and a paper of Sutton and Leiva dealing with the photochemistry of the dinitrogen complexes $(\eta^5\text{-}C_5Me_5)Re(CO)(L)N_2$, (L = phosphites and PMe_2Ph) with chlorobenzene [4], are the only previous publications related to this work reported in the literature. By considering our interest on the chemistry and photochemistry of the rhenium complexes and the significant interest in the reductive dechlorination of aryl chlorides, mainly for the neutralization of toxic polychloroaromatics (*e.g.*, polychlorobiphenyls, PCBs) in the enviroment [5], we were prompted to study further developments of the photochemistry of $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ in presence of lower chlorinated benzenes. We are also including the reactions of *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2(2,4,5\text{-}C_6Cl_3H_2)Cl$ with $AgBF_4$ to produce the cationic complex $[cis\text{-}(\eta^5\text{-}C_5Me_5)Re(CO)_2(2,4,5\text{-}C_6Cl_3H_2)(MeCN)]^+$ and the transformation of the latter to the fulvene complex $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(2,4,5\text{-}C_6Cl_3H_2)$.

EXPERIMENTAL

All manipulations were carried out under nitrogen using standard Schlenk techniques. Photolysis reactions were carried out at 350 nm with a Rayonet RPR 100 photoreactor in Pyrex tubes. All solvents were purified and dried by conventional methods [6], and distilled under nitrogen prior to use. $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ was prepared according to the procedures reported by Gladysz [7]. 1,2,4,5-Tetrachlorobenzene (98%) and 1,3,5-trichlorobenzene (99%) from Aldrich were used as received. Infrared spectra were recorded in solution (NaCl cell) on a Perkin-Elmer FT-1605 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 instrument.

All ^1H NMR chemical shifts were referenced using the chemical shifts of residual solvent resonances ($CDCl_3$, δ 7.27). ^{13}C NMR chemical shifts were referenced to solvent peaks ($CDCl_3$, δ 77.0). Mass spectra and elemental analyses were obtained at the Chemistry Department of the University of York, England, and the Centro de Instrumentación of Pontificia Universidad Católica de Chile, Santiago, Chile.

Preparation of *Trans*-(η^5-C_5Me_5)$Re(CO)_2$(2,4,5-$C_6Cl_3H_2$)Cl (1)

(η^5-C_5Me_5)$Re(CO)_3$ (100 mg, 0.247 mmol) was dissolved in 40 mL of a saturated solution of 1,2,4,5-tetrachlorobenzene in hexanes. The solution was bubbled with nitrogen for 10 min and then irradiated at $\lambda = 350$ nm for 18 h. The mixture turned yellow and yellow–orange crystals were formed in the wall of the tube overnight. The crystals of **(1)** were separated from the solution and washed with cold hexanes. The solution which contains the unreacted tricarbonyl and dissolved product was evaporated to dryness under vaccum. The residue was column chromatographed over silica gel 60 (Merck). Hexanes washes a mixture of tetrachlorobenzene and the unreacted (η^5-C_5Me_5)$Re(CO)_3$ and the yellow band which contains complex **(1)** was eluted with a mixture of hexanes-CH_2Cl_2 (9 : 1). The residue obtained after solvent evaporation, and the crystals were dissolved in the minimum of CH_2Cl_2, and a layer of hexanes was slowly poured into the flask. After 24 h at −10°C, yellow–orange crystals were formed. Yield: 48 mg (33%). The compound decomposed over 130°C. Elemental analysis ($C_{18}H_{17}O_2Cl_4Re$); calculated: C, 36.44; H, 2.86%. Found: C, 36.25; H, 2.61%. MS (electron impact, based on ^{187}Re and ^{35}Cl) m/z: 592 (M^+), 564 (M^+—CO), 536 (M^+—2CO). IR (CH_2Cl_2, cm^{-1}): 2044 (m) and 1962 (vs) (ν(CO)). ^1H NMR ($CDCl_3$) δ: 1.76 (s, 15H, C_5Me_5), 7.51 (s, 1H, $C_6Cl_3H_2$), 7.81 (s, ^1H, $C_6Cl_3H_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 9.6 (s, C_5Me_5), 104.7 (s, C_5Me_5), 128.9, 130.6, 141.3, 145.3, 147.2 and 148.3, ($C_6Cl_3H_2$), 193.0 (s, CO).

