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Reactions of rhenium trialkylphosphite complexes $(\eta^5\text{-}C_5Me_5)Re(CO)_2\{P(OR)_3\}$ (R = Me or Et) with halogens and $SbCl_5$: reversible Arbuzov-like dealkylation to form rhenium dialkylphosphonate complexes $(\eta^5\text{-}C_5Me_5)ReX(CO)_2\{PO(OR)_2\}$

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Abstract

The cationic complexes of general formula $[(\eta^5\text{-}C_5Me_5)ReX(CO)_2\{P(OR)_3\}]^+$ (R = Me; X = Cl (**2a**), Br (**3a**) or I (**4a**)) and (R = Et; X = Cl (**2b**), Br (**3b**) an I (**4b**)) have been synthesized by reactions of $(\eta^5\text{-}C_5Me_5)Re(CO)_2\{P(OR)_3\}$ with either halogens X_2 or $SbCl_5$. Each is obtained as a mixture of *cis* and *trans* isomers of a typical four-legged piano-stool geometry and has been fully characterized in solution by a combination of IR and ^1H, ^{13}C and ^{31}P nuclear magnetic resonance spectroscopy. It is observed that under appropriate conditions these cationic complexes undergo transformation to the corresponding neutral dialkylphosphonate complexes of general formula *trans*-$(\eta^5\text{-}C_5Me_5)ReX(CO)_2\{PO(OR)_2\}$ (**5a–7a** and **5b–7b**) where R = Me (**a**) or Et (**b**) and X = Cl (**5**), Br (**6**) and I (**7**). This is ascribed to a Michaelis–Arbuzov-type dealkylation reaction involving a nucleophilic attack at the alkyl group by the counter-anion, and it is possible to render the cation more (or less) stable to this transformation by suitable choice of the counter-anion and the phosphite. The cationic triethylphosphite complexes exhibit a decreased tendency to undergo the dealkylation reaction. Most interestingly, the product (*i.e.* cationic phosphite or neutral dialkylphosphonate) in the reaction of $(\eta^5\text{-}C_5Me_5)Re(CO)_5\{P(OR)_3\}$ with Br_2 at −78°C is dependent on the molar ratio of the reactants; when examined in detail, this is found to result from a counter-ion dependent *reversible* alkylation–dealkylation process. Thus the dialkylphosphonate is unchanged by treatment with alkylbromide alone but is completely transformed back to the cationic trialkylphosphite complex by alkyl bromide *and bromine*.

Key words: Rhenium; Halogen; Phosphite; Phosphonate

1. Introduction

In a previous paper [1] we demonstrated that the trimethylphosphine complex $Cp^*Re(CO)_2(PMe_3)$ ($Cp^* = \eta^5\text{-}C_5Me_5$) reacts with halogens X_2 (X = Cl, Br or I) in diethyl ether or with $SbCl_5$ in CH_2Cl_2 to produce salts of the cations $[Cp^*ReX(CO)_2(PMe_3)]^+$. The particular isomers observed for these four-legged piano-stool complex cations depended upon the halogen and the synthetic method. Reactions with X_2 directly gave the *trans* isomers for X = Cl or Br, but the *cis* isomer for X = I; for X = Br, isomerization from *trans* to *cis* occurred in CH_2Cl_2 solution, and the *cis* isomer for X = Cl was obtained directly by using $SbCl_5$. Here, we report the results of an investigation of corresponding reactions with the trialkylphosphite complexes $Cp^*Re(CO)_2\{P(OR)_3\}$ (R = Me or Et). In these cases the chemistry is complicated by the possibility of a Michaelis–Arbuzov-like dealkylation reaction, whereby the nucleophilic anion attacks the phosphite ligand in the cationic complex to give rise to a neutral phosphonate complex $Cp^*ReX(CO)_2\{PO(OR)_2\}$. Cationic halide complexes of the unsubstituted carbonyls $CpRe(CO)_3$ or $Cp^*Re(CO)_3$, *e.g.* $[Cp^*Re(CO)_3X]^+$, have been known for some time [2–4], and the triphenylphosphite complex $[Cp^*Re(CO)_2\{P(OPh)_3\}I][I_3]$ was recently reported [5a]. A vibrational analysis of the chloro, bromo and iodo

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dimethylphosphonate complexes $Cp^*Re(CO)_2\{PO(OMe)_2\}X$ (X = Cl, Br or I) described in this paper has already appeared [5b].

2. Experimental details

All reactions were carried out under an atmosphere of nitrogen using Schlenk tube techniques. Solvents were dried by conventional methods, distilled under nitrogen and used immediately. IR were measured using a Bomem model Michelson-120 Fourier transform IR instrument, usually for solutions in CaF_2 cells. ^1H, ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectra were measured by M.M. Tracey on a Bruker WM-400 instrument at 400.13, 100.16 and 162.0 MHz respectively and are referenced to $SiMe_4$ (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Mass spectra were obtained by G. Owen using a Hewlett–Packard model 5985 mass spectrometer utilizing electron impact (EI) or xenon fast-atom-bombardment (FAB) techniques. For the latter, the sample was dissolved in *m*-nitrobenzyl alcohol (NOBA). The masses are reported for ^{35}Cl, ^{79}Br and ^{187}Re. Microanalyses were performed by the Simon Fraser University Microanalytical Laboratory. The preparation of $(\eta^5\text{-}C_5Me_5)Re(CO)_2\{P(OEt)_3\}$ has been reported elsewhere [5a].

2.1. Preparation of $(\eta^5\text{-}C_5Me_5)Re(CO)_2\{P(OMe)_3\}$ (1)

A solution of $Cp^*Re(CO)_3$ (0.30 g, 0.74 mmol) and $P(OMe)_3$ (0.11 g, 0.89 mmol) in 200 ml of tetrahydrofuran (THF) was irradiated in a quartz tube at 0°C for 90 min. During the photolysis a slow flux of N_2 was maintained. After this time, the IR spectrum of the solution showed a 70% conversion to the trimethyl phosphite complex. Solvent was removed under vacuum and the residual yellow solid was dissolved in hexane and chromatographed on a neutral alumina column prepared in hexane. Elution with hexane–diethyl ether (3:1) eluted only the trimethyl phosphite complex. It was recrystallized from hexane at −4°C to yield the product as white crystals ((0.25 g (73%)). M.p. = 114°C. IR (CH_2Cl_2): ν(CO) 1929, 1856 cm^{-1}. ^1H NMR ($CDCl_3$): 2.08 (s, 15H, $\eta^5\text{-}C_5Me_5$); 3.50 (d, 9H, $^3J_{P-H}$ = 12.2 Hz, $P(OMe)_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 10.6 (s, $C_5\mathit{Me}_5$); 51.6 (s, O*Me*); 96.6 (s, C_5Me_5); 203.9 (s, *C*O) ppm. ^{31}P NMR (acetone–acetone-d_6): 142.6 ppm. MS (EI): *m/z* 502 $(M)^+$, 471 $(M - CO - 2H)^+$. Anal. Found: C, 35.62; H, 4.70. $C_{15}H_{24}O_5PRel$ calcd: C, 35.85; H, 4.81%.

