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Synthesis and Cis–Trans Isomerism of (Pentamethylcyclopentadienyl)rhenium(III) Halide Complexes Formed by Oxidative Addition of X_2 or HX (X = Cl, Br, I) to (η^5-C_5Me_5)Re(CO)$_2$(PMe$_3$) or (η^5-C_5Me_5)Re(CO)(PMe$_3$)(N$_2$)

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The cis isomers of the dihalide complexes $Cp^*Re(CO)(PMe_3)X_2$ (**2**: X = Cl (**a**), Br (**b**), I (**c**)) have been synthesized from the reaction of $Cp^*Re(CO)(PMe_3)(N_2)$ (**1**) with X_2 in hexane (Cp^* = η^5-C_5Me_5). These complexes were not observed to isomerize to the trans isomers when UV-irradiated, but instead decomposed. The trans isomer of **2b** was synthesized by treatment of *trans*-$Cp^*Re(CO)(PMe_3)(H)(Br)$ (**4b**) with *N*-bromosuccinimide, at 0 °C, but a corresponding synthetic route failed to give trans isomers of **2a** or **2c**. Reactions of $Cp^*Re(CO)_2(PMe_3)$ with X_2 in diethyl ether resulted in salts of the cations $[Cp^*Re(CO)_2(PMe_3)X]^+$ (**3**: X = Cl (**a**), Br (**b**), I (**c**)). The resulting isomers were trans for **3a** and **3b** but cis for **3c**; **3b** isomerized to the cis form in CH_2Cl_2 solution, and *cis*-**3a** was synthesized from $Cp^*Re(CO)_2(PMe_3)$ and $SbCl_5$ as the $[SbCl_6]^-$ salt. Trans isomers of the hydride halide complexes $Cp^*Re(CO)(PMe_3)(H)(X)$ (**4**: X = Cl (**a**), Br (**b**), I (**c**)) were synthesized from the reaction of **1** in diethyl ether with aqueous HX. The stereochemistry of the complexes **2**–**4** has been assigned on the basis of NMR coupling constants and by comparison with the known complexes $Cp^*Re(CO)_2X_2$ and $Cp^*Re(CO)_2(H)(Br)$.

Introduction

In a previous paper,[2] we reported synthetic, spectroscopic, and X-ray structural studies of the cis and trans isomers of the series of (pentamethylcyclopentadienyl)dicarbonylrhenium dihalides $Cp^*Re(CO)_2X_2$ (Cp^* = η^5-C_5Me_5; X = Cl, Br, I), together with related work on those cyclopentadienyl analogues $CpRe(CO)_2X_2$ (Cp = η^5-C_5H_5) that were not already known at that time. The Cp^* complexes were shown to be conveniently synthesized from the dinitrogen complex $Cp^*Re(CO)_2(N_2)$ by reaction with HX (or, less cleanly, X_2).[3] In connection with our studies of the related trimethylphosphine complex $Cp^*Re(CO)(PMe_3)(N_2)$ (**1**),[4] which we have noted to be very effective in photochemical C–H activation of hydrocarbons,[5] we now report on the related phosphine compounds $Cp^*Re(CO)(PMe_3)X_2$ (**2**). As will emerge, $Cp^*Re(CO)_2(N_2)$ and $Cp^*Re(CO)(PMe_3)(N_2)$ differ in their reactions toward HX and X_2, with the result that the hydride halide complexes of the latter (i.e., $Cp^*Re(CO)(PMe_3)(H)(X)$ (**4**)) have also been synthesized in this study. So also have the cationic complexes $[Cp^*Re(CO)_2(PMe_3)X]^+$ (**3**) been prepared, from reactions of the dicarbonyl $Cp^*Re(CO)_2(PMe_3)$ with X_2 or $SbCl_5$.

Experimental Section

General Considerations. All reactions were carried out under dry N_2 in a Schlenk apparatus connected to a double manifold providing a low vacuum or a nitrogen supply. Solvents were dried by conventional methods, distilled under N_2, and used immediately. Infrared spectra were measured by using CaF_2 solution cells and a Perkin-Elmer Model 983G instrument. ^1H and ^{13}C NMR spectra were measured by M. M. Tracey at 400 and 100 MHz, respectively, on a Bruker WM-400 instrument. Mass spectra were obtained by G. Owen using a Hewlett-Packard 5985 mass spectrometer with electron impact (EI) or fast-atom-bombardment (FAB; Phrasor Scientific Inc. accessory) sources. Masses are quoted for the isotopes ^{187}Re, ^{35}Cl, and ^{79}Br where these elements are present. Microanalyses were performed by M. K. Yang of the SFU Microanalytical Laboratory (C, H) or by the Canadian Microanalytical Service, Vancouver, BC, Canada (halogen). Rhenium was purchased as $Re_2(CO)_{10}$ (Strem Chemical Co.) and was converted to $Cp^*Re(CO)_3$ and $Cp^*Re(CO)(PMe_3)(N_2)$ as previously described.[4] $Cp^*Re(CO)_2(PMe_3)$ was synthesized by the photolysis of $Cp^*Re(CO)_3$ in tetrahydrofuran to give $Cp^*Re(CO)_2(THF)$ followed by addition of PMe_3 and workup. Photochemical reactions were conducted in quartz tubes irradiated by means of a Hanovia Model 654A-0360 200-W high-pressure mercury vapor lamp.

Synthesis. Preparation of *cis*-$Cp^*Re(CO)(PMe_3)Cl_2$ (*cis*-2a). This complex was prepared by following the same procedure used to prepare *cis*-**2b** (see below), with a dilute hexane solution of Cl_2 (prepared by bubbling Cl_2 gas into hexane for few minutes). *cis*-**2a** was obtained as a red solid in 88% yield. It melted at 183 °C with decomposition. Anal. Calcd for *cis*-**2a**: C, 33.87; H, 4.84. Found: C, 33.73; H, 4.77. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1899 (vs). ^1H NMR ($CDCl_3$): δ 1.76 (d, J = 10.41 Hz, 9 H, PMe_3), 1.82 (d, J = 0.4 Hz, 15 H, Cp^*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.46 (s, $C_5\mathit{Me}_5$), 17.89 (d, J = 41.2 Hz, $P\mathit{Me}_3$), 103.69 (s, C_5Me_5), 222.90 (d, J = 24.6 Hz, CO). MS (EI): m/z 496 (M^+), 468 ($M^+ - CO$), 433 ($M^+ - CO - Cl$), 392 ($M^+ - CO - PMe_3$).