Preparation of *Trans*-(η^5-C_5Me_5)$Re(CO)_2$(3,5-$C_6Cl_2H_3$)Cl (2)

A procedure similar to that described for the above complex gave **(2)** as red crystals in 23% yield. This complex started to decompose above 125°C. Elemental analysis ($C_{18}H_{18}O_2Cl_3Re$); calculated: C, 38.68; H, 3.25%. Found: C, 38.80; H, 3.13%. MS (electron impact, based on ^{187}Re and ^{35}Cl) m/z: 558(M^+), 530(M^+—CO), 502 (M^+—2CO). IR (CH_2Cl_2, cm^{-1}): 2038 (m) and 1960 (vs) (ν(CO)). ^1H NMR ($CDCl_3$) δ: 1.73 (s, 15H, C_5Me_5), 7.10 (m, 1H, $C_6Cl_2H_3$), 7.44 (m, 2H, $C_6Cl_2H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$)

δ: 9.4 (s, C_5Me_5), 103.8 (s, C_5Me_5), 125.3, 130.4, 134.4 and 142.7, ($C_6Cl_2H_3$), 196.4 (s, CO).

Preparation of [*Cis*-(η^5-C_5Me_5)Re(CO)$_2$(2,4,5-$C_6Cl_3H_2$)(MeCN)]BF_4

Complex (**1**) (88 mg, 0.147 mmol) was dissolved in 10 mL of dry CH_3CN at room temperature. To this orange–red solution an excess of solid $AgBF_4$ (93 mg, 0478 mmol) was added. The mixture was stirred for four h, at 40°C. After this time the IR spectrum showed the disappearance of the starting complex and the presence of only two ν(CO) absorptions at 2047 and 1976 cm^{-1}. The solvent was pumped off and the residual brown oily solid was dissolved in CH_2Cl_2 and washed with a saturated aqueous solution of NaCl. Evaporation of CH_2Cl_2 yielded a light yellow solid which was crystallized from CH_3CN–Et_2O at −10°C. The cationic complex was isolated as yellow–white microcrystalline solid in 93% yield (94mg). The extreme moisture-sensitivity of this complex, precuded us from measuring the melting point and obtaining the elemental analysis. IR (CH_3CN, cm^{-1}): 2047 (vs) and 1976 (s) (ν(CO)). ^1H NMR (CD_3CN) δ: 2.15 (s, 15H, C_5Me_5), 2.60 (s, 3H, CH_3CN), 7.23 (s, 1H, $C_6Cl_3H_2$), 7.72 (s, 1H, $C_6Cl_3H_2$). $^{13}C\{^1H\}$ NMR (CD_3CN) δ: 4.5 (s, CH_3CN), 10.5 (s, C_5Me_5), 110.5 (s, C_5Me_5), 136.6 (s, CH_3CN), 130.7, 131.6, 132.0, 143.6, 145.4 and 146.4 ($C_6Cl_3H_2$), 199.0 and 200.7 (s, CO).

Isomerization of (1)

Complex ***trans*-1** was dissolved in dry acetonitrile and monitored by IR spectroscopy at room temperature. After 15 h of stirring, the ν(CO) bands observed at 2044 and 2024 cm^{-1} for the *trans* and *cis* isomers, respectively, remain unchanged. A ratio 1:0.8 (*cis* to *trans*) was determined by quantification of the ν(CO) absorption bands by FTIR. In $CDCl_3$ a ratio of 0.3:1 was found by integration of the (η^5-C_5Me_5) resonances in the ^1H NMR spectrum. IR (CH_2Cl_2, cm^{-1}): 2025 (vs) and 1950 (s) (ν(CO)), IR (MeCN, cm^{-1}): 2024 (vs) and 1949 (s) (ν(CO)). ^1H NMR ($CDCl_3$) δ: 2.03 (s, 15H, C_5Me_5), 7.04 (s, 1H, $C_6Cl_3H_2$), 7.51 (s, 1H, $C_6Cl_3H_2$).