2.2. cis- and trans-$[(\eta^5\text{-}C_5Me_5)ReCl(CO)_2\{P(OMe)_3\}][SbCl_6]$ (2aSbCl$_6$)

A solution of $SbCl_5$ (in CH_2Cl_2) was added dropwise to $(\eta^5\text{-}C_5Me_5)Re(CO)_2\{P(OMe)_3\}$ (1) (0.15 g, 0.30 mmol.) in hexane (6 ml), resulting in the immediate formation of a yellow precipitate. The solvent was removed and the solid was washed with hexane (2 × 5 ml). The yellow solid residue was recrystallized from dichloromethane–hexane to yield yellow crystals of the product (0.256 g (98%)). IR (CH_2Cl_2): ν(CO) 2064 m, 2004 s cm^{-1}. ^1H NMR (acetone-d_6): (*trans* : *cis* ratio, 6:1), *trans* isomer 2.19 (s, 15H, $\eta^5\text{-}C_5Me_5$); 4.18 (d, 9H, $^3J_{P-H}$ = 12.2 Hz, $P(OMe)_3$); *cis* isomer 2.22 (d, 15H, J_{P-H} = 1.3 Hz, $\eta^5\text{-}C_5Me_5$); 4.00 (d, 9H, $^3J_{P-H}$ = 12.0 Hz, $P(OMe)_3$) ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): *trans* isomer) 10.0 (s, $C_5\mathit{Me}_5$); 58.3 (d, $^2J_{P-C}$ = 10 Hz, O*Me*); 110.5 (s, C_5Me_5); 192.8 (d, $^2J_{P-C}$ = 33.1 Hz, *C*O) ppm. ^{31}P NMR (acetone–acetone-d_6): *trans* isomer 92.4, *cis* isomer 85.9 ppm. MS (FAB): *m/z* 537 $(M)^+$, 509 $(M - CO)^+$, 447 $(M - CO - OCH_3)^+$. Anal. Found: C, 22.41; H, 3.01. $C_{15}H_{24}Cl_7O_5PReSb$ calcd: C, 20.67; H, 2.76%.

2.3. trans-$[(\eta^5\text{-}C_5Me_5)ReBr(CO)_2\{P(OMe)_3\}][Br_3]$ (3aBr$_3$)

A solution of **1** (0.20 g, 0.40 mmol) in THF (2 ml) was added dropwise to Br_2 (0.19 g, 0.80 mmol) in THF (1 ml) at −78°C. The resulting mixture was stirred for 5 min to produce an orange solution. The product was precipitated with hexane. The solvent was removed and the yellow–orange solid was washed with hexane (2 × 5 ml) and then dried under vacuum (0.314 g (96%)). IR (THF): ν(CO) 2052 m, 1990 s cm^{-1}. ^1H NMR ($CDCl_3$): 2.28 (s, 15H, $\eta^5\text{-}C_5Me_5$); 4.08 (d, 9H, $^3J_{P-H}$ = 12.2 Hz, $P(OMe)_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 10.7 (s, $C_5\mathit{Me}_5$); 57.9 (d, $^2J_{C-P}$ = 10 Hz, O*Me*); 109.5 (s, C_5Me_5); 190.5 (d, $^2J_{C-P}$ = 33.7 Hz, *C*O) ppm. ^{31}P NMR (acetone–acetone-d_6): 77.6 ppm. MS (FAB): *m/z* 581 $(M)^+$, 553 $(M - CO)^+$, 521 $(M - CO - OCH_3)^+$, Anal. Found: C, 21.39; H, 2.96. $C_{15}H_{24}Br_4O_5PRel$ calcd: C, 21.94; H, 2.95%.

2.4. cis- and trans-$[(\eta^5\text{-}C_5Me_5)ReI(CO)_2\{P(OMe)_3\}][I_3]$ (4aI$_3$)

A solution of **1** (0.100 g, 0.20 mmol) in THF (2 ml) was added dropwise to I_2 (0.101 g, 0.40 mmol) in THF (1 ml) at −78°C. The resulting mixture was stirred for 10 min to produce a red solution. The product was precipitated with hexane. The solvent was removed and the orange solid was washed with hexane (2 × 4 ml) and then dried under vacuum (0.202 g (99%)). IR (CH_2Cl_2): ν(CO) 2047 s, 1989 s cm^{-1}. ^1H NMR ($CDCl_3$): (*trans* : *cis* ratio, 1:4) *trans* isomer 2.38 (s, 15H, $\eta^5\text{-}C_5Me_5$); 4.05 (d, 9H, $^2J_{P-H}$ = 12.1 Hz, $P(OMe)_3$); *cis* isomer 2.37 (s, 15H, $\eta^5\text{-}C_5Me_5$); 3.88 (d, 9H, $^3J_{P-H}$ = 12.1 Hz, $P(OMe)_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): *trans* isomer 11.7 (s, C_5Me_5); 57.8 (d, $^2J_{C-P}$ = 9.6 Hz, OMe); 107.5 (s, C_5Me_5); 186.7 (d, $^2J_{C-P}$ =

33.1 Hz, CO); *cis* isomer 11.6 (s, C_5Me_5); 58.3 (d, $^2J_{C-P}$ = 8.4 Hz, O*Me*); 107.8 (s, C_5Me_5); 198.1 (d, $^2J_{C-P}$ = 33.1 Hz, *CO cis* to P); 186.2 (d, $^2J_{C-P}$ = 20.7 Hz, *CO trans* to P) ppm. ^{31}P NMR (acetone–acetone-d_6): *trans* isomer 91.3; *cis* isomer 81.8 ppm. MS (FAB): *m/z* 629 $(M)^+$, 601 $(M - CO)^+$, 569 $(M - CO - OCH_3)^+$. Anal. Found: C, 19.62; H, 2.67. $C_{15}H_{24}I_4O_5PReI$ calcd: C, 17.85; H, 2.40%.

2.5. trans-$(\eta^5\text{-}C_5Me_5)ReCl(CO)_2\{PO(OMe)_2\}$ (5a)

A solution of **1** (0.15 g, 0.30 mmol) in THF (3 ml) was treated with Cl_2 gas at −78°C and the resulting mixture was stirred for 15 min. The mixture was allowed to warm to room temperature and the solvent and volatile compounds were removed under vacuum. The remainder was dissolved in hexane (1 ml) and filtered through a short neutral alumina column. The column was eluted first with hexane (10 ml), then with diethyl ether (5 ml) and finally with acetone (10 ml); the latter fraction contained the product. After the acetone had been removed under vacuum, the yellow solid **5** was obtained in 98% yield. IR (CH_2Cl_2): ν(CO) 2045, 1973 s, ν(P=O) 1182 cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.02 (s, 15H, η^5-C_5Me_5); 3.72 (d, 6H, $^3J_{P-H}$ = 11.6 Hz, $PO(OMe)_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 9.6 (s, C_5Me_5); 52.7 (d, $^2J_{C-P}$ = 9.0 Hz, OMe); 105.4 (s, C_5Me_5); 195.1 (d, $^2J_{C-P}$ = 31 Hz, *CO*) ppm. ^{31}P NMR (acetone–acetone-d_6): 50.7 ppm. MS (EI): *m/z* 522 $(M)^+$, 494 $(M - CO)^+$, 466 $(M - 2CO)^+$, 388 $(M - 2CO - PO_2CH_3)^+$. Anal. Found: C, 32.05; H, 4.10. $C_{14}H_{21}ClO_5PRe$ calcd: C, 32.18; H, 4.02%.

