Activation of Dichloromethane by Basic Rhodium(I) and Iridium(I) Phosphine Complexes. Synthesis and Structures of *fac*-[Rh(PMe$_3$)$_3$Cl$_2$(CH$_2$PMe$_3$)]Cl·CH$_2$Cl$_2$ and *trans*-[Rh(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl(CH$_2$Cl)]Cl

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Sixteen-electron Rh^{I} complexes of basic phosphines react with CH$_2$Cl$_2$ yielding either RhCH$_2$Cl or RhCH$_2$PMe$_3$ complexes; an example of each has been structurally characterized.

There has been considerable recent interest[1,2] in the activation of dihalogenomethanes by late transition metal complexes as a means of generating the synthetically useful MCH$_2$X unit avoiding the use of α-halogenoethers. In certain cases,[3] dinuclear μ-CH$_2$ complexes result directly from CH$_2$X$_2$ activation. Elegant studies by Werner *et al.*[1] on the (η-C$_5$H$_5$)Rh(L)$_2$ half-sandwich systems demonstrated the possibility of ligand migrations of the form given in equation (1) (L = tertiary phosphine), as well as attack on the RhCH$_2$X group by external nucleophiles (*e.g.* pyridine, methoxide). It is interesting to note that most of these reactions have involved CH$_2$I$_2$, CH$_2$Br$_2$, or CH$_2$ICl, there being few examples of CH$_2$Cl$_2$ activation.[1b,2b,3c] We report herein that square-planar rhodium(I) complexes incorporating basic phosphine ligands react rapidly with CH$_2$Cl$_2$ yielding either chloromethyl Rh^{III} or Rh^{III}CH$_2$PR$_3$ ylide complexes in high yields.

$$\mathrm{Rh(L)(CH_2X)} \longrightarrow \mathrm{Rh(X)(CH_2L)} \qquad (1)$$

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Interest in our laboratory in the stoicheiometric[4] and catalytic[5] reactions of the cationic $[L_nM]Cl$ complexes (**1**)[6] and (**2a,b**)[7,4b] and the neutral $[(PMe_3)_3RhCl]$ (**3**)[6] complexes led us to explore their stability in the useful solvent CH_2Cl_2. Complexes (**1**) and (**3**) are reportedly unstable in chlorinated solvents CH_2Cl_2, $CHCl_3$, and CCl_4.[6]‡ We also find that (**1**) and (**3**) react with CH_2Cl_2 and report herein the nature of the reaction products.

$[L_nM]Cl$
(**1**) L = PMe_3, M = Rh, $n = 4$
(**2a**) L = dmpe, M = Rh, $n = 2$
(**2b**) L = dmpe, M = Ir, $n = 2$

dmpe = $Me_2PCH_2CH_2PMe_2$

$[(PMe_3)_3RhCl]$
(**3**)

fac-$[Rh(PMe_3)_3Cl_2(CR_2PMe_3)]Cl{\cdot}CR_2Cl_2$
(**4a**) R = H
(**4b**) R = D

trans-$[(dmpe)_2MCl(CH_2Cl)]Cl{\cdot}CH_2Cl_2$

(**5a**) M = Rh
(**5b**) M = Ir

mer, cis-$[(PMe_3)_3RhCl_2(CH_2Cl)]$
(**6a**)

$[(PMe_3)_2RhCl_3(CH_2PMe_3)]$
(**6b**)

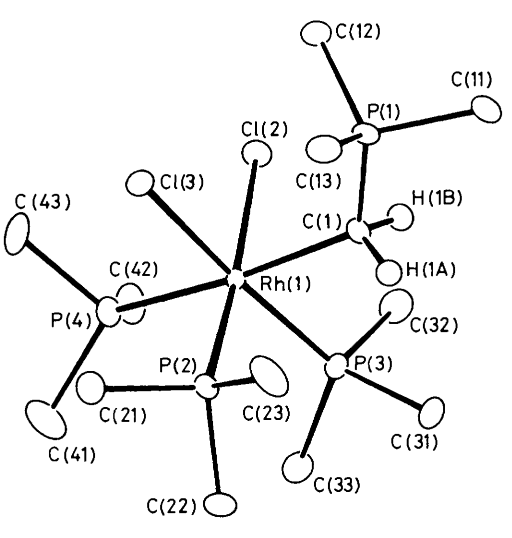
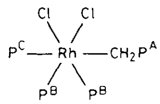
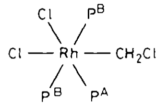


Figure 1. ORTEP drawing of a molecule of (**4a**). Selected bond distances (Å) and angles (°): Rh(1)-P(2) 2.280(1), Rh(1)-P(4) 2.380(1), Rh(1)-Cl(2) 2.431(1), Rh(1)-C(1) 2.160(3), P(1)-C(1) 1.782(3), P(3)-Rh(1)-C(1) 83.4(1), Rh(1)-C(1)-P(1) 125.2(2).