Preparation of *cis*-$Cp^*Re(CO)(PMe_3)Br_2$ (*cis*-2b). To a stirred solution of the dinitrogen complex **1** (50 mg) in hexane was added a dilute hexane solution of Br_2 dropwise until all the starting material disappeared (by IR spectroscopy). Upon addition of the bromine solution, a red precipitate was formed. Hexane was pipetted off and the precipitate dried under vacuum. The resulting red-brown solid was chromatographed on a neutral alumina column. The column was washed with hexane and the product then eluted with acetone. Removal of the acetone under vacuum resulted in a red-brown solid. Recrystallization from CH_2Cl_2/hexane at −15 °C gave *cis*-**2b** (62 mg) as dark red microcrystals in 97% yield. The compound decomposed above 210 °C. Anal. Calcd for *cis*-**2b**: C, 28.72; H, 4.10. Found: C, 28.88; H, 4.11. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1902 (vs). ^1H NMR ($CDCl_3$): δ 1.84 (d, J = 10.2 Hz, 9 H, PMe_3), 1.89 (d, J = 0.4 Hz, 15 H, Cp^*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.83 (s, $C_5\mathit{Me}_5$), 19.20 (d, J = 41.5 Hz, PMe_3), 102.67 (s, C_5Me_5), 220.28 (d, J = 24.9 Hz, CO). MS (EI): m/z 584 (M^+), 556 ($M^+ - CO$), 505 ($M^+ - Br$), 480 ($M^+ - CO - PMe_3$).

Preparation of *trans*-$Cp^*Re(CO)(PMe_3)Br_2$ (*trans*-2b). *trans*(*H*,*Br*)-$Cp^*Re(CO)(PMe_3)(H)(Br)$ (40 mg) was dissolved in 10 mL of freshly distilled THF. To this yellow solution at 0 °C was added 16 mg of solid *N*-bromosuccinimide. The color changed immediately to orange-red, and the ν(CO) absorption in the IR spectrum was replaced by one 40 cm^{-1} to higher wavenumber. Evaporation of THF, extraction with hexane, and recrystallization from hexane at −78 °C gave 42.5 mg (95% yield) of *trans*-**2b** as an orange-red solid. The compound slowly decomposed above 185 °C. Anal. Calcd for *trans*-**2b**: C, 28.72; H, 4.10. Found: C, 28.99; H, 4.06. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1937 (vs). IR (THF, cm^{-1}): 1943. ^1H NMR ($CDCl_3$): δ 1.63 (d, J = 9.6 Hz, 9 H, PMe_3), 1.85 (s, 15 H, Cp^*). ^{13}C NMR ($CDCl_3$): δ 10.33 (q, J = 128.1 Hz, $C_5\mathit{Me}_5$), 16.13 (q of d, $^1J_{CH}$ = 130.3 Hz, $^1J_{CP}$ = 36.0 Hz, PMe_3), 101.25 (s, C_5Me_5), 205.20 (d, $^2J_{CP}$ = 3.7 Hz, CO). MS (EI): m/z 584 (M^+), 556 ($M^+ - CO$), 505 ($M^+ - Br$), 480 ($M^+ - CO - PMe_3$). Isomerization trans → cis was observed to occur in the dark at room temperature in C_6H_6 after 1 day to about 10% (by IR spectroscopy) and after 5 days to 80%. After 1 day in $CDCl_3$ at room temperature in the presence of daylight the conversion was 25% (by IR spectroscopy).

Preparation of *cis*-$Cp^*Re(CO)(PMe_3)I_2$ (*cis*-2c). A procedure similar to that used in the synthesis of the *cis*-**2b** complex, with a hexane solution of I_2, gave the product in 90% yield as brown-red microcrystals, MP 191 °C dec. Anal. Calcd for *cis*-**2c**: C, 24.71; H, 3.53. Found: C, 25.01; H, 3.60. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1902 (vs). ^1H NMR ($CDCl_3$): δ 1.95 (d, J = 9.8 Hz, 9 H, PMe_3), 2.04 (d, J = 0.64 Hz, Cp^*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.77 (s, $C_5\mathit{Me}_5$), 21.82 (d, $^1J_{CP}$ = 41.7 Hz,

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PMe_3), 100.80 (s, C_5Me_5), 217.25 (d, $^2J_{CP}$ = 26.3 Hz, CO). MS (EI): *m/z* 680 (M^+), 652 (M^+ − CO), 576 (M^+ − CO − PMe_3), 553 (M^+ − I).

Preparation of *trans*-$[Cp^*Re(CO)_2(PMe_3)Cl][HCl_2]$ (*trans*-3a(HCl_2)). A concentrated yellow solution of chlorine in diethyl ether (5 mL) was added dropwise to a solution of $Cp^*Re(CO)_2(PMe_3)$ (26 mg, 5.7 × 10^{-2} mmol) in diethyl ether (5 mL) with stirring. A precipitate formed, and addition was continued until all the rhenium complex had reacted (by IR spectroscopy). The supernatant was decanted, and the remaining yellow solid was washed several times with diethyl ether and then dried under a vacuum. The analytical sample was recrystallized from CH_2Cl_2/diethyl ether. Anal. Calcd for $[Cp^*Re(CO)_2(PMe_3)Cl][HCl_2]$: C, 32.12; H, 4.49; Cl, 18.96. Found: C, 31.48, 31.56; H, 4.43, 4.64; Cl, 21.19, 20.71. $[Cp^*Re(CO)_2(PMe_3)Cl]Cl$ requires the following: C, 34.35; H, 4.61; Cl, 13.52. $[Cp^*Re(CO)_2(PMe_3)Cl][Cl_3]$ requires the following: C, 30.26; H, 4.06; Cl, 23.82. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2050 (s), 1985 (vs). ^1H NMR ($CDCl_3$): δ 1.95 (d, *J* = 10.9 Hz, 9 H, PMe_3), 2.23 (s, 15 H, Cp^*). FABMS (xenon source, sulfolane solution): *m/z* 489 (M^+), 461 (M^+ − CO), 431 (M^+ − 2 CO − 2 H), 355 (M^+ − 2 CO − PMe_3 − 2 H).

