Reactions of (Cyclopentadienyl)rhenium Halide Complexes (η^5-C_5H_5)Re(NO)(PPh_3)(X) with *n*-BuLi/TMEDA; Generation and Methylation of Lithio- and Dilithiocyclopentadienyl Ligands

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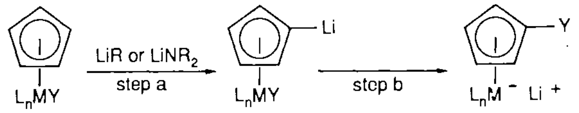
Reactions of halide complexes (η^5-C_5H_5)Re(NO)(PPh_3)(X) [1, X = Cl (a), Br (b), I (c)] with *n*-BuLi/TMEDA (1.1 equiv., THF, −78°C) give lithiocyclopentadienyl complexes (η^5-C_5H_4Li)-Re(NO)(PPh_3)(X) (2), as assayed by NMR and subsequent methylation to (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(X) (3). Reaction of 2a with further *n*-BuLi/TMEDA affords (0°C) dilithiocyclopentadienyl complex (η^5-1,3-$C_5H_3Li_2$)Re(NO)(PPh_3)(Cl) (4), as assayed by NMR and methylation to [η^5-1,3-$C_5H_3(CH_3)_2$]Re(NO)(PPh_3)-(Cl) (5). No significant migration of the halide ligand to the lithiocyclopentadienyl ligand is observed. New compounds 3a−c and 5 are characterized by NMR (^{1}H, ^{13}C, ^{31}P), IR, mass spectrometry, and microanalysis.

There has been a great deal of recent interest in reactions of cyclopentadienyl transition-metal complexes with strong bases such as lithium alkyls and lithium dialkylamides[1−8]. Both synthetically useful[1−4] and mechanistically novel[5−8] processes have been discovered. Often, cyclopentadienyl ligand deprotonation occurs, giving a lithiocyclopentadienyl ligand (eq i, step a). Depending upon the nature of the remaining ligands, subsequent rearrangement to a metal centered anion can occur (eq i, step b)[5−8]. These migrations are now known to be relatively common, and resemble well-established anionic rearrangements of organic compounds[9].

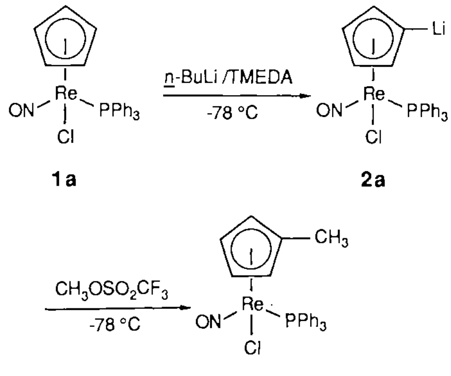


(i)

Migratory aptitudes can provide valuable information on rearrangement mechanisms. The migration of silyl or germyl ligands to lithiocyclopentadienyl ligands has been previously reported by Graham[5a], Malisch[5c], Berryhill[5d], Pasman[5g], Pannell[5h] and ourselves[8]. Similar migrations of acyl ligands have been described by ourselves[6] and Davies[5f]. We have also reported related examples of hydride ligand migrations[7]. However, data on the migratory aptitudes of halide ligands are lacking. We have recently become interested in the physical and chemical properties of (cyclopentadienyl)rhenium halide complexes (η^5-C_5H_5)Re(NO)(PPh_3)(X) (1)[10] and alkyl halide complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(XR)]$^+BF_4^-$[11]. Hence, we set out to study reactions of the former with alkyllithium reagents. We anticipated either initial deprotonation to give a lithiocyclopentadienyl ligand, or halogen/lithium exchange to give the previously characterized rhenium anion Li^+ [(η^5-C_5H_5)-Re(NO)(PPh_3)]$^-$[7].