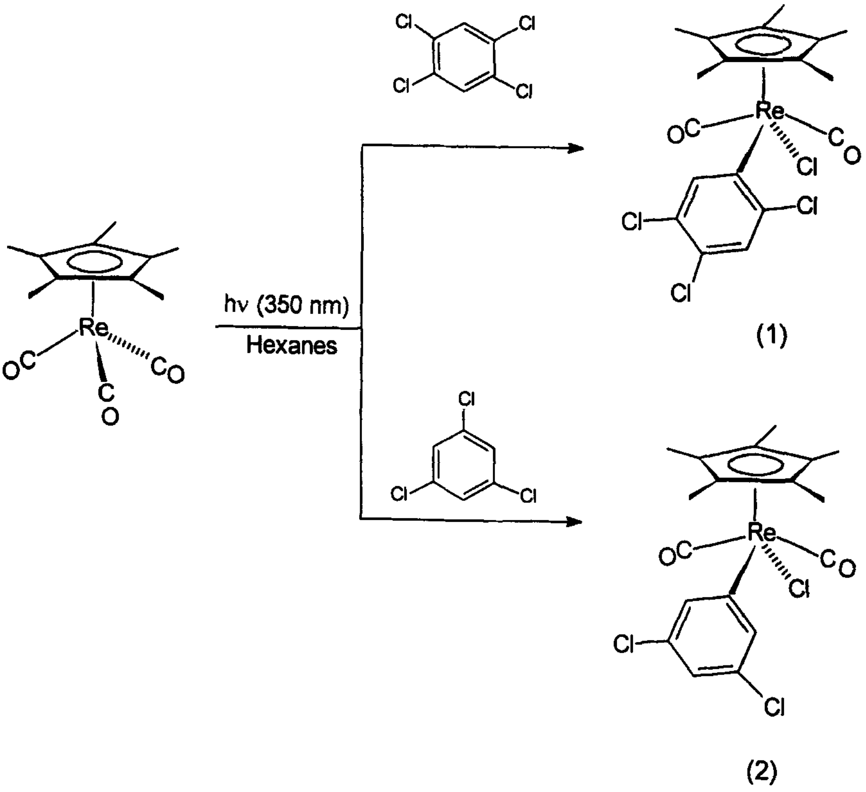
Preparation of (η^6-$C_5Me_4CH_2$)Re(CO)$_2$(2,4,5-$C_6Cl_3H_2$) (3)

To a solution of [*cis*-(η^5-C_5Me_4)Re(CO)$_2$(2,4,5-$C_6Cl_3H_2$)(MeCN)]BF_4 (90 mg, 0.134 mmol) in THF (10 mL) 4.2 mL (0.515 mmol) a solution of Et3N · 3HF (Aldrich, prepared by dissolving 0.1 mL in 5 mL of THF), was added by syringe. The mixture was stirred at room temperature until the IR spectrum showed the disappearance of the cation and new strong bands at 1989 and 1907 cm^{-1}. The THF was pumped off and the oily residue was extracted with several portions of hexanes and filtered through Celite. **(3)** was isolated as yellow needles after crystallization from hexanes at −15°C (27 mg, 36% yield). Complex **(3)** decomposes above 138°C without melting. Elemental analysis ($C_{18}H_{16}O_2Cl_3Re$); calculated: C, 38.81; H, 2.88%. Found: C, 38.92; H, 3.00% MS (electron impact, based on ^{187}Re and ^{35}Cl) m/z: 556(M^+) and 500 (M^+—2CO). IR (hexane, cm^{-1}): 2004 (s) and 1923 (vs) (ν(CO)). ^1H NMR ($CDCl_3$) δ: 1.77 (s, 6H, $C_5Me_4CH_2$), 2.00 (s, 2H, $C_5Me_4CH_2$), 7.40 (s, 1H, $C_6Cl_3H_2$), 7.71 (s, 1H, $C_6Cl_3CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 9.3 (s, $C_5Me_4CH_2$), 9.8 (s, $C_5Me_4CH_2$), 47.9 (s, $C_5Me_4CH_2$), 107.5 (s, $C_5Me_4CH_2$), 108.3 (s, $C_5Me_4CH_2$), 128.6, 128.9, 129.5, 145.6 and 148.1 ($C_6Cl_3H_2$), 199.2 (s, CO).