Preparation of *cis*-$[Cp^*Re(CO)_2(PMe_3)Cl][SbCl_6]$ (*cis*-3a($SbCl_6$)). A solution of $Cp^*Re(CO)_2(PMe_3)$ (32 mg, 7.1 × 10^{-2} mmol) in CH_2Cl_2 (5 mL) was treated with $SbCl_5$ (0.8 g, 3 mmol) and stirred for 1 h. The solution became dark orange-brown. The product was precipitated with diethyl ether. It was recrystallized as yellow crystals (decomposition above 154 °C) by dissolving in CH_2Cl_2, filtering through Celite, adding diethyl ether, and storing at −10 °C. Anal. Calcd for $[Cp^*Re(CO)_2(PMe_3)Cl][SbCl_6]$: C, 21.88; H, 2.94. Found: C, 21.70; H, 3.03. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2051 (vs), 1982 (s). ^1H NMR ($CDCl_3$): δ 1.79 (d, *J* = 10.8 Hz, 9 H, PMe_3), 2.11 (s, 15 H, Cp^*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2): δ 10.74 (s, $C_5\mathit{Me}_5$), 15.80 (d, *J* = 40.4 Hz, PMe_3), 109.1 (s, C_5Me_5), 192.4 (d, *J* = 14.3 Hz, CO), 204.6 (d, *J* = 24.0 Hz, CO). FABMS: *m/z* 489 (M^+), 461 (M^+ − CO), 431 (M^+ − 2 CO − 2 H), 355 (M^+ − 2 CO − PMe_3 − 2 H).

Preparation of *trans*-$[Cp^*Re(CO)_2(PMe_3)Br][Br_3]$ (*trans*-3b(Br_3)). A solution of $Cp^*Re(CO)_2(PMe_3)$ (20 mg, 4.5 × 10^{-2} mmol) in diethyl ether was treated with a solution of Br_2 in diethyl ether (5 mL) until precipitation was complete and all of the rhenium complex had reacted (by IR spectroscopy). The yellow solid was separated and recrystallized from CH_2Cl_2/diethyl ether at −10 °C. Anal. Calcd for $[Cp^*Re(CO)_2(PMe_3)Br][Br_3]$: C, 23.30; H, 3.13. Found: C, 23.45; H, 3.25. $[Cp^*Re(CO)_2(PMe_3)Br]Br$ requires the following: C, 29.37; H, 3.94. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2045 (s), 1981 (vs). ^1H NMR ($CDCl_3$): δ 1.95 (d, *J* = 10.6 Hz, 9 H, PMe_3), 2.30 (s, 15 H, Cp^*). FABMS: *m/z* 533 (M^+), 505 (M^+ − CO), 475 (M^+ − CO − 2 H), 399 (M^+ − 2 CO − PMe_3 − 2 H).

Preparation of *cis*-$[Cp^*Re(CO)_2(PMe_3)Br][Br_3]$ (*cis*-3b(Br_3)). A solution of the trans isomer in CH_2Cl_2 isomerized within 3 days completely to the cis isomer, as indicated by the resulting spectroscopic data. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2045 (vs), 1977 (s). ^1H NMR ($CDCl_3$): δ 2.10 (d, *J* = 10.6 Hz, 9 H, PMe_3), 2.33 (s, 15 H, Cp^*).

Preparation of *cis*-$[Cp^*Re(CO)_2(PMe_3)I][I_3]$ (*cis*-3c(I_3)). A solution of $Cp^*Re(CO)_2(PMe_3)$ (100 mg, 0.22 mmol) in diethyl ether (8 mL) was treated with a saturated solution of I_2 in diethyl ether with stirring until all of the rhenium complex had reacted (by IR spectroscopy). The red precipitate formed was separated, washed with diethyl ether, and dried under a vacuum: yield 209 mg (99%); mp 125–126 °C. Anal. Calcd for $[Cp^*Re(CO)_2(PMe_3)I][I_3]$: C, 18.74; H, 2.52. Found: C, 18.90, 18.85; H, 2.46, 2.44. $[Cp^*Re(CO)_2(PMe_3)I]I$ requires the following: C, 25.47; H, 3.42. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2039 (vs), 1973 (s). ^1H NMR ($CDCl_3$): δ 2.12 (d, *J* = 10.3 Hz, 9 H, PMe_3), 2.37 (d, *J* = 0.9 Hz, 15 H, Cp^*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.85 (s, $C_5\mathit{Me}_5$), 19.99 (d, *J* = 41.7 Hz, PMe_3), 107.02 (s, C_5Me_5), 187.72 (d, *J* = 15.3 Hz, CO), 202.45 (d, *J* = 24.8 Hz, CO). FABMS: *m/z* 581 (M^+), 553 (M^+ − CO), 523 (M^+ − 2 CO − 2 H), 505 (M^+ − PMe_3), 477 (M^+ − CO − PMe_3), 447 (M^+ − 2 CO − PMe_3 − 2 H).

Preparation of *trans*(*H,Cl*)-$Cp^*Re(CO)(PMe_3)(H)(Cl)$ (4a). In a procedure similar to that described below for **4b**, with 37% aqueous HCl solution, the hydride chloride complex **4a** was obtained in 85% yield as a yellow solid, mp 75 °C (*cis*-**2a** was also obtained in about 10% yield from the aqueous layer). Anal. Calcd for **4a**: C, 36.36; H, 5.41. Found: C, 36.20; H, 5.38. IR (hexane, cm^{-1}): ν(CO) 1920 (vs). ^1H NMR (C_6D_6): δ −9.35 (d, $^2J_{PH}$ = 56.10 Hz, 1 H, Re–H), 1.58 (d, *J* = 9.6 Hz, 9 H, PMe_3), 1.97 (s, 15 H, Cp^*). ^{13}C NMR (C_6D_6): δ 10.98 (q, *J* = 127.5 Hz, $C_5\mathit{Me}_5$), 19.33 (q of d, $^1J_{CH}$ = 130.8 Hz, $^1J_{CP}$ = 35.4 Hz, PMe_3), 96.38 (s, C_5Me_5), 207.80 (d, $^2J_{CH}$ = 10.0 Hz (singlet in $^{13}C\{^1H\}$ NMR spectrum), CO). MS (EI): *m/z* 462 (M^+), 432 (M^+ − CO).