Results

Chloride complex (η^5-C_5H_5)Re(NO)(PPh_3)(Cl) (**1a**) was treated with *n*-BuLi/TMEDA (1.1 equiv.) in THF at −78°C. Subsequent addition of $CH_3OSO_2CF_3$ gave methylcyclopentadienyl complex (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(Cl) (**3a**) in 78% yield after workup (eq ii). The ^{1}H- and ^{13}C-NMR spectra of **3a** showed patterns characteristic of a monosubstituted cyclopentadienyl ligand (Table)[6−8]. The corresponding bromide and iodide complexes (η^5-C_5H_5)-Re(NO)(PPh_3)(X) [X = Br (**1b**), I (**1c**)] gave identical chemistry, and the corresponding methylcyclopentadienyl complexes (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(X) [X = Br (**3b**), I (**3c**); Table] were isolated in 68 and 65% yields, respectively.



1a **2a** **3a**

(ii)

The spectroscopic detection of intermediates in the above transformations was attempted. The reaction of **1a** with *n*-BuLi/TMEDA was monitored at −78°C by ^{31}P NMR. Complex **1a** (17.79 ppm) immediately disappeared, and a new complex (**2a**, 21.60 ppm) appeared. Such ca. 4 ppm downfield shifts have been previously shown to be characteristic of cyclopentadienyl ligand monolithiation[6−8], and subsequent addition of $CH_3OSO_2CF_3$ gave methylcyclopentadienyl complex **3a** as above. Hence, the intermediate was assigned the structure (η^5-C_5H_4Li)Re(NO)(PPh_3)(Cl) (**2a**). Analogous ^{31}P-NMR experiments were conducted with bromide complex **1b** (16.07 ppm) and iodide complex **1c** (14.13 ppm). In both cases, lithiocyclopentadienyl complexes (η^5-C_5H_4Li)-Re(NO)(PPh_3)(X) (**2b**, 19.69 ppm; **2c**, 17.26 ppm) rapidly formed and underwent clean methylation.

In a separate experiment, lithiocyclopentadienyl complex **2a** was allowed to warm. Above 0°C, decomposition occurred to give some material (10−20%) with ^{31}P-NMR resonances (45−47 ppm) characteristic of rhenium-centered anions Li^+ [(η^5-C_5H_4X)Re(NO)-(PPh_3)]$^-$. However, due to the low yield we were not able to spectroscopically (or by chemical trapping) distinguish this material from the parent anion Li^+ [(η^5-C_5H_5)Re(NO)(PPh_3)]$^-$. Identical results were obtained from analogous experiments with lithiocyclopentadienyl bromide and iodide complexes **2b** and **2c**.

Interestingly, lithiocyclopentadienyl chloride complex **2a** reacted with another equivalent of *n*-BuLi/TMEDA (0°C, 30 min) to give *di*lithiocyclopentadienyl complex (η^5-1,3-$C_5H_3Li_2$)Re(NO)(PPh_3)-(Cl) (**4**, eq iii), as assayed by ^{31}P NMR (26.22 ppm) and subsequent methylation (CH_3I, 0°C) to dimethylcyclopentadienyl complex [η^5-1,3-$C_5H_3(CH_3)_2$]Re(NO)(PPh_3)(Cl) (**5**, 18.38 ppm). In a preparative experiment, **5** was isolated in 63% yield. The assignment of the 1,3-substitution pattern was made on the basis of a split IR C−H

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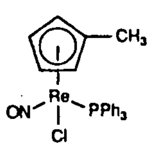
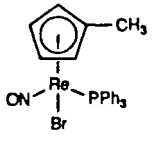
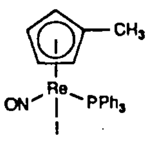
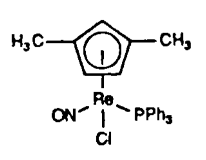
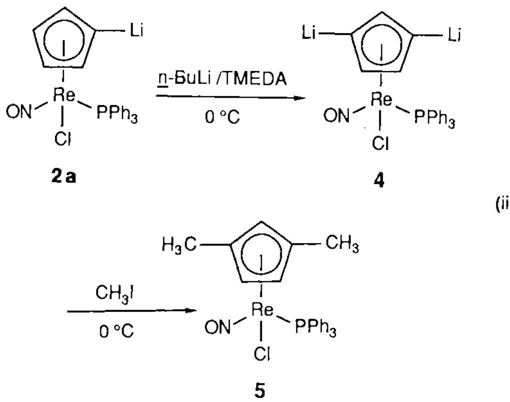
Table. NMR characterization of new cyclopentadienyl-substituted complexes