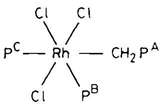
Brief dissolution of (**1**) in CH_2Cl_2 followed by precipitation with Et_2O gives the cationic ylide species *fac*-$[Rh(PMe_3)_3Cl_2(CH_2PMe_3)]Cl{\cdot}CH_2Cl_2$ (**4a**) as white microcrystals in quantitative yield. The ^1H and ^{31}P n.m.r. spectra§ of (**4a**) indicate three different PMe_3 environments in a 1:2:1 ratio. The ^1H n.m.r. spectrum indicates a molecule of CH_2Cl_2 of crystallization is present. The resonance due to the ylide CH_2 group is apparently obscured by the PMe_3 resonances. Reaction of (**1**) with CD_2Cl_2 gives the analogous $RhCD_2PMe_3$ species (**4b**) and the ^2H n.m.r. spectrum of isolated (**4b**) in CH_2Cl_2 shows a sharp singlet at δ 5.32 for the CD_2Cl_2 of crystallization and a broad peak of approximately equal integrated intensity at δ 1.6 for $RhCD_2PMe_3$. The $^{13}C\{^1H\}$ n.m.r. spectrum of (**4a**) shows the $RhCH_2PMe_3$ carbon as a well resolved dddt indicating coupling to ^{103}Rh, two distinct, ^{31}P nuclei, and two equivalent ^{31}P nuclei. An *X*-ray diffraction



(**4a**)



(**6a**)



(**6b**)

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‡ There are significant discrepancies between our results and those reported in ref. 6. We defer a detailed discussion of these and additional findings to a subsequent report.

§ *Spectroscopic data* for (**4a**): ^1H n.m.r. (360 MHz, CD_2Cl_2) δ 5.35 (s, 2H, CH_2Cl_2), 2.02 [d, $^2J(PH)$ 14 Hz, 9H, PMe_3] , 1.73 [d, $^2J(PH)$ 10 Hz, 18H, $2PMe_3$], 1.58 [d, $^2J(PH)$ 9 Hz, 9H, PMe_3]; $^{31}P\{^1H\}$ n.m.r. (121.69 MHz, CD_2Cl_2, positive chemical shifts are to high frequency of external 85% H_3PO_4) δ 35.26 [d of quartets, $^3J(P^CP^A)$ 6, $^3J(P^BP^A)$ 4, $^2J(RhP^A)$ 4 Hz, P^A], 7.53 [ddd, $J(RhP^B)$ 117, $^3J(P^AP^B)$ 4, $^2J(P^CP^B)$ 26 Hz, $2P^B$], −19.42 p.p.m. [ddt, $J(RhP^c)$ 78, $^3J(P^AP^C)$ 6, $^2J(P^BP^C)$ 26 Hz, P^C]; $^{13}C\{^1H\}$ n.m.r. (75.59 MHz, CD_2Cl_2) δ 55.51 (s, CH_2Cl_2), 18.60 (m, 2 × P^BMe_3), 16.50 [d, $J(PC)$ 28 Hz, PMe_3], 15.38 [dd, $J(PC)$ 55, 3 Hz, PMe_3], 5.59 p.p.m. [dddt, $^2J(P^BC)$ 8, $^2J(P^CC)$ 120, $^2J(P^AC)$ + $J(RhC)$ 40, 21 Hz, $RhCH_2P$].

(**4b**): ^2H N.m.r. (46.14 MHz, CH_2Cl_2, relative to Me_4Si) δ 5.35 (s, 2D, CD_2Cl_2), 1.70 p.p.m. (br. s, 2D, $RhCD_2P$).

(**5a**): ^1H N.m.r. (360 MHz, CD_2Cl_2) δ 3.37 [d of quintets, ^2J (RhH) 2.3, $^3J(PH)$ 5.6 Hz, 2H, $RhCH_2Cl$], 2.25 (m, 4H, PCH_2CH_2P), 2.00 (m, 4H, PCH_2CH_2P), 1.76 (br. s, 12H, PMe), 1.71 (br. s, 12H, PMe); $^{31}P\{^1H\}$ n.m.r. (121.69 MHz, CD_2Cl_2) δ 38.1 p.p.m. [d, $J(RhP)$ 93 Hz]; $^{13}C\{^1H\}$ n.m.r. (75.59 MHz, CD_2Cl_2) δ 32.60 [d of quintets, $J(RhC)$ 30, $^2J(PC)$ 6 Hz, $RhCH_2Cl$], 28.05 (apparent quintet, J 13 Hz, CH_2P), 13.13 (apparent quintet, J 9 Hz, PMe), 11.62 (apparent quintet, J 8 Hz, PMe).