Preparation of *trans*(*H,Br*)-$Cp^*Re(CO)(PMe_3)(H)(Br)$ (4b). The dinitrogen complex **1** (50 mg) in diethyl ether was stirred with an excess of aqueous HBr solution (0.5 mL, 48%). The reaction was followed by IR spectroscopy until all the dinitrogen complex reacted (ca. 10 min), giving a yellow organic layer and a brownish aqueous layer that contained the dibromide *cis*-**2b** in less than 10% yield. The yellow solution was separated and the solvent pumped off. The yellow product from the ether layer was then dissolved in hexane and the solution filtered through Celite, resulting in a yellow solid when dried under vacuum: yield 50 mg (90%); mp 120 °C. Anal. Calcd for **4b**: C, 32.20; H, 4.94. Found: C, 32.99; H, 4.95. IR (hexane cm^{-1}): ν(CO) 1922 (vs). ^1H NMR (C_6D_6): δ −10.33 (d, $^2J_{PH}$ = 55.74 Hz, 1 H, Re–H), 1.38 (d, *J* = 9.30 Hz, 9 H, PMe_3), 1.84 (s, 15 H, Cp^*). ^{13}C NMR (C_6D_6): δ 11.23 (q, *J* = 127.5 Hz, $C_5\mathit{Me}_5$), 20.68 (q of d, $^1J_{CH}$ = 128.0 Hz, $^1J_{CP}$ = 36.9 Hz, PMe_3), 95.37 (s, C_5Me_5), 206.45 (d, $^2J_{CH}$ = 8.71 Hz (singlet in $^{13}C\{^1H\}$ NMR spectrum), CO). MS (EI): *m/z* 506 (M^+), 476 (M^+ − CO − 2 H).

Preparation of *trans*(*H,I*)-$Cp^*Re(CO)(PMe_3)(H)(I)$ (4c). A procedure similar to that used in the synthesis of the previous hydride halide complexes, with 47% aqueous HI solution, gave the product in 82% yield as a yellow solid. A small amount (ca. 5%) of *cis*-**2c** was also obtained from the aqueous layer; mp 140 °C. Anal. Calcd for **4c**: C, 30.32; H, 4.51. Found: C, 30.12; H, 4.46. IR (hexane, cm^{-1}): ν(CO) 1925 (vs). ^1H NMR (C_6D_6): δ −11.46 (d, $^2J_{PH}$ = 56.1 Hz, 1 H, Re–H), 1.45 (d, *J* = 9.1 Hz, 9 H, PMe_3), 1.89 (s, 15 H, Cp^*). ^{13}C NMR (C_6D_6): δ 11.85 (q, *J* = 127.7 Hz, $C_5\mathit{Me}_5$), 23.05 (q of d, $^1J_{CH}$ = 130.6 Hz, $^1J_{CP}$ = 36.5 Hz, PMe_3), 95.11 (s, C_5Me_5), 204.32 (d, $^2J_{CH}$ = 10.8 Hz (singlet in $^{13}C\{^1H\}$ NMR spectrum, CO). MS (EI): *m/z* 554 (M^+), 524 (M^+ − CO − 2 H).

Reaction of $Cp^*Re(CO)_2(N_2)$ with Anhydrous HBr. $Cp^*Re(CO)_2(N_2)$ (118 mg; 0.30 mmol) was dissolved in diethyl ether and degassed twice in a high-vacuum system. To this pale yellow solution was added an excess amount of redistilled gaseous anhydrous HBr, and the mixture was stirred over a period of 5 days. During this time a golden yellow crystalline solid gradually precipitated from a more intensely yellow solution, which was identified as *trans*-$Cp^*Re(CO)_2(H)(Br)$. Evaporation of the yellow solution followed by successive recrystallization from hexane at −78 °C yielded some further product and ca. 35 mg of unreacted $Cp^*Re(CO)_2(N_2)$. The yield of *trans*-$Cp^*Re(CO)_2(H)(Br)$ was 40 mg (43%). The compound decomposed above 75 °C. Anal. Calcd for $Cp^*Re(CO)_2(H)(Br)$: C, 31.44; H, 3.49. Found: C, 31.42; H, 3.48. IR (hexane, cm^{-1}): ν(CO) 2030 (m), 1964 (vs). ^1H NMR (C_6D_6): δ −9.98 (s, 1 H, Re–H), 1.64 (s, 15 H, Cp^*). ^{13}C NMR (C_6D_6): δ 10.49 (q, *J* = 128.6 Hz, $C_5\mathit{Me}_5$), 99.85 (s, C_5Me_5), 195.75 (d, *J* = 13.6 Hz (singlet in $^{13}C\{^1H\}$ NMR spectrum), CO). MS (EI): *m/z* 458 (M^+), 430 (M^+ − CO). This complex is stable in dry diethyl ether under N_2; however, when aqueous HBr was added and the solution was stirred, it converted quantitatively to the dibromide *cis*-$Cp^*Re(CO)_2Br_2$, identified by comparison with an authentic sample.[2]

Results

The transformations observed in this study are summarized in Schemes I and II. Spectroscopic properties of the complexes are summarized in Table I. These observations are discussed in the section which follows.

Discussion

(a) Dihalide Complexes $Cp^*Re(CO)(PMe_3)X_2$ (2). The *cis*-dihalides $Cp^*Re(CO)(PMe_3)X_2$ (**2**: X = Cl (**a**), Br (**b**), I (**c**)) were easily prepared by the reaction of the dinitrogen complex $Cp^*Re(CO)(PMe_3)(N_2)$ (**1**) in hexane with the halogens X_2 (eq 1, Scheme I).