Complex	IR (cm^{-1}, KBr)	^1H NMR (δ, $CDCl_3$)[a]	$^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$)[b]	$^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$)[c]
 **3a**	$\nu_{N\equiv O}$ 1653 s	7.54-7.37 (m, 3 C_6H_5); C_5H_4 (br m) at 5.57, 5.52, 4.54, 4.06; 1.80 (s, CH_3).	PC_6H_5 at 135.28 (d, J = 53.5, ipso), 134.38 (d, J = 11.3), 130.92 (s, p), 128.90 (d, J = 11.3); C_5H_4 at 119.71 (s, ipso), 93.80 (s), 86.26 (br s), 85.10 (s), 84.87 (d, J = 6.6); 13.74 (s, CH_3).	17.98 (s)
 **3b**	$\nu_{N\equiv O}$ 1654 s	7.54-7.39 (m, 3 C_6H_5); C_5H_4 (br m) at 5.51, 5.42, 4.57, 4.18; 1.97 (s, CH_3).	PC_6H_5 at 135.71 (d, J = 53.4, ipso), 134.39 (d, J = 11.3), 130.88 (s, p), 128.85 (d, J = 11.2); C_5H_4 at 117.08 (s, ipso), 93.39 (s), 88.30 (s), 85.54 (s), 84.32 (s); 14.23 (s, CH_3).	16.61 (s)
 **3c**	$\nu_{N\equiv O}$ 1655 s	7.54-7.36 (m, 3 C_6H_5); C_5H_4 (br m) at 5.42 (1H), 5.21 (1H), 4.55 (2H); 2.18 (s, CH_3).	PC_6H_5 at 136.57 (d, J = 53.8, ipso), 134.56 (d, J = 10.1), 130.94 (s, p), 128.90 (d, J = 10.1); C_5H_4 at 112.12 (s, ipso), 92.70 (d, J = 2.5), 91.64 (s), 86.61 (s), 84.47 (d, J = 2.5); 14.92 (s, CH_3).	14.60 (s)
 **5**	$\nu_{N\equiv O}$ 1642 s δ_{C-H} 750 m 738 m	7.58-7.34 (m, 3 C_6H_5); C_5H_3 (br m) at 5.49, 5.36, 3.42; 1.88 (s, CH_3); 1.69 (s, CH_3).	PC_6H_5 at 135.50 (d, J = 53.2, ipso), 134.06 (d, J = 9.5), 130.51 (s, p), 128.54 (d, J = 11.3); C_5H_3 at 122.83 (s, ipso), 100.88 (s, ipso), 91.11 (s), 86.45 (d, J = 6.9), 79.63 (s); 2 CH_3 at 13.83 (s), 12.55 (s).	18.38 (s)

[a] At 300 MHz and ambient probe temperature and referenced to internal $(CH_3)_4Si$; all couplings (Hz) are to hydrogen. – [b] At 75 MHz and ambient probe temperature and referenced to internal $(CH_3)_4Si$; all couplings are to phosphorus. – [c] At 32.2 MHz and ambient probe temperature and referenced to external 85% H_3PO_4.

bending absorption at 750 cm^{-1}. Based upon extensive data on substituted ferrocenes[12], the 1,2-isomer would show a single C—H bending absorption in this region. Lithiocyclopentadienyl complexes **2b** and **2c** did not react with additional *n*-BuLi/TMEDA at 0°C.