(**5b**): ^1H N.m.r. (360 MHz, CD_2Cl_2) δ 3.64 [quintet, $^3J(PH)$ 5 Hz, 2H, $IrCH_2Cl$], 2.2 (m, 4H, PCH_2CH_2P), 1.9 (m, 4H, PCH_2CH_2P), 1.84 (s, 12H, PMe), 1.77 (s, 12H, PMe); $^{31}P\{^1H\}$ n.m.r. (121.69 MHz, CD_2Cl_2) 7.96 (s).

(**6a**): ^1H N.m.r. (360 MHz, C_6D_6) δ 4.30 [tt, $^2J(RhH) = {}^3J(P^AH)$ 2.3, $^3J(P^BH)$ 4.4 Hz, 2H, $RhCH_2Cl$], 1.32 [virtual t, $J(PH)$ 3.5 Hz, 18H, P^BMe_3], 1.19 [d, $^2J(PH)$ 10.2 Hz, 9H, P^AMe_3]; $^{31}P\{^1H\}$ n.m.r. (121.69 MHz, C_6D_6) δ 8.7 [dt, $J(RhP)$ 137, $^2J(PP)$ 28 Hz, P^A], −7.6 p.p.m. [dd, $J(RhP)$ 98, $^2J(PP)$ 28 Hz, 2 × P^B]; ^{13}C n.m.r. (100.16 MHz, C_6D_6) δ 41.39 [td quartet, $J(CH)$ 154, $J(RhC)$ 29, $^2J(PC)$ 6 Hz, $RhCH_2Cl$], 18.71 [quartet of d, $J(CH)$ 130, $J(PC)$ 34 Hz, P^AMe_3], 15.43 [quartet of virtual t, $J(CH)$ 130, $J(PC)$ 16 Hz, P^BMe_3].

(**6b**): ^1H N.m.r. {360 MHz, $[^2H_8]$tetrahydrofuran (THF)} δ 1.86 [d, $^2J(PH)$ 14 Hz, 9H, PMe_3], 1.49 [overlapping doublets, $^2J(PH)$ 10, $^2J(PH)$ 11 Hz, 18H, 2 × PMe_3], $RhCH_2P$ not observed; $^{31}P\{^1H\}$ n.m.r. (121.69 MHz, $[^2H_8]$THF) δ 31.5 [approx. dt, $^3J(P^CP^A) \simeq {}^3J(P^BP^A)$ 5—7 Hz, $^2J(RhP)$ 9 Hz, P^A], 10.7 [ddd, $^3J(P^AP^B)$ 7, $^2J(P^CP^B)$ 26, $^2J(RhP)$ 120 Hz, P^B] −15.6 p.p.m. [ddd, $^3J(P^AP^C)$ 5, $^2J(PP)$ 26, $J(RhP)$ 84 Hz, P^C].

(**7**) ^1H N.m.r. (360 MHz, CD_2Cl_2) δ 3.64 [d of quintets, $^2J(RhH)$ 2.6, $^3J(PH)$ 6.0 Hz, 2H, $RhCH_2Cl$], 1.70 (br.s, 36 H, 4 × PMe_3); $^{31}P\{^1H\}$ n.m.r. (121.69 MHz, CD_2Cl_2) δ −8.99 p.p.m. [d, $J(RhP)$ 93 Hz].

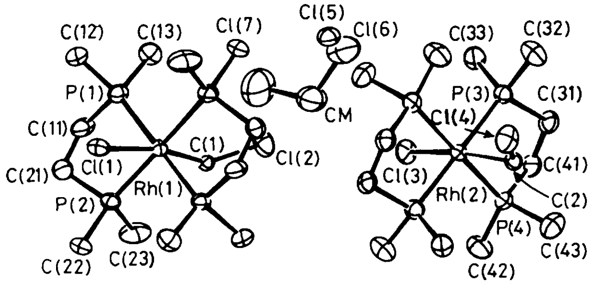

Figure 2. ORTEP drawing of a unit cell containing two molecules of (**5a**). Selected bond distances (Å) and angles (°). Rh(1)–P(1) 2.344(1), Rh(1)–C(1) 2.161(2), Rh(1)–Cl(1) 2.445(3), Cl(2)–C(1) 1.754(11); Cl(1)–Rh(1)–C(1) 168.5(3); Rh(1)–C(1)–Cl(2) 119.9(7). CM is the carbon atom of a CH_2Cl_2 solvent molecule.

analysis¶ confirmed the structure shown in Figure 1. In order to inhibit the apparent phosphine migration step, complexes (**2a,b**), incorporating the chelating dmpe ligand, were treated with an excess of CH_2Cl_2. Precipitation with Et_2O gave *trans*-[$(dmpe)_2MCl(CH_2Cl)]Cl{\cdot}CH_2Cl_2$ [M = Rh, (**5a**); M = Ir, (**5b**)]§ complexes in high yields and reasonably high purity as evidenced by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ n.m.r. spectroscopy. The *trans* geometry is demonstrated by the equivalence of all four ^{31}P nuclei in the $^{31}P\{^1H\}$ n.m.r. spectra, the coupling of the MCH_2Cl protons to four equivalent ^{31}P nuclei in the ^1H n.m.r. spectra, and the observation of two resonances for the dmpe Me groups in both the ^1H and $^{13}C\{^1H\}$ n.m.r. spectra. The molecular structure of (**5a**)¶ is shown in Figure 2.