2.6. trans-$(\eta^5\text{-}C_5Me_5)ReBr(CO)_2\{PO(OMe)_2\}$ (6a)

A solution of (**3a**Br_3) (0.10 g, 0.12 mmol) in THF (6 ml) was heated at 60°C for 3 h. The solvent was removed under vacuum, and the residue was extracted with dichloromethane (2 ml). The product was chromatographed on a neutral alumina column made up in hexane and eluted with acetone. The fraction containing the product was evaporated and the residue was recrystallized from hexane at −4°C to afford pale-yellow crystals (0.06 g, (78%)). IR (CH_2Cl_2): ν(CO) 2041 m, 1971 s, ν(P=O) 1177 cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.09 (s, 15H, η^5-C_5Me_5); 3.73 (d, 6H, $^3J_{P-H}$ = 11.6 Hz, $PO(OMe)_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 9.9 (s, C_5Me_5); 52.6 (d, $^2J_{C-P}$ = 9.3 Hz, OMe); 105.4 (s, C_5Me_5); 193.3 (d, $^2J_{C-P}$ = 31 Hz, *CO*) ppm. ^{31}P NMR (acetone–acetone-d_6): 48.7 ppm. MS (EI): *m/z* 566 $(M)^+$, 538 $(M - CO)^+$, 510 $(M - 2CO)^+$, 432 $(M - 2CO - PO_2CH_3)^+$. Anal. Found: C, 29.48; H, 3.90. $C_{14}H_{21}BrO_5PRe$ calcd: C, 29.62; H, 3.71%.

2.7. trans-$(\eta^5\text{-}C_5Me_5)ReI(CO)_2\{PO(OMe)_2\}$ (7a)

This complex was synthesized analogously to **6a** as a pale yellow crystalline solid with an 80% yield. IR (CH_2Cl_2): ν(CO) 2031 m, 1964 s, ν(P=O) 1180 cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.20 (s, 15H, η^5-C_5Me_5); 3.73 (d, 6H, $^3J_{P-H}$ = 14.0 Hz, $PO(OMe)_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 10.5 (s, C_5Me_5); 52.5 (d, $^2J_{C-P}$ = 9 Hz, OMe); 104.2 (s, C_5Me_5); 190.7 (d, $^2J_{C-P}$ = 30 Hz, *CO*) ppm. ^{31}P NMR (acetone–acetone-d_6): 47.6 ppm. MS (EI): *m/z* 614 $(M)^+$, 586 $(M - CO)^+$, 558 $(M - 2CO)^+$, 480 $(M - 2CO - PO_2CH_3)^+$. Anal. Found: C, 27.18; H, 3.59. $C_{14}H_{21}IO_5PRe$ calc. Calcd: C, 27.36; H, 3.42%.

2.8. cis- and trans-$[(\eta^5\text{-}C_5Me_5)ReCl(CO)_2\{P(OEt)_3\}][SbCl_6]$ (2b $SbCl_6$)

A solution of $SbCl_5$ (in CH_2Cl_2) was added dropwise to $(\eta^5\text{-}C_5Me_5)Re(CO)_2\{P(OEt)_3\}$ (0.20 g, 0.37 mmol) in hexane (4 ml), resulting in the immediate formation of a yellow precipitate. The solvent was removed and the solid was washed with hexane (2 × 4 ml). The yellow solid residue was recrystallized from acetone–ether to yield yellow crystals of the product (0.17 g (78%)). IR (CH_2Cl_2): ν(CO) 2062 m, 2006 s cm^{-1}. ^{1}H NMR ($CDCl_3$): (*trans*:*cis* ratio, 2:1) *cis* isomer 1.50 (t, 9H, $^3J_{H-H}$ = 7.0 Hz, CH_3); 2.15 (s, 15H, η^5-C_5Me_5); 4.18 (multiplet, 6H, CH_2); *trans* isomer 1.40 (t, 9H, $^3J_{H-H}$ = 7.0 Hz, CH_3); 2.10 (s, 15H, η^5-C_5Me_5); 4.35 (quintet, 6H, $^3J_{P-H}$ = $^3J_{H-H}$ = 7.0 Hz, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): *trans* isomer 10.2 (s, C_5Me_5); 15.9 (s, $POCH_2CH_3$); 67.6 (s, CH_2); 109.0 (s, C_5Me_5); 192.3 (d, $^2J_{C-P}$ = 31.0 Hz, *CO*) ppm. ^{31}P NMR (acetone–acetone-d_6): *trans* isomer 84.8; *cis* isomer 80.7. MS (FAB): *m/z* 579 $(M)^+$, 551 $(M - CO)^+$. Anal. Found: C, 25.32; H, 3.44. $C_{18}H_{30}Cl_7O_5PReSb$ calcd: C, 29.72; H, 4.16%.

2.9. cis-$[(\eta^5\text{-}C_5Me_5)ReCl(CO)_2\{P(OEt)_3\}][Cl_3]$ (2bCl_3)

A solution of $(\eta^5\text{-}C_5Me_5)Re(CO)_2\{P(OEt)_3\}$ (0.05 g, 0.09 mmol) in hexane (4 ml) was treated with Cl_2 gas at −78°C. There was immediate precipitation. The supernatant liquid was removed and the solid was washed with hexane (2 × 5 ml). The product was dried under vacuum (0.04 g, (68%). ^{1}H NMR ($CDCl_3$): 1.34 (t, 9H, $^3J_{H-H}$ = 7.0 Hz, CH_3); 2.05 (s, 15H, η^5-C_5Me_5); 4.24 (multiplet, 6H, CH_2) ppm. Anal. Found: C, 31.53; H, 4.84. $C_{18}H_{30}Cl_4O_5PRe$ calcd: C, 31.50; H, 4.38%.

2.10. cis- and trans-$[(\eta^5\text{-}C_5Me_5)ReBr(CO)_2\{P(OEt)_3\}][Br_3]$ (3bBr_3)

A solution of $(\eta^5\text{-}C_5Me_5)Re(CO)_2\{P(OEt)_3\}$ (0.05 g, 0.09 mmol) in hexane (30 ml) was added dropwise to Br_2 (0.09 g, 0.54 mmol) in hexane (4 ml). There was an immediate precipitate. The supernatant was removed, and the product was washed with hexane (2 × 5 ml). After the hexane was removed the yellow–red residue was recrystallized from dichloromethane–hexane to

yield the product as orange crystals (0.07 g, (90%)). IR (CH_2Cl_2): ν(CO) 2056 m, 1993 s cm^{-1}. ^1H NMR ($CDCl_3$): (*trans* : *cis* ratio, 4:1) *trans* isomer 1.50 (t, 9H, $^3J_{H-H} = 7.0$ Hz, CH_3); 2.23 (s, 15H, η^5-C_5Me_5), 4.48 (quintet, 6H, $^3J_{P-H} = {}^3J_{H-H} = 7.0$ Hz, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): *trans* isomer 10.6 (s, C_5Me_5); 16.0 (s, $POCH_2CH_3$), 67.4 (s, CH_2); 108.7 (s, C_5Me_5); 190.5 (d, $^2J_{C-P} = 34.1$ Hz, CO) ppm. ^{31}P NMR (acetone–acetone-d_6): *trans* isomer 83.5; *cis* isomer 78.4. MS (FAB): m/z 623 $(M)^+$, 595 $(M - CO)^+$. Anal. Found: C, 25.30; H, 3.38. $C_{18}H_{30}Br_4O_5PRe$ calcd: C, 25.04; H, 3.47%.