(iii)

Discussion

Although the deprotonation of cyclopentadienyl ligands by alkyllithium reagents was reported soon after the discovery of ferrocene[13], only very recently have migrations of ancillary ligands to lithiocyclopentadienyl ligands been recognized as a class of reactions. This study establishes that halide ligands have, at best, poor migratory aptitudes. Comparison to previous work with (cyclopentadienyl)rhenium complexes of the formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)$ gives the following order of ligand migratory aptitudes: acyl > silyl > hydride > halide ⩾ alkyl. Our new results support the previous suggestion by Berryhill[5d] and ourselves[6] that the best migrating ligands should have low-lying acceptor orbitals.

Cyclopentadienyl-halide complexes **1** do, however, rapidly undergo deprotonation by *n*-BuLi/TMEDA. Comparison with the studies cited above gives the relative rates halide ≃ acyl > alkyl ⩾ silyl ≃ hydride. This correlates well with the electron-withdrawing capabilities of these ligands. The strong electron-withdrawing capability of the chloride ligand likely facilitates further lithiation to give the $1,3\text{-}C_5H_3Li_2$ ligand. The polylithiation of ferrocene has been reported[14], but this is to our knowledge the first example of a *cleanly* generated $1,3\text{-}C_5H_3Li_2$ ligand.

Finally, we note that lithiocyclopentadienyl metal complexes are useful intermediates for the synthesis of bi- and polymetallic complexes[4]. Further studies of reactions of (cyclopentadienyl)rhenium complexes with strong bases are in progress.

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Experimental

General: All reactions were conducted under dry N_2. — IR spectra: Perkin Elmer 1500 (FT) spectrometer. — NMR spectra: Varian XL-300 (^{1}H, ^{13}C) and FT-80A (^{31}P) spectrometers. — Mass spectra: VG 770 spectrometer. — Microanalyses: Galbraith Laboratories.

Solvents were purified as follows: THF and benzene, distilled from Na/benzophenone; hexane, distilled from Na; CH_2Cl_2 and $CDCl_3$, distilled from P_2O_5; ethyl acetate, used as received. Base *n*-BuLi (Aldrich) was standardized before use[15]. TMEDA (Aldrich) and $CH_3OSO_2CF_3$ (Aldrich) were distilled from CaH_2. CH_3I was distilled from P_2O_5 and stored over Cu. Halide complexes (η^5-C_5H_5)Re(NO)(PPh_3)(X) were prepared as previously described[10a].

Preparation of (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(Cl) (**3a**): A Schlenk tube was charged with (η^5-C_5H_5)Re(NO)(PPh_3)(Cl) (**1a**, 0.17 g, 0.21 mmol), THF (10 ml), and a stir bar. The solution was cooled to −24°C, and TMEDA (0.031 g, 0.27 mmol) and *n*-BuLi (0.11 ml, 2.4 M in hexane) were added with stirring. After 0.5 h, $CH_3OSO_2CF_3$ (0.085 g, 0.52 mmol) was added. After 0.5 h, the solution was transferred to a round bottom flask and solvent was removed by rotary evaporation. The residue was extracted with benzene. The extract was filtered, and the solvent was removed from the filtrate by rotary evaporation. The resulting red oil was dissolved in ca. 10 ml of CH_2Cl_2, the solution layered with hexane and kept at −24°C for 2 days. Small red crystals formed, which were collected and dried in vacuo at 78°C to give 0.097 g (0.16 mmol, 78%) of **3a**, m.p. 174–175°C (dec.). — Mass spectrum (17 eV; ^{187}Re, ^{35}Cl): *m/z* (%) = 593 (M^+, 41), 563 (M^+ − NO, 6), 449 (M^+ − Cl − NO−$C_5H_4CH_3$, 3), 262 (PPh_3^+, 100).