The neutral complex (**3**) was treated with *ca.* 2.4 equivalents of CH_2Cl_2 in benzene to yield two new complexes (**6a,b**). Complex (**6a**), *mer*, *cis*-[$(PMe_3)_3RhCl_2(CH_2Cl)$], is fairly soluble in benzene and can be isolated by filtration [a mixture of (**6b**) and some (**6a**) is collected at this stage] and vacuum removal of solvent. Complex (**6b**) appears to be the ylide species [$(PMe_3)_2RhCl_3(CH_2PMe_3)$], in which one PMe_3 ligand is *trans* to the ylide moiety and one PMe_3 ligand is *cis* to the ylide. Interestingly, no significant decomposition or rearrangement to (**6b**) occurred when (**6a**) was heated to 60 °C in [$^2H_8$]tetrahydrofuran for 10 days. In addition, preliminary evidence suggests that (**6a**) reacts slowly with an excess of PMe_3 in CH_2Cl_2 *via* Cl^- displacement from Rh rather than $RhCH_2Cl$ and the complex *trans*-[$(PMe_3)_4RhCl(CH_2Cl)]Cl$ (**7**) was observed by *in situ* ^1H and $^{31}P\{^1H\}$ n.m.r. spectroscopy.§ Finally, it seems unlikely that CH_2PMe_3 ligands are derived from direct reaction of PMe_3 with CH_2Cl_2 as this reaction is quite slow compared with the reactions discussed above.

These results suggest that isomerization of [$(PMe_3)RhCH_2Cl$] to [$(Cl)RhCH_2PMe_3$] is promoted by the presence of a PMe_3 ligand *trans* to the chloromethyl group, consistent with a buildup of positive charge on the α-carbon during the phosphine–halide exchange.

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¶ *Crystal data* for (**4a**): $RhCl_5P_4C_{14}H_{40}$, monoclinic-*b*, $P2_{1/c}$ (No. 14), $a = 9.965(2)$, $b = 12.293(2)$, $c = 22.799(4)$ Å, $\beta = 94.45(2)°$, $T = -75$ °C, $U = 2784.4$ Å^3, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 13.16\ \text{cm}^{-1}$; Enraf-Nonius CAD4, Mo-$K_\alpha$ radiation, 8640 data collected using the ω-scan method, $1.8° \leqslant 2\theta \leqslant 60.0°$, 5566 unique reflections with $I \geqslant 3.0\sigma(I)$ used in solution and refinement; solution by direct methods (MULTAN), refinement by full-matrix least squares, weights $\alpha[\sigma^2(I) + 0.0009I^2]^{-1/2}$, 225 parameters, all non-H atoms anisotropic, H atoms calculated [except for H's on C(1) located on a difference map and refined isotropically]; $R = 0.036$, $R_w = 0.041$.

(**5a**): $RhCl_5P_4C_{14}H_{36}$, triclinic, $P\bar{1}$ (No. 2), $a = 10.819(2)$, $b = 11.669(1)$, $c = 10.542(3)$ Å, $\alpha = 91.49(1)$, $\beta = 108.23(2)$, $\gamma = 87.36(1)°$, $T = -70$ °C, $U = 1263$ Å^3, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 14.5\ \text{cm}^{-1}$; Enraf-Nonius CAD4, Mo-$K_\alpha$ radiation, 6774 data collected using the ω-scan method, $4° \leqslant 2\theta \leqslant 55°$, 3223 unique reflections with $I > 3.0\sigma(I)$ used in solution and refinement; solution by Patterson analysis, refinement by full-matrix least squares, weights $\alpha[\sigma(F^2) + 0.02\ F^2]$, 237 parameters, all non-H atoms (except C of $RhCH_2Cl$ group) anisotropic, C of $Rh{-}CH_2Cl$ group isotropic, H atoms fixed (except H's on $RhCH_2Cl$ and CH_2Cl_2 not included); the two cations are located at centres of symmetry with a disorder occurring between the $-Cl$ and $-CH_2Cl$ ligands which are mutually *trans*. $R = 0.047$, $R_w = 0.041$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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