2.11. *cis- and trans-*$[(\eta^5\text{-}C_5Me_5)ReI(CO)_2\{P(OEt)_3\}][I_3]$ (**4bI$_3$**)

This complex was prepared in a similar manner to **3b**Br_3 using I_2 and 0.10 g of $(\eta^5\text{-}C_5Me_5)Re(CO)_2\{P(OEt)_3\}$. The product was obtained as a dark red solid (97%). IR (CH_2Cl_2): ν(CO) 2045 s, 1987 s cm^{-1}. ^1H NMR ($CDCl_3$): (*trans* : *cis* ratio, 1:3) *trans* isomer 1.45 (t, 9H, $^3J_{H-H} = 7.0$ Hz, CH_3); 2.36 (s, 15H, η^5-C_5Me_5); 4.34 (quintet, 6H, $^3J_{H-H} = {}^3J_{P-H} = 7.0$ Hz, CH_2); *cis* isomer 1.42 (t, 9H, $^3J_{H-H} = 7.0$ Hz, CH_3); 2.36 (s, 15H, η^5-C_5Me_5); 4.17 (multiplet, 6H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): *trans* isomer 11.5 (d, C_5Me_5); 16.28 (s, $POCH_2CH_3$); 67.7 (s, CH_2); 107.2 (s, C_5Me_5); 187.8 (d, $^2J_{C-P} = 34.2$ Hz, CO); *cis* isomer 11.5 (s, C_5Me_5); 15.8 (s, $POCH_2CH_3$); 67.6 (s, CH_2); 107.6 (s, C_5Me_5); 186.8 (d, $^2J_{C-P} = 21.0$ Hz, CO);198.9 (d, $^2J_{C-P} = 32.1$ Hz, CO) ppm. ^{31}P NMR (acetone–acetone-d_6): *trans* isomer 83.7; *cis* isomer 75.9 ppm. MS (FAB): m/z 671 $(M)^+$, 643 $(M - CO)^+$. Anal. Found: C, 20.64; H, 2.84. $C_{18}H_{30}I_4O_5PRe$ calcd: C, 20.57; H. 2.86%

2.12. *trans-*$(\eta^5\text{-}C_5Me_5)ReCl(CO)_2\{PO(OEt)_2\}$ (**5b**)

A solution of **2b**Cl_3 (0.12 g, 0.18 mmol) in THF (6 ml) was heated at 60°C for 5 h. The solvent was removed under vacuum, and the remainder was extracted in hexane (3 ml). This hexane extract was placed on a neutral alumina column. Elution with acetone removed the product. Evaporation of the solvent resulted in a pale-yellow solid (0.05 g (50%)). IR (CH_2Cl_2): ν(CO) 2045 m, 1973 s, ν(P=O) 1179 cm^{-1}. ^1H NMR ($CDCl_3$): 1.29 (t, 6H, $^3J_{H-H} = 7.0$ Hz, CH_3); 2.02 (s, 15H, η^5-C_5Me_5); 4.12 (m, 4H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 9.6 (s, C_5Me_5); 16.3 (s, CH_3); 61.1 (s, CH_2); 105.8 (s, C_5Me_5); 197.6 (d, $^2J_{C-P} = 31$ Hz, CO) ppm. ^{31}P NMR (acetone–acetone-d_6): 47.3 ppm. MS (EI): m/z 550 $(M)^+$, 522 $(M - CO)^+$, 494 $(M - 2CO)^+$, 402 $(M - 2CO - PO_2Et)^+$. Anal. Found: C, 35.03; H, 4.46. $C_{16}H_{25}ClO_5PRe$ calcd: C, 34.93; H, 4.55%.

2.13. *trans-*$(\eta^5\text{-}C_5Me_5)ReBr(CO)_2\{PO(OEt)_2\}$ (**6b**)

A solution of **3b**Br_3 (0.11 g, 0.20 mmol) in acetone (20 ml) was treated with NaI (in excess), and the resulting mixture was stirred for 12 h. The solvent was removed under vacuum, and the remainder dissolved in dichloromethane (2 ml) and filtered through a short Celite column. This dichloromethane extract was placed on a neutral alumina column. Elution with acetone removed the product. Evaporation of the solvent resulted in a pale-yellow solid (0.07 g, (60%)). IR (CH_2Cl_2): ν(CO) 2040 m, 1969 s, ν(P=O) 1181 cm^{-1}. ^1H NMR ($CDCl_3$): 1.29 (t, 6H, $^3J_{P-H} = 7.0$ Hz, CH_3); 2.08 (s, 15H, η^5-C_5Me_5); 4.12 (m, 4H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 9.9 (s, C_5Me_5); 16.0 (s, CH_3); 61.6 (s, CH_2); 105.5 (s, C_5Me_5); 193.7 (d, $^2J_{C-P} = 31$ Hz, CO) ppm. ^{31}P NMR (acetone–acetone-d_6): 45.2 ppm. MS (EI): m/z 594 $(M)^+$, 566 $(M - CO)^+$, 538 $(M - 2CO)^+$, 446 $(M - 2CO - PO_2Et)^+$. Anal. Found: C, 32.31; H, 4.21. $C_{16}H_{25}BrO_5PRe$ calcd: C, 32.32; H, 4.2%.

2.14. *trans-*$[(\eta^5\text{-}C_5Me_5)ReI(CO)_2\{PO(OEt)_2\}]$ (**7b**)

This complex was prepared following the same procedure as above, but the solvent was methanol and the complex **4b**I_3 was stirred and refluxed for 22 h. The product was pale yellow and obtained with a 30% yield. IR (CH_2Cl_2): ν(CO) 2031 m, 1964 s, ν(P=O) 1155 cm^{-1}. ^1H NMR ($CDCl_3$): 1.29 (t, 6H, $^3J_{H-H} = 7.0$ Hz CH_3); 2.20 (s, 15H, η^5-C_5Me_5); 4.10 (m, 4H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 9.9 (s, C_5Me_5); 16.0 (s, CH_3); 61.6 (s, CH_2); 105.1 (s, C_5Me_5); 193.7 (d, $^2J_{C-P} = 31$ Hz, CO) ppm. ^{31}P NMR (acetone–acetone-d_6): 43.9 ppm. MS (EI): m/z 642 $(M)^+$, 614 $(M - CO)^+$, 586 $(M - 2CO)^+$, 494 $(M - 2CO - PO_2Et)^+$. Anal. Found: C, 29.87; H, 3.84. $C_{16}H_{25}IO_5PRe$ calcd: C, 29.91; H, 3.89%.