$C_{24}H_{22}ClNOPRe$ (593.2) Calcd. C 48.60 H 3.75
Found C 48.30 H 3.77

(η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(Br) (**3b**) was prepared from (η^5-C_5H_5)Re(NO)(PPh_3)(Br) (**1b**, 0.11 g, 0.18 mmol), TMEDA (0.029 g, 0.25 mmol), *n*-BuLi (0.10 ml, 2.5 M in hexane), and $CH_3OSO_2CF_3$ (0.073 g, 0.44 mmol) in a manner identical to the preparation of **3a**. This gave 0.78 g (0.12 mmol, 68%) of **3b**, m.p. 186–187°C. — Mass spectrum (17 eV; ^{187}Re, ^{79}Br): *m/z* (%) = 637 (M^+, 33), 607 (M^+ − NO, 5), 449 (M^+ − Br − NO−$C_5H_4CH_3$, 4), 345 (M^+ − NO − PPh_3, 3), 262 (PPh_3^+, 100).

$C_{24}H_{22}BrNOPRe$ (637.6) Calcd. C 45.21 H 3.49
Found C 45.30 H 3.63

(η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(I) (**3c**) was prepared from (η^5-C_5H_5)Re(NO)(PPh_3)(I) (**1c**, 0.076 g, 0.11 mmol), TMEDA (0.020 g, 0.17 mmol), *n*-BuLi (0.060 ml, 2.5 M in hexane), and $CH_3OSO_2CF_3$ (0.062 g, 0.38 mmol) in a manner identical to the preparation of **3a**. This gave 0.049 g (0.072 mmol, 65%) of **3c**, m.p. 178–179°C. — Mass spectrum (70 eV; ^{187}Re): *m/z* (%) = 685 (M^+, 56), 655 (M^+ − NO, 2), 558 (M^+ − I, 12), 528 (M^+ − I − NO, 16), 449 (M^+ − I − NO−$C_5H_4CH_3$, 10), 423 (M^+ − PPh_3, 3), 393 (M^+ − PPh_3 − NO, 2), 262 (PPh_3^+, 100).

$C_{24}H_{22}INOPRe$ (684.6) Calcd. C 42.11 H 3.25
Found C 41.94 H 3.14

Preparation of [η^5-1,3-$C_5H_3(CH_3)_2$]Re(NO)(PPh_3)(Cl) (**5**): A Schlenk tube was charged with **1a** (0.074 g, 0.13 mmol), THF (5 ml), and a stir bar. The solution was cooled to 0°C, and TMEDA (0.038 g, 0.33 mmol) and *n*-BuLi (0.13 ml, 2.5 M in hexane) were added with stirring. After 50 min, CH_3I (0.099 g, 0.70 mmol) was added. After 0.5 h, the reaction was transferred to a round bottom flask, and the solvent was removed by rotary evaporation. The residue was extracted with benzene. The extract was filtered, and the solvent was removed from the filtrate by rotary evaporation. The resulting red oil was chromatographed on a 15 × 2.5 cm silica gel column with ethyl acetate/hexane (20:80 v/v). The major orange band was collected and concentrated to a red oil. The oil was dissolved in ca. 5 ml of CH_2Cl_2, the solution layered with hexane and kept at −24°C for 3 days. Small red crystals formed, which were collected by filtration and dried in vacuo at 78°C to give 0.050 g (0.082 mmol, 63%) of **5**, m.p. 203–205°C (dec.). — Mass spectrum (17 eV; ^{187}Re, ^{35}Cl): *m/z* (%) = 607 (M^+, 36), 592 (M^+ − CH_3, 2), 577 (M^+ − 2 CH_3, 4), 262 (PPh_3^+, 100).

$C_{25}H_{24}ClNOPRe$ (607.2) Calcd. C 49.45 H 3.99
Found C 49.67 H 4.24

CAS Registry Numbers

1a: 92761-70-1 / **1b**: 92695-33-5 / **1c**: 92695-34-6 / **2a**: 110852-93-2 / **2b**: 110852-94-3 / **2c**: 110852-95-4 / **3a**: 110852-89-6 / **3b**: 110852-90-9 / **3c**: 110852-91-0 / **4**: 110874-20-9 / **5**: 110852-92-1

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