Oxidative additions of dichloromethane and *cyclo*-octasulfur to rhodium(I) complexes containing (2-aminoethyl)-dimethylphosphine or -diphenylphosphine

Kazuo Kashiwabara,*[,a] Akira Morikawa,[a] Takayoshi Suzuki,*[,b] Kiyoshi Isobe[c] and Kazuyuki Tatsumi[a]

[a] *Department of Chemistry, Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-01, Japan*

[b] *Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka 560, Japan*

[c] *Department of Material Science, Faculty of Science, Osaka City University, Sumiyoshi, Osaka 558, Japan*

The oxidative-addition reactions of dichloromethane and *cyclo*-octasulfur with rhodium(I) complexes containing (2-aminoethyl)dimethylphosphine (edmp) or (2-aminoethyl)diphenylphosphine (edpp) have been examined. The reactions of $[\{RhCl(cod)\}_2]$ (cod = cycloocta-1,5-diene) with edmp and with edpp in dichloromethane yield cationic adducts *trans*(*Cl*,*C*)*cis*(*P*,*P*′)-$[RhCl(CH_2Cl)(edmp)_2]^+$ **1** and *trans*(*Cl*,*C*)*cis*(*P*,*P*′)-$[RhCl(CH_2Cl)(edpp)_2]^+$ **2**, respectively. X-Ray analyses of these complexes revealed that the Rh−Cl bond lengths are considerably elongated compared with those of the corresponding dichloro complexes *trans*(*Cl*,*Cl*′)*cis*(*P*,*P*′)-$[RhCl_2(edmp)_2]^+$ and *trans*(*Cl*,*Cl*′)*cis*(*P*,*P*′)-$[RhCl_2(edpp)_2]^+$ due to the strong *trans* influence of the chloromethyl donor group. The Rh−C bonds in complexes **1**, **2** and *trans*-$[RhCl(CH_2Cl)(dmpe)_2]^+$ are 2.050(7) < 2.078(7) < 2.162(2) Å, respectively. This order reflects the differences in the steric bulk around rhodium(III) centre as well as the strength of the *trans* influence toward the *trans*-positioned Rh−Cl bond. Complex **2** reacted further with S_8 to give a mixture of *trans*(*P*,*N*)-$[Rh(S_4)(edpp)_2]^+$ **3a** and *trans*(*P*,*N*)-$[Rh(S_5)(edpp)_2]^+$ **3b**, however such a reaction does not occur for **1**. On the other hand, direct addition of S_8 to $[Rh(edmp)_2]^+$ in methanol resulted in the formation of *trans*(*N*,*N*′)-$[Rh(S_4)(edmp)_2]^+$ **4a** and a small amount of the S_5 complex **4b**. The analogous reaction with $[Rh(edpp)_2]^+$ gave a mixture of **3a** and **3b**. X-Ray analyses revealed that **3a** and **3b** are cocrystallized in the ratio of 1 : 1. The preparation of *trans*(*N*,*N*′)-$[Rh(O_2)(edmp)_2]^+$ **5** is also described.

Oxidative-addition reactions of various small molecules with rhodium(I) phosphine complexes have been extensively studied.[1] In most cases the phosphine ligands employed are monodentate tertiary phosphines and didentate diphosphines such as 1,2-bis(dimethylphosphino)ethane (dmpe) and 1,2-bis(diphenylphosphino)ethane (dppe). We are interested in introducing into rhodium(I) complexes hybrid donor-type phosphines which carry a set of phosphorus and nitrogen donor atoms such as (2-aminoethyl)dimethylphosphine (edmp) and (2-aminoethyl)diphenylphosphine (edpp).[2] The amino donor group is classified as a hard base and forms a weaker, more labile bond to rhodium(I) than does the softer phosphorus donor group. Therefore, given the possibility of reorientation of the P−N hybrid ligands during oxidative-addition reactions, the products obtained from their rhodium(I) complexes are expected to have different structures and characteristics to those from the corresponding diphosphine complexes. In this paper we report on the oxidative additions of dichloromethane and *cyclo*-octasulfur to $[RhL_2]^+$-type complexes (L = edmp or edpp).