3. Results

3.1. *Synthesis of the cationic complexes* $[Cp^*ReX(CO)_2\{P(OR)_3\}]^+$

The reaction of a solution of $SbCl_5$ in CH_2Cl_2 with $Cp^*Re(CO)_2\{P(OMe)_3\}$ (**1**) in hexane at room temperature gave a yellow precipitate of $[Cp^*ReCl(CO)_2\{P(OMe)_3\}][SbCl_6]$ (**2a**$SbCl_6$) which was recrystallized from CH_2Cl_2. The ν(CO) absorptions at 2064 m and 2004 s cm^{-1} for (**2a**$SbCl_6$) in CH_2Cl_2 exhibited an intensity pattern indicative of a *trans* four-legged piano stool geometry (**I**) (Scheme 1), which was supported by the observation of a single ^{13}C NMR carbonyl resonance at $\delta = 192.8$ ppm coupled to the *cis* phosphorus atom with $^2J_{P-C} = 33.1$ Hz. The ^1H NMR spectrum in acetone-d_6 exhibited the expected resonances at $\delta = 2.19$ ppm (Cp*) and $\delta = 4.18$ ppm

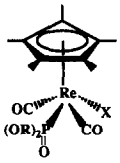
Cationic Trialkylphosphite Complexes

(I) trans

(II) cis

	R	Me	Et
X =	Cl	(2a)	(2b)
	Br	(3a)	(3b)
	I	(4a)	(4b)

Neutral Dialkylphosphonate Complexes



(III) trans

	R	Me	Et
X =	Cl	(5a)	(5b)
	Br	(6a)	(6b)
	I	(7a)	(7b)

Scheme 1.

$(P(OMe)_3)$; these were accompanied by much weaker resonances at $\delta = 2.22$ ppm (Cp*) and $\delta = 4.00$ ppm $(P(OMe)_3)$ attributed to a small amount (less than 15%) of the *cis* isomer **II**.

The ^{13}C NMR spectrum exhibited signals for the Cp* and $P(OMe)_3$ carbon atoms for both isomers, but the *cis* isomer concentration was insufficient for the carbonyl resonances to be detected. The ^{31}P NMR spectrum exhibited a major resonance at $\delta = 92.4$ ppm for the *trans* isomer and a less intense resonance at $\delta = 85.9$ ppm for the *cis* isomer. All the cationic complexes **2a–4a** and **2b–4b** measured in this study consistently show the ^{31}P NMR resonance of the *trans* isomer at a slightly greater δ value than the *cis* isomer. Solutions of **2a**$SbCl_6$ in CH_2Cl_2 or CD_2Cl_2 slowly converted to the phosphonate complex **5a** as evidenced by growth of resonances at $\delta = 2.02$ ppm (Cp*) and $\delta = 3.72$ ppm $(PO(OMe)_2)$ in the ^1H NMR spectrum. An overnight ^{13}C NMR spectrum run in CD_2Cl_2 resulted in about equal amounts of the phosphonate **5a** and the cation **2a**$SbCl_6$. However, no conversion of **2a**$SbCl_6$ to **5a** was detected by IR in THF even when refluxed for 2 h. Addition of aqueous NaI to a stirred CH_2Cl_2 solution of **2a**$SbCl_6$ immediately and quantitatively converted it to **5a**. Notably, the reaction of **1** with Cl_2 did not afford the cation **2a** but resulted in the phosphonate complex **5a** instead (see below).

The reaction of excess Br_2 or I_2 in THF with **1** at -78°C followed by precipitation with hexane resulted in the corresponding salts $[Cp^*ReBr(CO)_2\{P(OMe)_3\}][Br_3]$ (**3a**Br_3) and $[Cp^*ReI(CO)_2\{P(OMe)_3\}][I_3]$ (**4a**I_3) as yellow–orange and orange solids respectively. Compound **3a**Br_3 was observed to have ν(CO) bands at 2052 m and 1990 s cm^{-1} in THF, with intensities indicative of the *trans* isomer **I**, again supported by the single ^{13}CO resonance at $\delta = 190.5$ ppm ($^2J_{P-C} = 33.7$ Hz). In this case, only very weak (about 4%) resonances attributable to the *cis* isomer **II** could be detected in the ^1H NMR spectrum at $\delta = 2.26$ ppm (Cp*) and $\delta = 3.90$ ppm $(P(OMe)_3)$. For the iodo compound **4a**I_3, however, the IR spectrum exhibited ν(CO) absorptions at 2047 s and 1989 s cm^{-1} which had nearly equal intensities, suggesting a mixture of both isomer **I** and isomer **II**. The Cp* methyl ^1H NMR resonances for these two isomers were almost coincident at $\delta = 2.38$ ppm but there were two well-separated doublets for the $P(OMe)_3$ protons of each isomer at $\delta = 3.88$ ppm ($^3J_{P-H} = 12.1$ Hz) and $\delta = 4.05$ ppm ($^3J_{P-H} = 12.1$ Hz) assigned to the *cis* and *trans* isomers respectively in 4:1 ratio. The ^{31}P NMR spectrum exhibited a resonance at $\delta = 81.8$ ppm assigned to the *cis* isomer which was more intense than that at $\delta = 91.3$ ppm for the *trans* isomer. The ^1H NMR spectrum of the mixture of isomers of **4a**I_3 in acetone-d_6 was measured over the temperature range 313–233 K and the reverse to test for thermodynamic equilibrium. At 298 K the *cis*:*trans* ratio was 1:4, and the proportion of *trans* isomer increased further with decrease in temperature (*e.g. cis*:*trans* ratio of 1:1.8 at 233 K) and returned to 1:4 at 298 K, showing the system to be at equilibrium at this temperature. The rate of isomerization was not measured but was too slow to give any observable spin saturation transfer between the $P(OMe)_3$ methyl signals for the two isomers at 298 K.

The related triethylphosphite complexes $[Cp^*ReX(CO)_2\{P(OEt)_3\}][X_3]$ for X = Br (**3b**Br_3) and X = I (**4b**I_3) were synthesized in a similar fashion as orange and dark-red crystalline solids respectively. In these cases both the *trans* isomer **I** and the *cis* isomers **II** are present in the isolated products, and the proportions can be easily determined from an inspection of the methylene proton resonances in the ^1H NMR spectrum. This is because the methylene protons are equivalent in **I** and give rise to a simple quintet pattern by coupling to the CH_3 protons and to phosphorus with identical $J = 7.0$ Hz, but the methylene protons in the *cis* isomer **II** are diastereotopic and the pattern at 400 MHz appears as a multiplet (an apparent quintet of doublets). The assignment was confirmed in detail for **4b**I_3 by appropriate decoupling procedures. Phospho-

rus decoupling reduced the $\delta = 4.17$ ppm signal to a simple quartet (*trans* isomer **I**). Irradiation at $\delta = 4.17$ ppm left the $\delta = 4.34$ ppm pattern unaffected, confirming that these resonances arise from separate isomers, and it reduced the methyl triplet at $\delta = 1.42$ ppm (*i.e.* the major triplet) to a singlet, thus confirming the major isomer to be *cis*, *i.e.* **II**. Correspondingly irradiation of the methylene signal at $\delta = 4.34$ ppm reduced the minor methyl triplet at $\delta = 1.50$ ppm (from the *trans* isomer **I**) to a singlet but left the resonances of the *cis* isomer unaffected. The *cis* : *trans* ratio for **4b**I_3 was determined from the ^{1}H NMR spectrum to be 3 : 1. The ^{1}H NMR spectrum of the bromo complex **3b**Br_3 exhibits similar features except that here the resonance pattern for the diasterotopic methylene protons is weaker than the methylene resonance for the other isomer, and therefore the *cis* isomer is the minor one in this case. The *cis* : *trans* ratio for **3b**Br_3 was estimated from ^{1}H NMR intensities to be 1 : 4. The ^{31}P NMR spectra were in accord with these *cis* : *trans* ratios; for example for **4b**I_3 a less intense resonance occurred at $\delta = 83.7$ ppm (*trans* isomer) downfield of a more intense peak at $\delta = 75.9$ ppm (*cis* isomer).