RESULTS

Photolysis of (η^5-C_5Me_5)Re(CO)$_3$ ($\lambda = 350$ mm) in a saturated hexane solution of 1,2,4,5-$C_6Cl_4H_2$ or 1,3,5-$C_6Cl_3H_3$ at room temperature, for 18 h, produced one major dicarbonyl product (see Scheme 1). Much longer irradiation times produced significant amounts of the dichloro complex (η^5-C_5Me_5)Re(CO)$_2$Cl$_2$ [8]. In both cases, the products were isolated as air stable yellow–orange crystals by recrystallization from CH_2Cl_2/hexane at −10°C and were identified as *trans*-(η^5-C_5Me_5)Re(CO)$_2$(2,4,5-$C_6Cl_3H_2$)Cl, **(1)** and *trans*-(η^5-C_5Me_5)Re(CO)$_2$(3,5-$C_6Cl_2H_3$)Cl, **(2)**. These crystalline solids are indefinitely stable under nitrogen at room temperature and appear not to deteriorate when exposed to air over a period of hours. They are stable, in the solid state at room temperature with respect to isomerization. However, complex **(1)** at room temperature, in $CDCl_3$ and CH_3CN solutions interconvert to the *cis* isomer, 0.3 : 1 and 1 : 0.8, *cis* to *trans* equilibrium ratios were determined by ^1H NMR and FTIR, after 15 h, respectively. Attempts to isomerize **(2)** under similar experimental conditions were unsuccessful, the complex was recovered unreacted. In boiling MeCN the complex slowly decomposed to an unidentified carbonyl containing complex, which showed absorptions at 1927 and 1840 cm^{-1} in the IR spectrum, in MeCN.

Complexes **(1)** and **(2)** exhibit only two ν(CO) absorptions in the IR spectra at about 2044 and 1960 cm^{-1} (in CH_2Cl_2 solution), and the lower wavenumber one is much more intense. On this criterion, as well as the



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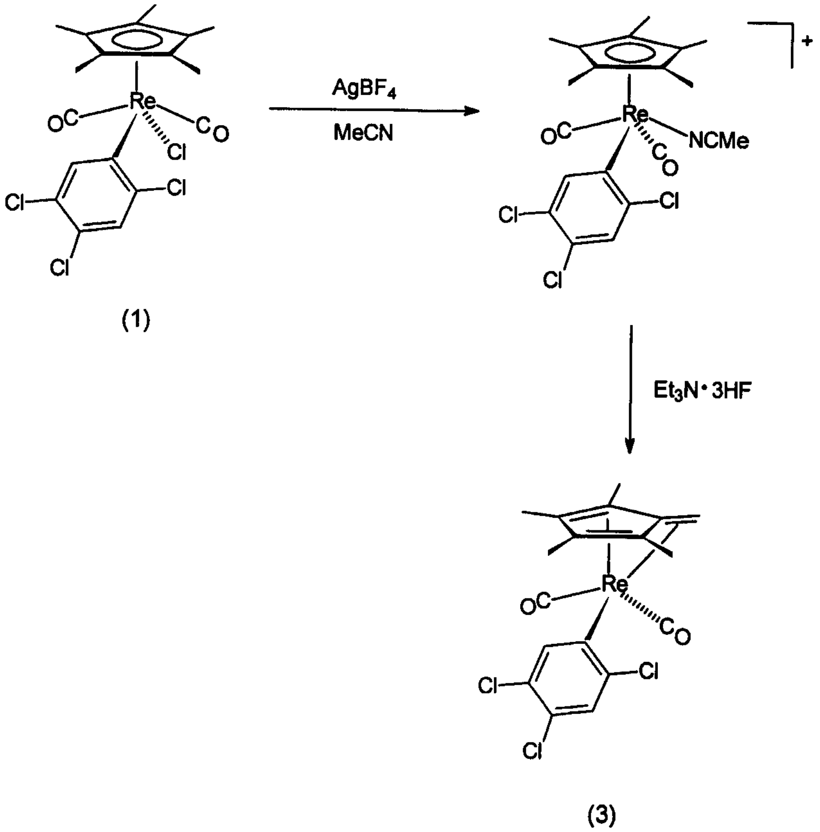
correspondence between our IR values and those reported for *trans*-(η^5-C_5Me_5)$Re(CO)_2(2,3,4,5$-$C_6Cl_4H)Cl$ [3], *trans*-(η^5-C_5Me_5)$Re(CO)_2(C_6H_5)I$ [9], *trans*-(η^5-C_5H_5)$Re(CO)_2(C_6F_5)Br$ [10], *trans*-(η^5-C_5Me_5)$Re(CO)_2(Et)Br$ [11] and *trans*-(η^5-C_5Me_5)$Re(CO)_2(Me)I$ [12], we consider that our products are also the *trans* isomers. The ^1H NMR spectra, in addition to (η^5-C_5Me_5), show the expected resonances for the protons of the chlorinated aryl ligands. The appearance of a single resonance for the CO in the $^{13}C\{^1H\}$ NMR spectra is further evidence for the *trans* orientation of the carbonyl ligands in this type of molecule. The mass spectra show the molecular ion for both complexes and fragments corresponding to the successive loss of the CO ligands.