These red or red-brown microcrystalline solids are indefinitely stable under N_2 and appear not to deteriorate when exposed to air over a period of days. They are very soluble in polar organic solvents such as acetone, $CHCl_3$, or CH_2Cl_2 and in benzene or toluene, and in these solutions they appear not to undergo thermal isomerization. No isomerization was detected even in boiling benzene or toluene, though the complexes soon decomposed under these conditions.

The spectroscopic properties (Table I) clearly show the presence of only a single isomer. Thus, there is a single ν(CO) absorption near 1900 cm^{-1}, and the ^1H and ^{13}C NMR spectra exhibit only the expected resonances for a single isomer. The mass spectra clearly establish the molecular ion and show the expected loss of CO, PMe_3, and halogen.

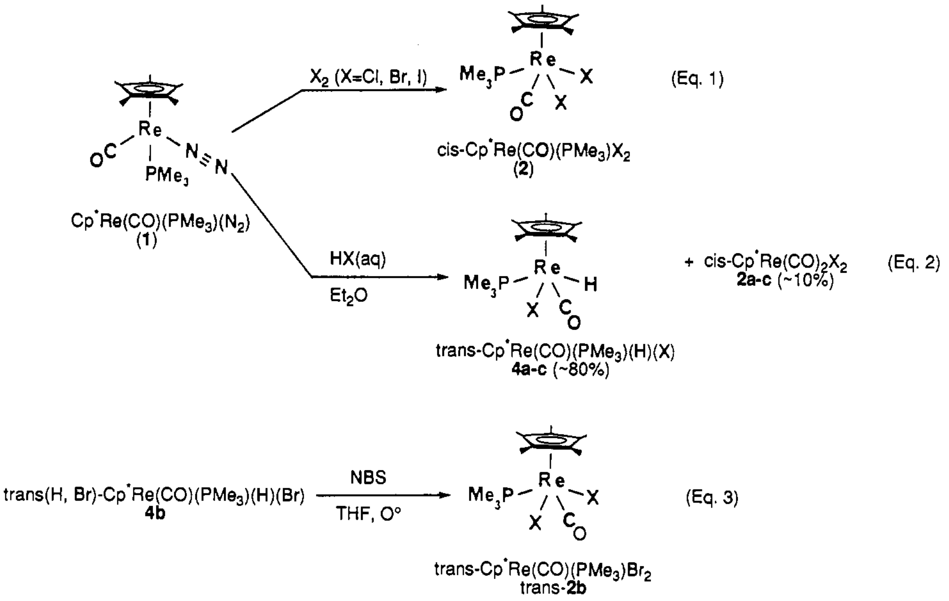
The stereochemistry of these complexes **2** is expected to be that of a four-legged piano stool, by analogy with the complexes $Cp^*Re(CO)_2X_2$, for which the stereochemistry was established by X-ray structures of *cis*-$Cp^*Re(CO)_2I_2$ and *trans*-$Cp^*Re(CO)_2Br_2$.[2] Whereas in these dicarbonyl dihalides the cis stereochemistry could be readily inferred from the relative intensities

Table I. Selected Spectroscopic Parameters

compd	$\nu(CO)^a$	$\delta(CO)^b$	$\delta(Re{-}H)^b$
cis-Cp*Re(CO)(PMe_3)Cl_2 (*cis*-**2a**)	1899^c	222.90 [24.6 (PC)]^d	
cis-Cp*Re(CO)(PMe_3)Br_2 (*cis*-**2b**)	1902^c	220.28 [24.9 (PC)]^d	
trans-Cp*Re(CO)(PMe_3)Br_2 (*trans*-**2b**)	1937^c	205.20 [3.7 (PC)]^d	
cis-Cp*Re(CO)(PMe_3)I_2 (*cis*-**2c**)	1902^c	217.25 [26.3 (PC)]^d	
trans-[Cp*Re$(CO)_2$(PMe_3)Cl][HCl_2] (*trans*-**3a**(HCl_2))	2050 s, 1985 vs^c		
cis-[Cp*Re$(CO)_2$(PMe_3)Cl][$SbCl_6$] (*cis*-**3a**($SbCl_6$))	2051 vs, 1982 s^c	192.4 [14.3 (PC)]^d 204.6 [24.0 (PC)]	
trans-[Cp*Re$(CO)_2$(PMe_3)Br][Br_3] (*trans*-**3b**(Br_3))	2045 vs, 1981 s^c		
cis-[Cp*Re$(CO)_2$(PMe_3)Br][Br_3] (*cis*-**3b**(Br_3))	2045 vs, 1977 s^c		
cis-[Cp*Re$(CO)_2$(PMe_3)I][I_3] (*cis*-**3c**(I_3))	2039 vs, 1973 s^c	187.72 [15.3 (PC)]^d 202.45 [24.8 (PC)]	
trans(*H*,*Cl*)-Cp*Re(CO)(PMe_3)(H)(Cl) (**4a**)	1920^e	207.80 [10.0 (CH)]^f	−9.35 [56.1 (PH)]^f
trans(*H*,*Br*)-Cp*Re(CO)(PMe_3)(H)(Br) (**4b**)	1922^e	206.45 [8.7 (CH)]^f	−10.33 [55.7 (PH)]^f
trans(*H*,*I*)-Cp*Re(CO)(PMe_3)(H)(I) (**4c**)	1925^e	204.32 [10.8 (CH)]^f	−11.46 [56.1 (PH)]^f
trans-(*H*,*Br*)-Cp*Re$(CO)_2$(H)(Br)	2030 m, 1964 vs	195.75 [13.6 (CH)]^f	-9.98^f

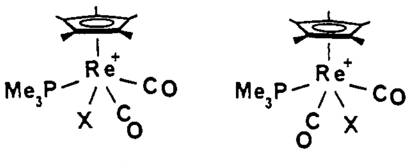
^{a} In cm^{-1}. ^{b} Coupling constants *J* (Hz) in brackets. ^{c} CH_2Cl_2 solvent. ^{d} $CDCl_3$ solvent. ^{e} Hexane solvent. ^{f} C_6D_6 solvent.