In an interesting contrast with $Cp^*Re(CO)_2\{P(OMe)_3\}$ (**1**) the reaction of the triethylphosphite complex $Cp^*Re(CO)_2\{P(OEt)_3\}$ with either $SbCl_5$ or Cl_2 gave in both cases the cation $[Cp^*ReCl(CO)_2\{P(OEt)_3\}]^+$ (**2b**) whereas the reaction of Cl_2 with **1** afforded only the phosphonate complex **5a**.

3.2. Synthesis of dialkylphosphonate complexes $Cp^*ReX(CO)_2\{PO(OR)_2\}$

The reaction of $Cp^*Re(CO)_2\{P(OMe)_3\}$ (**1**) with Cl_2 in THF at -78°C gave upon work-up a high yield of the trans isomer of the dimethylphosphonate complex $Cp^*ReCl(CO)_2\{PO(OMe)_2\}$ (**5a**) as a yellow solid (Scheme 1, **III**). The assignment of the stereochemistry of **5a** was straightforward from the ν(CO) intensities and the single CO resonance at $\delta = 195.1$ ppm ($^2J_{P-C} = 31$ Hz). The corresponding bromo analogue **6a** and iodo analogue **7a** were synthesized as pale-yellow crystals by the thermolysis of **3a**Br_3 and **4a**I_3 respectively in THF at 60°C for 3 h followed by extraction into CH_2Cl_2, chromatography and recrystallization from hexane. These also were obtained exclusively as the *trans* isomers. The corresponding diethylphosphonate complexes $Cp^*ReX(CO)_2\{PO(OEt)_2\}$ (X = Br (**6b**) or I (**7b**)) were obtained as pale yellow solids by treating the triethylphosphite complexes **3b**Br_3 or **4b**I_3 with NaI. Thermolysis at 60°C in THF for 4 h was also carried out for **3b**Br_3 and gave **6b** as expected by analogy with the trimethylphosphite examples. Again, only the *trans* isomers were obtained for **6b** and **7b**. The chloride $Cp^*ReCl(CO)_2\{PO(OEt)_2\}$ (**5b**) was prepared similarly, by thermolysis of $[Cp^*ReCl(CO)_2\{P(OEt)_3\}]^+$ (**2b**) (prepared from $Cp^*Re(CO)_2\{P(OEt)_3\}$ and Cl_2) at 60°C in THF for 5 h. The ^{31}P NMR spectra of the dialkylphosphonate complexes all exhibit a single resonance consistent with the presence of only the *trans* isomer in each case. The chemical shift region, about 43–51 ppm, is characteristic and readily distinguishes the phosphonate from the relatively more deshielded resonances of the parent cationic trialkylphosphite complexes.

3.3. Reversible formation of the cationic phosphite and neutral phosphonate complexes

When $Cp^*Re(CO)_2\{P(OMe)_3\}$ (**1**) was reacted with one equivalent of Br_2 at -78°C in THF the solution obtained did not contain the trimethylphosphite complex cation $[Cp^*ReBr(CO)_2\{P(OMe)_3\}]^+$ (**3a**) but was a mixture of the phosphonate complex **6a** and unreacted **1**. Addition of a second equivalent of Br_2 converted the remaining **1** to the phosphonate complex **6a** and the spectrum now indicated also the presence of a small amount of the trimethylphosphite complex cation **3a**. Addition of a third equivalent of Br_2 resulted in disappearance of most of the phosphonate complex **6a** in favour of the cationic trimethylphosphite complex **3a**. In order to probe in more detail the competing reactions that give rise to this behaviour, some further reactions were carried out. When the phosphonate **6a** was treated with CH_3Br gas in THF, there was no evidence of a change in the IR spectrum. However, addition of MeBr and Br_2 to **6a** resulted in formation of the trimethylphosphite complex cation **3a** as the only rhenium product. When the isolated Br_3^- salt of the trimethylphosphite complex **3a**, *i.e.* (**3a**Br_3), was dissolved in CH_2Cl_2 at room temperature the IR spectrum showed, within 15 min, the appearance of absorptions resulting from the phosphonate complex **6a** and this could be completely reversed by the addition of Br_2 to the solution. Exactly similar behaviour was observed for the bromo diethylphosphonate complex **6b**. Addition of EtBr and Br_2 converted this quantitatively to the cationic complex **3b**.

4. Discussion

4.1. Synthesis and interconversions of cationic phosphite complexes and neutral phosphonate complexes

The trialkylphosphite complexes $Cp^*Re(CO)_2\{P(OR)_3\}$ (R = Me, or Et) behave similarly to $CpRe(CO)_3$ [3,4], $Cp^*Re(CO)_3$ [2], $Cp^*Re(CO)_2(PMe_3)$ [1], $Cp^*Re(CO)_2\{P(OPh)_3\}$ [5] and $Cp^*Re(CO)_2(PPh_3)$ [6] in forming a cationic electrophilic addition product, in this case $[Cp^*ReX(CO)_2\{P(OR)_3\}]^+$, in reactions with X_2 (X = Br or I) or $SbCl_5$. Because of the possibility of

subsequent nucleophilic attack by the anion on the trialkylphosphite ligand in a Michaelis–Arbuzov type of reaction [7*] to give a dialkylphosphonate ligand (*vide infra*), the success in isolating these cationic trialkylphosphite complexes is very dependent on the reaction conditions. The use of $SbCl_5$ is very straightforward and both **2a** and **2b** precipitate readily and can be recrystallized from CH_2Cl_2 without further reaction because of the low nucleophilicity of the $[SbCl_6]$ counter anion:

$$Cp^*Re(CO)_2\{P(OR)_3\} + 2SbCl_5 \rightarrow [Cp^*ReCl(CO)_2\{P(OR)_3\}][SbCl_6] + SbCl_3 \quad (1)$$

By way of comparison, the use of Cl_2 directly, even at $-78°C$, gives on subsequent isolation a high yield of the dialkylphosphonate complex (*i.e.* **5a**) in the case of trimethylphosphite (but not triethylphosphite). This we attribute to initial formation of cations **2a** or **2b**, *i.e.*

$$Cp^*Re(CO)_2\{P(OR)_3\} + Cl_2 \rightarrow [Cp^*ReCl(CO)_2\{P(OR)_3\}]Cl \quad (2)$$

and **2a** then immediately reacts according to

$$[Cp^*ReCl(CO)_2\{P(OR)_3\}]Cl \rightarrow Cp^*ReCl(CO)_2\{PO(OR)_2\} + RCl \quad (3)$$

(whereas **2b** requires heating) owing to the much higher nucleophilicity of the chloride anion (or possibly other anionic chlorine species such as Cl_3^-) now present compared with $[SbCl_6]^-$. It has previously been observed that triethylphosphite ligands are more resistant than trimethylphosphite to dealkylation [7a*,8a]. In the cases of Br_2 and I_2, however, an excess of these reagents in THF at $-78°C$ followed by precipitation with hexane produced excellent yields of the solid bromo and iodo cationic trialkylphosphite complexes **3a**, **3b**, **4a** and **4b** as the $[Br_3]^-$ or $[I_3]^-$ salts:

$$Cp^*Re(CO)_2\{P(OR)_3\} \xrightarrow[(X=Br\text{ or }I)]{\text{excess}X_2} [Cp^*ReX(CO)_2\{P(OR)_3\}][X_3] \quad (4)$$

Each of these salts is sufficiently stable in THF or $CDCl_3$ solution during short periods of time to enable the IR, ^1H and ^{13}C NMR spectra to be obtained. Over longer periods in solution there is significant conversion to the neutral dialkylphosphonate complexes **6a**, **6b**, **7a** and **7b**. For example a solution of **3a**Br_3 in $CDCl_3$ after 1 h exhibited a ^1H NMR spectrum indicating a *trans*-**3a**: *cis*-**3a** and phosphonate **6a** ratio of approximately 1:1:9. This occurs more rapidly at higher temperatures, as expected, giving good yields of these phosphonate complexes as the *trans* isomers in each case.