The complex *cis*-(η^5-C_5Me_5)$Re(CO)_2(2,4,5$-$C_6Cl_3H_2)Cl$ was not isolated pure and was identified by IR and ^1H NMR, in the mixture with the *trans* isomer (see experimental section).

The cationic complex $[cis\text{-}(\eta^5\text{-}C_5Me_5)Re(CO)_2(2,4,5\text{-}C_6Cl_3H_2)(MeCN)]^+$ was prepared by reaction of **(1)** with $AgBF_4$ in acetonitrile, at 40°C (see Scheme 2). This compound, isolated as a red-brown microcrystalline solid in almost quantitative yield, did not give satisfactory elemental analysis, even after several crystallizations from MeCN/ether, presumably due to its extreme moisture sensitivity. For the above reason, the cation was only characterized by IR and NMR. The $\nu(CO)$ absorptions at 2047 and $1976\,cm^{-1}$ in MeCN, exhibited an intensity pattern indicative of a *cis* "four-legged piano stool" geometry, that is, the lower wavenumber band is the less intense of the pair. A similar pattern has been observed for the analogous complex $[cis\text{-}(\eta^5\text{-}CMe_5)Re(CO)_2(C_6F_5)(MeCN)]^+$ reported previously from our laboratory [1]. A CH_2Cl_2 solution of this complex appears not to undergo isomerization at room temperature, though it does



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not survive under these conditions for more than 6 h. The most interesting feature of the NMR data obtained for this complex, is the presence of two signals in the carbonyl region observed in the $^{13}C\{^1H\}$ NMR spectrum. The inequivalency of the CO's, is further evidence for the *cis* orientation of these complexes.

The tetramethylfulvene complex **(3)** was isolated as orange microcrystals after recrystallization from hexane. It is stable as a solid and in solutions of organic solvents. Spectroscopic measurements of **(3)** clearly indicate the presence of the tetramethylfulvene ligand. Thus, there are two singles at δ 1.77 and 2.00 for the two distinct methyl groups and a low field singlet at δ 4.06, assigned to the methylene group of the fulvene ligand. The above assignment was confirmed by ^{13}C NMR the spectrum of this complex shows resonances at δ 9.3 and 9.8, and 47.9 for the methyls and methylene carbons, respectively. Both ^1H and ^{13}C NMR parameters found for this complex are in agreement with those determined for the closely related complexes $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(C_6X_4H)$, $(X = F$ and $Cl)$ [2,3], and $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2(C_6F_4R)$, $(R = F$ and $CF_3)$ [1]. The mass spectrum of **(3)** shows peaks for the M^+, $[M^+\text{—}CO]$ and $[M^+\text{—}2CO]$ fragments.