Scheme I



Scheme II

$$Cp^*Re(CO)_2(PMe_3) \xrightarrow[Et_2O]{X_2} \underset{3\ (X = a,\ Cl;\ b,\ Br;\ c,\ I)}{[Cp^*Re(CO)_2(PMe_3)X]^+} \qquad (Eq.\ 4)$$



cis 3 trans 3

of the ν(CO) absorptions, this is of course not possible for the monocarbonyls **2**. In this case we have used the magnitude of the $^2J_{CP}$ coupling constant in the ^{13}C NMR spectrum of the CO group. Previous studies on the ^{13}C NMR spectra of cis and trans isomers of CpMo$(CO)_2$(PPh_3)X (X = Cl, Br, I) have indicated that in these piano-stool complexes the $^2J_{CP}$ values for the coupling of phosphorus to the carbonyl carbon differ significantly: a CO group cis to PPh_3 resonates at larger δ and has $^2J_{CP}$ near 28 Hz, whereas a CO group trans to PPh_3 resonates at smaller δ and has $^2J_{CP}$ near 5 Hz.[6,7] The observed value of $^2J_{CP}$ in *cis*-**2a–c**, about 25 Hz, is in good agreement with values observed in closely related compounds with cis phosphine and CO groups, for example *trans*-CpMo$(CO)_2$(PPh_3)Cl (27.2 Hz) and *cis*-CpMo$(CO)_2$(PPh_3)I (28.6 Hz).[6,7] *cis*-**2a–c** also exhibit a small (ca. 0.5 Hz) coupling of phosphorus to the Cp* methyl protons in ^1H NMR spectra, not observed in *trans*-**2a–c**.

Isomerism of the cis dicarbonyl dihalides Cp*Re$(CO)_2X_2$ to the trans isomers was previously observed to occur readily upon UV irradiation.[2] In the case of the phosphine complexes **2** no such isomerization could be established, since **2a–c** all decomposed upon UV irradiation to give intractable products. Nevertheless, in one example, namely the bromide, we were successful in obtaining the trans isomer by an alternate route. Thus, *trans*-Cp*Re(CO)(PMe_3)Br_2 could be obtained by the reaction of *trans*(*H*,*Br*)-Cp*Re(CO)(PMe_3)(H)(Br) (**4b**) (vide infra) with *N*-bromosuccinimide (NBS) in THF at 0 °C (eq 3, Scheme I).

In contrast, *trans*(*H*,*Cl*)- and *trans*(*H*,*I*)-Cp*Re(CO)(PMe_3)(H)(X) (**4a**,**c**) were recovered unreacted when treated with *N*-chloro- and *N*-iodosuccinimide, respectively, at 0 °C under similar conditions; at room temperature, a slow reaction was observed but only cis isomers of the dihalides **2a** and **2c** resulted. It is possible that the trans isomers were first formed but rearranged to the more stable cis isomers, as indeed is the case now described with the bromide **2b**.

trans-Cp*Re(CO)(PMe_3)Br_2 (*trans*-**2b**) was isolated as an orange-red solid in almost quantitative yield. In the ^{13}C NMR spectrum the carbonyl carbon resonance is a doublet with a much smaller J_{PC} value of 3.7 Hz, compared with 24.9 Hz for the cis isomer, and is shifted to smaller δ by 15.1 ppm with respect to

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the signal for *cis*-**2b**; this is consistent with previous ^{13}C NMR results for mutually trans carbonyl and phosphine groups.[6,7] This isomer is unstable in solution at room temperature: about 80% conversion to *cis*-**2b** occurred in benzene in the dark over 5 days.

(b) Cationic Complexes $\mathbf{[Cp^*Re(CO)_2(PMe_3)X]^+}$ (3). The much greater ease of substitution of the N_2 ligand in $\mathrm{Cp^*Re(CO)(N_2)(PMe_3)}$ (**1**) compared with that of CO in $\mathrm{Cp^*Re(CO)_2(PMe_3)}$ is well illustrated by their reactions with halogens. Above, we have described that the N_2 ligand in **1** is readily lost and oxidative addition of X_2 occurs to give the cis isomers of the dihalides **2a**–**c**. In the case of the dicarbonyl complex reactions with halogens under similar conditions resulted in the cations $\mathrm{[Cp^*Re(CO)_2(PMe_3)X]^+}$ (**3**: X = Cl (**a**), Br (**b**), I (**c**)) without CO displacement (eq 4, Scheme II).

It is reasonable to infer from this that the corresponding unstable cationic intermediate $\mathrm{[Cp^*Re(CO)(N_2)(PMe_3)(X)]^+}$ is likely formed in the mechanism of the reaction of the dinitrogen complex **1** with X_2 (eq 1, Scheme I). Subsequent nucleophilic attack of the halide (or polyhalide) anion that is also generated results in the formation of *cis*-**2a**–**c**, either after N_2 loss or in a concerted process.

The cations **3** are also presumed to adopt the four-legged piano-stool geometry displayed by the dihalides **2**. In the IR spectra two ν(CO) absorptions are observed, as expected, but the relative intensities of these two absorptions show interesting changes as X is varied from Cl to Br to I, indicating stereochemical changes. For **3a** (Cl) and **3b** (Br) the higher wavenumber band ν_{sym}(CO) is weaker than ν_{asym}(CO), which we interpret to indicate that these are trans isomers. For **3c** (I) the reverse is true, an indication that this is the cis isomer. It was further observed that **3b** actually undergoes conversion in solution to an isomer in which the relative intensity of the ν(CO) bands is similar to that in **3c**, which we interpret as a trans–cis isomerization. On this basis it would appear that the cis configuration becomes preferred to trans as the halogen is changed from Cl through Br to I. This view must be treated with caution, however, as the observed isomer may well reflect the mechanism of the reaction, which may differ with different halogens, or may be influenced by the counterion. In this regard it is significant that the synthesis of **3a** as the $\mathrm{[SbCl_6]}$ salt from the reaction of $\mathrm{Cp^*Re(CO)_2(PMe_3)}$ with $\mathrm{SbCl_5}$ produced the cis isomer, as indicated by the relative ν(CO) intensities.