Although the reactions with excess X_2 yield the trialkylphosphite complex cations **3a**, **4a**, **3b** and **4b** it is interesting that, following the reaction of **1** with Br_2 in a 1:1 ratio at room temperature, none of the cationic complex **3a** is observed spectroscopically; rather, there is formed a mixture of unreacted **1** with the phosphonate complex **6a**. Then, addition of a further equivalent of Br_2 consumes all of **1** but the product is still substantially **6a** (with a small amount of the cation **3a** now observable). Only after a third equivalent of Br_2 is added, is complex **3a** the major product. This result, and the results of the reactions described above in which the phosphonate **6a** can be reconverted to the cationic phosphite complex **3a** only with MeBr and Br_2 together but not by MeBr alone; this can be understood in terms of the equilibrium between Br^- and $[Br_3]^-$ as given by

$$Br^- + Br_2 \rightleftharpoons [Br_3]^- \quad (5)$$

with the assumption that Br^- is sufficiently nucleophilic to dealkylate the $P(OR)_3$ ligand rapidly, but that in $[Br_3]^-$ this tendency is much reduced. Thus we propose that the first step is formation of the cation **3a**:

$$\underset{\mathbf{1}}{Cp^*Re(CO)_2\{P(OMe)_3\}} + Br_2 \rightleftharpoons \underset{\mathbf{3a}Br}{[Cp^*ReBr(CO)_2\{P(OMe)_3\}]Br} \quad (6)$$

However, in the presence of one equivalent of Br_2 this does not go to completion and much of **1** remains because much of the Br_2 is unavailable for reaction with **1** owing to its involvement in complexing with Br^- to give $[Br_3]^-$ as shown in eqn. (5). We now propose that cation **3a** is rapidly dealkylated by nucleophilic attack of Br^- (but not by $[Br_3]^-$) to give the phosphonate **6a** and MeBr as in the following equation, so that, at a 1:1 ratio of reactants, only **1** and **6a** are observed:

$$\underset{\mathbf{3a}}{[Cp^*ReBr(CO)_2\{P(OMe)_3\}]^+} + Br^- \rightleftarrows \underset{\mathbf{6a}}{Cp^*ReBr(CO)_2\{PO(OMe)_2\}} + MeBr \quad (7)$$

Addition of excess Br_2 displaces the equilibrium position in eqn. (5) in favour of the poorly nucleophilic $[Br_3]^-$ ion and shifts eqn. (7) in favour of the cationic complex **3a** which can be isolated as the $[Br_3]^-$ salt. The addition of MeBr by itself to **6a** in solution is ineffective in converting **6a** to **3a** because of the over-

* A reference number with an asterisk indicates a note in the list of references.

whelming forward reaction in eqn. (7) owing to the strong nucleophilicity of Br^-, but, when assisted by Br_2 addition (which consumes Br^- as the weakly nucleophilic $[Br_3]^-$), transformation of **6a** to **3a** is observed to be essentially quantitative.

In the case of I_2, addition to **1** in a 1:1 ratio at −78°C again only consumes about half of **1** but the product at this stage is mainly the cation **4a** rather than the phosphonate **7a**. This is presumably because I^- is virtually completely complexed with further I_2 as $[I_3]^-$ which is not nucleophilic enough to convert **4a** to the phosphonate **7a** at a sufficient rate at this temperature. At room temperature eventually all of **1** is consumed and the cationic complex disappears in favour of the phosphonate complex **7a** presumably as a result of the increased rate of dealkylation by $[I_3]^-$ (or I^-) at the higher temperature.

4.2. Stereochemistry of phosphite and phosphonate complexes

The complexes **2–7** are all presumed to adopt the four-legged piano-stool geometry that has been well established for $CpML_4$ type of complexes [8b]. In the particular case of the phosphonate complex $Cp^*ReI(CO)_2\{PO(OMe)_2\}$ (**7a**) this has been confirmed by an X-ray crystal structure determination as shown in Fig. 1 [9]. Furthermore, the structure determination unequivocally showed **7a** to adopt the *trans* geometry **III** and this is in agreement with the relative intensities of the ν(CO) bands in the IR spectrum, where the intensity of the higher wavenumber symmetric stretching mode (ν_{sym}) is weaker than the lower wavenumber antisymmetric stretching mode (ν_{asym}). A similar pattern of intensities is observed for all the phosphonate complexes **5–7** and all exhibit a ^{13}CO resonance for equivalent CO groups in the ^{13}C NMR spectrum. Accordingly we are confident that all adopt the *trans* geometry, and this is the geometry which places the bulky phosphonate and halogen atoms in the least mutually sterically hindered positions [8a].

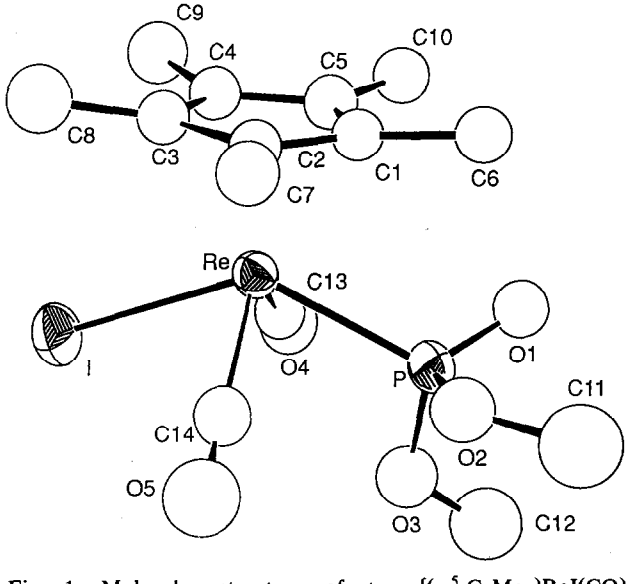


Fig. 1. Molecular structure of *trans*-[$(\eta^5\text{-}C_5Me_5)ReI(CO)_2\{PO(OMe)_2\}$] (**7a**).

In agreement with the compilation of Brill and Landon [7a*], we find that the ^{31}P resonances for the phosphonate complexes, in the range 43–51 ppm, are all shifted to smaller δ values compared to the parent cationic trialkylphosphite complexes. However, both occur rather upfield of the tabulated ranges of phosphonate and phosphite complexes quoted in that review [7a*].