DISCUSSION

The $(\eta^5\text{-}C_5Me_5)Re(CO)_2$ fragment is often generated photochemically from the tricarbonyl [13] or dicarbonyl(dinitrogen) [14] complexes. Recently we demonstrated that the dominant photochemical reaction of $(\eta^5\text{-}C_5Me_5)$ $Re(CO)_3$ with C_6F_5H and 1,2,3,4-$C_6F_4H_2$ is C—H bond activation to form the corresponding hydrido complex $(\eta^5\text{-}C_5Me_5)Re(CO)_2(C_6F_4R)H$, $(R = F$ and H) [2], whereas the reaction with C_6Cl_5H is C—Cl bond activation to form $(\eta^5\text{-}C_5Me_5)Re(CO)_2(C_6Cl_4H)Cl$ [3]. In an anologous manner to the latter reaction, the current paper demonstrate that the dominant photochemical reaction of 1,2,4,5-tetrachlorobenzene and 1,3,5-trichlorobenzene with the tricarbonyl complex, is also C—Cl bond activation. Under the experimental conditions used, neither coordination nor C—H bond activation products of the chlorinated benzenes was observed in these reactions. Instead the dichloro complex *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Cl_2$ [8] is formed upon longer irradiation times, presumably by photodecomposition of the C—Cl activation products.

The exclusive appearance of the *trans* isomers for these C—Cl activation products is not unusual considering that all photochemically induced, oxidative addition reactions to the $(\eta^5\text{-}C_5Me_5)Re(CO)_2$ fragment occur under this stereochemistry [2, 15]. We have also observed that *cis* isomers of complexes possessing a four-legged piano-stool type of structure, are readily isomerized to the *trans* isomers by UV irradiation [8]. It may be possible that the kinetic products for these reactions are the *cis* isomers, but they isomerize to the thermodynamically more stable *trans* isomers. The *trans* to *cis* isomerization observed for complex (1) in polar organic solvents, occurs in a similar manner to that observed for its tetrachlorophenyl analog *trans*-(η^5-C_5Me_5)Re(CO)$_2$(C_6Cl_4H)Cl [3] and contrasts with the unidirectional thermal isomerization (*cis* to *trans*) observed for (η^5-C_5H_4R)Re(CO)$_2$Br$_2$ [16] and (η^5-C_5H_5)Re(CO)$_2$H$_2$ [17] when dissolved in the same type of solvents. The reluctance of complex (2) to interconvert to the *cis* isomer, is a matter of further study in this field.

The formation of the cationic complex [*cis*-(η^5-C_5Me_5)Re(CO)$_2$(2,4,5-$C_6Cl_3H_2$)(MeCN)]$^+$ from the reaction of (1) with $AgBF_4$ in acetonitrile, (see Scheme 2), is associated with the isomerization of the precursor. Only the complex *cis*-(η^5-C_5Me_5)Re(CO)$_2$(2,4,5-$C_6Cl_3H_2$)Cl, which is more polar than its *trans* isomer, reacts with $AgBF_4$, this feature also explain the reluctance of (2) to form the cation, in reaction with silver salt.

The reaction of the cation with $Et_3N \cdot 3HF$, which has been recommended as an effective fluorinating agent [18], resulted in the formation of the new fulvene complex (η^6-$C_5Me_4CH_2$)Re(CO)$_2$(2,4,5-$C_6Cl_3H_2$) (3) instead of the neutral fluoro derivative (η^5-C_5Me_5)Re(CO)$_2$(2,4,5-$C_6Cl_3H_2$)F. The latter compound presumably eliminated HF which is scavenged by the glassware rather than reacting with the product or precursor. Support for the above assignment is provided by HF formation observed in the reaction of the photogenerated fragment (η^5-C_5Me_5)Re(CO)$_2$ with C_6F_6 to produce the analogous complex (η^6-$C_5Me_4CH_2$)Re(CO)$_2$(C_6F_5) [1], thus, the thermodynamic driving force for these reactions is the simultaneous C—H activation of one of the ring methyl groups and the release of HF.

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