While the main feature of interest in these compounds is the cation, some comment on the anions is warranted. When synthesized from $\mathrm{Cl_2}$, the chloro complex **3a** did not give satisfactory analytical data for the presence of either $\mathrm{[Cl]^-}$ or $\mathrm{[Cl_3]^-}$ as the anion. The C, H data gave reasonable agreement with a formulation in which the anion is $\mathrm{[HCl_2]^-}$. However, we have no direct evidence for this as the ^{1}H NMR spectrum showed no resonance for the proton (which could be unobservably broad or could be exchanged with traces of water in the solvent). Chlorine analyses obtained extramurally, while in better agreement with this formulation than the others, were erratic, possibly as a result of the rather unstable sample deteriorating during transit. It was because of this uncertainty that the rather more stable $\mathrm{[SbCl_6]}$ salt was synthesized, albeit as a different isomer. The bromo complex gave a satisfactory analysis for the salt of the tribromide ion $\mathrm{[Br_3]^-}$, a counterion that is established to occur in bromination reactions.[8] The presence of the $\mathrm{[I_3]^-}$ counterion in the case of the iodide is expected and was observed previously in the related complex $\mathrm{[Cp^*Re(CO)_3I][I_3]}$.[2]

The ^{13}C NMR spectra have been measured for the more stable cis complexes *cis*-$\mathrm{[Cp^*Re(CO)_2(PMe_3)Cl][SbCl_6]}$ (*cis*-**3a**($\mathrm{SbCl_6}$)) and *cis*-$\mathrm{[Cp^*Re(CO)_2(PMe_3)I][I_3]}$ (*cis*-**3c**($\mathrm{I_3}$)). Of interest are the $^2J_{\mathrm{PC}}$ values for the two CO groups, which are as follows: (i) in *cis*-**3a**($\mathrm{SbCl_6}$), δ 192.4 (J = 14.3 Hz) and δ 204.6 (J = 24.0 Hz); (ii) in *cis*-**3c**($\mathrm{I_3}$), δ 187.7 (J = 15.3 Hz) and δ 202.4 (J = 24.8 Hz). We tentatively assign the resonance at higher δ value, having the greater $^2J_{\mathrm{PC}}$ value, to the CO group cis to the $\mathrm{PMe_3}$ group, in a manner consistent with precedent[6,7] and with the assignments made above for the CO groups in the cis and trans isomers of $\mathrm{Cp^*Re(CO)(PMe_3)Br_2}$ (**2b**) (CO cis to $\mathrm{PMe_3}$ δ 220.28, J = 24.9 Hz; CO trans to $\mathrm{PMe_3}$, δ 205.20, J = 3.7 Hz). However, the much larger observed J values (14.3, 15.3 Hz) for the CO assigned to be trans to $\mathrm{PMe_3}$ compared with J = 3.7 Hz in *trans*-**2b** (and with J = 5.0 Hz reported for *cis*-$\mathrm{CpMo(CO)_2(PMe_3)I}$)[6,7] must be noted.

(c) Hydride Halide Complexes $\mathbf{Cp^*Re(CO)(PMe_3)(H)(X)}$ (4). The trimethylphosphine dinitrogen complex **1** reacted with an excess of concentrated aqueous hydrogen halides (HX) to produce primarily *trans(H,X)*-$\mathrm{Cp^*Re(CO)(PMe_3)(H)(X)}$ (**4**: X = Cl (**a**), Br (**b**), I (**c**)) in over 80% yield, with only less than 10% of the corresponding *cis*-dihalide (*cis*-**2**) being formed (eq 2, Scheme I).

In all cases, the complexes *trans*-**4a**–**c** were isolated as yellow solids that were indefinitely stable under N_2. They are very soluble in the majority of organic solvents, including hexane and cyclohexane. They show in the IR spectra a single very strong ν(CO) absorption at about 1922 cm^{-1} in hexane. The presence of the hydride ligand (which could not be observed in the IR spectra) was clearly determined from the ^{1}H NMR spectra (Table I), in which there appears a doublet of relative intensity 1 H in the high-field region at ca. δ −10.0 with $^2J_{\mathrm{PH}}$ near 56 Hz. This value is in reasonable agreement with those observed in other four-legged piano-stool complexes containing a *cis*-H–M–P moiety, e.g. $\mathrm{[CpMn(CO)_2(PMe_2Ph)(H)]^+}$ (52 Hz),[9] $\mathrm{CpMo(CO)_2(PR_3)H}$ (64–67 Hz),[10] and $\mathrm{[CpRe(CO)_2(PPh_3)H]^+}$ (39 Hz).[11] In a *trans*-H–M–P arrangement, $^2J_{\mathrm{PH}}$ is expected, from various precedents, to be 2–3 times smaller than that observed in the cis arrangement.[9-11] In the proton-coupled ^{13}C NMR spectrum the carbonyl carbon resonance is a doublet with $^2J_{\mathrm{CH}} \approx$ 8–11 Hz, and it is a singlet in the proton-decoupled spectrum with no observable coupling to ^{31}P. These values of $^2J_{\mathrm{CH}}$ are comparable to the value of 13.6 Hz that we have observed in *trans*-$\mathrm{Cp^*Re(CO)_2(H)(Br)}$ (see below), for which the trans geometry follows from the relative ν(CO) intensities in the IR spectrum, and are thus a further indication of the correctness of the proposed geometry for *trans*-**4a**–**c** in which there is a cis arrangement of CO and hydride ligands.

The formation of these hydride halide complexes in the case of the phosphine dinitrogen complex **1** contrasts with the previously published results[2] with the unsubstituted dicarbonyl $\mathrm{Cp^*Re(CO)_2(N_2)}$, where it was observed instead that only the dihalides $\mathrm{Cp^*Re(CO)_2X_2}$ were formed when either aqueous or undried gaseous HX compounds were used. To shed more light on this, we carried out a reaction of $\mathrm{Cp^*Re(CO)_2(N_2)}$ with HBr under scrupulously anhydrous conditions. This resulted in a dramatic difference; none of the dibromo complex was produced, but instead the new hydrido bromo complex *trans*-$\mathrm{Cp^*Re(CO)_2(H)(Br)}$ was formed and fully characterized. The trans geometry of the CO groups followed from the relative intensities of $\nu_{\mathrm{sym}}(\mathrm{CO}) < \nu_{\mathrm{asym}}(\mathrm{CO})$ and the observation of a single resonance for CO in the ^{13}C NMR spectrum. Notably the hydride coupling constant $^2J_{\mathrm{CH}}$ = 13.6 Hz for this resonance provides a useful value for a *cis*-(H)(CO) system by which to compare the values of $^2J_{\mathrm{CH}}$ observed for the phosphine complexes **4** (above) and supports the assignment of these phosphine complexes **4** as trans isomers, as discussed above.