The crystal structure of several other phosphonate complexes have been reported, including $CpFe(CO)_2\{PO(OEt)_2\}$ [10], $Hg\{PO(OEt)_2\}_2$ [11], $HgCl\{PO(OEt)_2\}$ [11], $CpCo\{P(OMe)_3\}\{PO(OMe)_2\}_2$ [12], $[CpCo(dppe)\{PO(OMe)_2\}]^+$ [13], $CpCOI\{PPh_2NHCH(Me)Ph\}\{PO(OMe)_2\}$ [14], $CpCo(C_3F_7)\{PPh_2NHCH(Me)Ph\}\{PO(OMe)_2\}$ [15], $Cp^*CoI\{PPh_2NHCH(Me)Ph\}\{PO(OMe)_2\}$ [16], $CpCr(CO)_2\{P(OMe)_3\}\{PO(OMe)_2\}$ [17], $Pt\{P(OH)(OMe)_2\}_2\{PO(OMe)_2\}_2$ [18], $ReOCl(OMe)\{PO(OMe)_2\}(PPh_3)_2$ [19], $[(C_6H_6)OsI\{PO(OMe)_2\}_2]^-$, $(C_6H_6)OsI\{PO(OMe)_2\}H$ [20] and $[Pt\{P(OMe)_3\}_3\{PO(OMe)_2\}]PF_6$ [21].

While all the phosphonates **5–7** are observed to be *trans* complexes, the stereochemistry of the cationic trialkylphosphite complexes **2–4** depends on the halogen and the particular alkyl group. Complex **2a**$SbCl_6$ was obtained mainly as the *trans* isomer, although spectroscopy indicated the presence of about 15% of the *cis* isomer also; however, **2a**Cl_3 was obtained exclusively as the *cis* isomer. This contrasts with $Cp^*Re(CO)_2(PMe_3)$, where reaction with $SbCl_5$ was reported to give the *cis* isomer of $[Cp^*ClRe(CO)_2(PMe_3)][SbCl_6]$ whereas Cl_2 produced the cation as the *trans* isomer [1]. In reactions with excess Br_2, $Cp^*Re(CO)_2\{P(OMe)_3\}$ gave predominantly the *trans* isomer of **3a**Br_3, while $Cp^*Re(CO)_2\{P(OEt)_3\}$ gave a mixture of both isomers of **3b**Br_3, with the *trans* : *cis* ratio about 4:1 in favour of *trans*. For the iodide **4a**I_3 the ratio is about 4:1 in favour of the *cis* isomer and for **4b**I_3 it is about 3:1 in favour of the *cis* isomer. Although the results as a whole show no parallel to those for $Cp^*Re(CO)_2(PMe_3)$ [1], it can be noted that, in this case also, formation of the *cis* isomer was predominant for the iodide.

Because of the tendency of these complexes to convert to the phosphonate in solution, we have not undertaken an exhaustive study of the conditions that

favour the formation of the particular isomers and have not attempted to isolate pure isomers. It has, however, been established for **4aI**$_3$ and **4bI**$_3$ that the observed ratio of the isomers in solution at ambient temperature is the thermodynamic equilibrium ratio.

5. Conclusion

In this study, we have demonstrated that the rhenium trialkylphosphite complexes $(\eta^5\text{-}C_5Me_5)Re(CO)_2\{P(OR)_3\}$ readily form the cationic halide derivatives $[(\eta^5\text{-}C_5Me_5ReX(CO)_2\{P(OR)_3\}]^+$ which are unstable with respect to a Michaelis–Arbuzov-like dealkylation by a sufficiently nucleophilic anion. We have further demonstrated that in this system this is a reversible process, and the resulting neutral dialkylphosphonate complex $(\eta^5\text{-}C_5H_5)ReBr(CO)_2\{PO(OR)_2\}$ may be completely reconverted to the cationic complex by the addition of, for example, alkyl bromide and Br_2 together, because the $[Br_3]^-$ anion thus generated is too weakly nucleophilic to effect the dealkylation reaction.

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References and notes

1 A.H. Klahn-Oliva, R.D. Singer, J.M. Aramini and D. Sutton, *Inorg. Chem., 28* (1989) 4217.
2 F.W.B. Einstein, A.H. Klahn-Oliva, D. Sutton and K.G. Tyers, *Organometallics, 5* (1986) 53.
3 N.E. Kolobova, Z.P. Valueva, and E.I. Kazimirchuk, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1981) 408.
4 R.B. King, *J. Inorg. Nucl. Chem., 29* (1967) 2119.
5 (a) A.H. Klahn, C. Leiva, K. Mossert and X. Zhang, *Polyhedron, 10* (1991) 1873; (b) M. Campos-Vallete, G. Diaz-Fleming, A.H. Klahn-Oliva and C. Leiva, *Vib. Spectrosc., 3* (1992) 305.
6 A.H. Klahn, unpublished results.
7 (a) For a review of the Arbuzov-like dealkylation reactions of transition metal phosphite complexes see T.B. Brill and S.J. Landon, *Chem. Rev., 84* (1984) 577; (b) For recent examples of phosphonate complexes see H.-L. Ji, J.H. Nelson, A. DeCian and J. Fischer, *Organometallics, 11* (1992) 1618; (c) H. Nakazawa, M. Yamaguchi, K. Kubo and K. Miyoshi, *J. Organomet. Chem. 428* (1992) 145, and references cited therein.
8 (a) R.B. King and R.H. Reimann, *Inorg. Chem., 15* (1976) 179; (b) P. Kubacek, R. Hoffmann and Z. Havlas, *Organometallics, 1* (1982) 180.
9 F.W.B. Einstein, C.E.F. Rickard, A.H. Klahn and C. Leiva, *Acta Crystallogr., Sect. C47* (1991) 862.
10 (a) H. Nakazawa, K. Morimasa, Y. Kushi and H. Yoneda, *Organometallics, 7* (1988) 458; (b) H. Nakazawa, K. Morimasa and H. Yoneda, *J. Coord. Chem., 18* (1988) 209.
11 G.G. Mather and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, (1973) 560.
12 D.K. Towle, S.J. Landon, T.B. Brill and T.H. Tulip, *Organometallics, 1* (1982) 295.
13 R.J. Sullivan, Q-B. Bao, S.J. Landon, A.L. Rheingold and T.B. Brill, *Inorg. Chim. Acta, 111* (1986) 19.
14 H. Brunner, C.R. Jablonski and P.G. Jones, *Organometallics, 7* (1988) 1283.
15 C.R. Jablonski, H. Ma, Z. Chen, R.C. Hynes, J.N. Bridson and M.P. Bubenik, *Organometallics, 12* (1993) 917, and references cited therein.
16 C. Jablonski, T. Burrow and P.G. Jones, *J. Organomet. Chem., 370* (1989) 173.
17 V.W. Doy, I. Tavanaiepour, S.S. Abdel-Meguid, J.F. Kirner, L.Y. Goh and E.L. Muetterties, *Inorg. Chem., 21* (1982) 657.
18 J.M. Solar, R.D. Rogers and W.R. Mason, *Inorg. Chem., 23* (1984) 373.
19 M. Fernanda, N.N. Carvalho, A.J.L. Pombeiro, D.L. Hughes and R.L. Richards, *J. Organomet. Chem., 335* (1987) C 23.
20 V. Schubert, R. Werner, L. Zinner and H. Werner, *J. Organometal Chem., 253* (1983) 363.
21 Q.-B. Bao, S.J. Geib, A.L. Rheingold and T.B. Brill, *Inorg. Chem., 26* (1987) 3453.