When *trans*-$\mathrm{Cp^*Re(CO)_2(H)(Br)}$ was treated with aqueous HBr,[12] it transformed smoothly to the previously observed[2] *cis*-dibromide *cis*-$\mathrm{Cp^*Re(CO)_2Br_2}$. It therefore appears that in the previously reported reactions[2] oxidative addition of HX to $\mathrm{Cp^*Re(CO)_2(N_2)}$ occurs first to produce $\mathrm{Cp^*Re(CO)_2(H)(X)}$

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[12] A sample of the solution during the synthesis of $\mathrm{Cp^*Re(CO)_2(H)(Br)}$ transformed completely to the dibromide when exposed to the atmosphere overnight.

and then this subsequently reacts in the presence of, at least, traces of water to give the dihalide $Cp^*Re(CO)_2X_2$. The function of the water has yet to be determined. In the case of the phosphine complex **1** some of the *cis*-dihalide complexes **2a–c** was always observed to be formed, also as a result of reaction of the hydride halide complexes **4a–c** with further aqueous HX. However, in the case of the phosphines this reaction is much slower, allowing the hydride halides to be isolated in good yield under conditions where they are not observed at all for the dicarbonyl.

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Registry No. **1**, 101835-36-3; *cis*-**2a**, 123002-21-1; *cis*-**2b**, 101915-09-7; *trans*-**2b**, 101835-39-6; *cis*-**2c**, 123002-22-2; *trans*-**3a**(HCl_2), 123002-24-4; *cis*-**3a**($SbCl_6$), 123050-32-8; *trans*-**3b**(Br_3), 123002-26-6; *cis*-**3b**(Br_3), 123050-34-0; *cis*-**3c**(I_3), 123002-28-8; **4a**, 123002-29-9; **4b**, 101835-40-9; **4c**, 123002-30-2; $Cp^*Re(CO)_2(PMe_3)$, 96791-01-4; $Cp^*Re(CO)_3$, 12130-88-0; $Cp^*Re(CO)_2N_2$, 92787-15-0; *trans*-$Cp^*Re(CO)_2(H)(Br)$, 123002-31-3; *cis*-$Cp^*Re(CO)_2Br_2$, 99341-48-7.

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Synthesis and Characterization of the Bis(1,3-bis(methylthio)-1,3-propanedithionate) Complexes $M[S_2C_3H(SCH_3)_2]_2$ ($M = Ni^{II}, Pd^{II}, Pt^{II}$)

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New dithionate (dtsacsac) complexes of the formula $M[S_2C_3H(SCH_3)_2]_2$ ($M = Ni^{II}, Pd^{II}, Pt^{II}$) have been synthesized by the reaction of reduced 3,5-bis(methylthio)-1,2-dithiolium triflate with nickel acetate, palladium acetate, and potassium tetrachloroplatinate(II), respectively. The new complexes show metal-dependent, reversible redox properties. $Ni(dtsacsac)_2$ is more planar and aromatic than the earlier reported nickel dithioacetylacetonato complex [$Ni(sacsac)_2$] and forms uniform stacks. The $Ni(dtsacsac)_2$ complex is also unreactive toward electrophilic aromatic substitution. Oxidation of the new complexes with iodine affords 1,3-bis(methylthio)-1,2-dithiolium triiodide.

Introduction

Planar complexes of d^8 metals have long been considered as possible components of molecular metals.[1] Recently, two molecular superconductors[2,3] based on dithiolene complexes have been reported. While metal dithiolene complexes[4] (where the metal is part of a five-membered chelate ring) have been extensively studied, the corresponding dithioacetylacetonate complexes, where the metal would be part of a six-membered ring, have received less attention. We reasoned that planar propanedithionates with sulfur substituents at the 1 and 3 positions would have several features in common with dithiolene complexes and might lead to highly conducting complexes. Also, in connection with our work on the Y-aromatic sulfocarbons,[5] we wished to examine the reactivity of γ-C–H in these metal complexes. If this C–H bond could be replaced by a CS_2 moiety, then an entry into methanetris(dithiocarboxylate) derivatives could be developed.

We note that a wide range of complexes of the ligand dithioacetylacetone, sacsac (pentane-2,4-dithione), with both divalent and trivalent transition metals have been prepared.[6] The synthesis of these complexes have been carried out by using the method of Martin et al.[7] by the reaction of the metal ion, the oxo ligand, and HCl in ethanol with H_2S at 0 °C. Some complexes have also been prepared by the reduction of 1,2-dithiolium salts[8] to the corresponding dithioacetylacetonate anion.

The planar ML_2-type complexes of the Ni triad (Ni, Pd, Pt) were shown to undergo two successive one-electron reductions.[6e] The reduction potentials of complexes of dithioacetylacetonate and its derivatives were found to be shifted positive relative to the respective complexes with oxygen donor atoms.[6b,9] They were, however, only slightly dependent on the metal center.[6d] This, together with the observation that the potential differences between the successive reduction steps were remarkably constant for the Ni, Pd, and Pt complex of the same ligand, was taken as evidence for the ligand-based character of these processes.[6d] Interestingly, the reduced complexes were subject to a subsequent dimerization reaction the extent of which increased in the order Ni ≪ Pd < Pt.[6d,e] The dimerization was largely suppressed by substituting bulkier groups for the methyl groups in the sacsac ligand.[6d] In contrast, the cyclic voltammetrc oxidation remained chemically irreversible up to high scan rates,[6e] with the notable exception of $Pt(sacsac)_2$, where a reversible oxidation was found.[6e]

In this paper we report the synthesis of novel 1,3-bis(methylthio)-1,3-propanedithionate complexes via a "one-pot" procedure. We also describe briefly the X-ray structure of the Ni complex

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