There have been several reports of oxidative-addition reactions of dichloromethane with rhodium(I) complexes containing dmpe,[3] dppe,[4,5] 2,6-bis(4,4-dimethyloxazolin-2-yl)pyridine,[6] $CNBu^t$[7] or macrocyclic $[14]aneS_4$ (1,4,8,11-tetrathiacyclotetradecane).[8] These reactions afford either chloromethyl (Rh^{III}–CH_2Cl) or methylene-bridged (Rh^{III}–CH_2–Rh^{III}) complexes. With the exception of 1,4,7,10-tetraazacyclododecane phosphorane (HL′),[9] no reports have appeared for rhodium(I) complexes containing P−N hybrid ligands. Burns *et al.*[9] reported that a reaction of dichloromethane with [RhCl(PPh$_3$)(L′−*P*,*N*)] led to a $\overline{\text{P−N−C−Rh}}^{\text{III}}$ metallacyclic complex $[RhCl_3(CH_2C_8H_{19}N_4P-P,C)]$, presumably *via* an intermediate containing a Cl−Rh−CH$_2$Cl moiety. In the case of oxidative addition of *cyclo*-octasulfur, the rhodium(I) complexes containing dmpe, dppe,[10] $PhP[(CH_2)_3PPh_2]_2$[11] and *cis*-$Ph_2AsCH{=}CHAsPh_2$[12] produced the corresponding η^2-S_2 complexes of rhodium(III), whereas $[Rh(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ led to $[Rh(\eta^5\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}S_n)]$ (n = 4–6).[13] There have been no published reports of oxidative addition of *cyclo*-octasulfur to complexes containing P−N hybrid ligands. For the oxidative addition of dioxygen, a few examples have been established for rhodium(I) complexes having such ligands, in particular $[Rh(O_2)(o\text{-}Ph_2PC_6H_4NMe_2)_2]SbF_6$[14] and $[Rh(O_2)(o\text{-}Ph_2PC_6H_4\text{-}CH{=}NR)_2]BPh_4$ (R = Et, Pr^n or Pr^i).[15] Here, we describe the structures of the oxidative-addition products, *trans*(*Cl*,*C*)*cis*(*P*,*P*′)-$[RhCl(CH_2Cl)L_2]^+$ (L = edmp **1** or edpp **2**), *trans*(*P*,*N*)-$[Rh(S_n)(edpp)_2]^+$ **3** and *trans*(*N*,*N*′)-$[Rh(S_n)(edmp)_2]^+$ **4** (n = 4 or 5) as well as the dioxygen complex *trans*(*N*,*N*′)-$[Rh(O_2)(edmp)_2]^+$ **5** and compare each with the structures of the related dmpe and dppe complexes.

Experimental

The compounds edmp[16] and edpp[17] were prepared according to literature methods, and dppe was obtained from Strem Chemicals Inc. All reactions were handled under a dinitrogen atmosphere using Schlenk techniques until such time that air-stable rhodium complexes were formed. All of the solvents used in the preparation of the phosphines and their complexes were deaerated with dinitrogen for 20 min immediately before use. The ^1H, ^{13}C-$\{^1H\}$ and ^{31}P-$\{^1H\}$ NMR spectra were recorded on a Hitachi R-90H or a JEOL GX400 spectrometer using tetramethylsilane as an internal reference for ^{1}H and ^{13}C-{^{1}H} and 85% H_3PO_4 as an external reference for ^{31}P-{^{1}H}, infrared spectra on a Perkin-Elmer System 2000 FT-IR spectrophotometer by the Nujol-mull method using polyethylene film.

Complex preparation

The complexes [{RhCl(cod)}$_2$]^{18} (cod = cycloocta-1,5-diene) and [Rh(cod)$_2$]BF_4^{19} were prepared by the literature methods.

***trans*(*Cl,C*)*cis*(*P,P′*)-[RhCl(CH$_2$Cl)(edmp)$_2$]Cl 1.** To a dichloromethane solution (45 cm^3) of [{RhCl(cod)}$_2$] (0.49 g, 1.0 mmol) was added a methanol solution (7 cm^3) of edmp (0.42 g, 4.0 mmol) with stirring. A pale yellow solution was obtained immediately. The solution was stirred for 3 h at room temperature and then concentrated under reduced pressure to *ca.* 5 cm^3. To the concentrate was added diethyl ether (70 cm^3). The resulting pale yellow precipitate was filtered off, washed with diethyl ether (5 cm^3 × 2) and dried *in vacuo*. The crude product was dissolved in the minimum volume of methanol and the filtered solution stored in a desiccator together with diethyl ether in an adjacent vessel to deposit a pale yellow *crystalline solid* (0.79 g, 91%) (Found: C, 25.15; H, 5.95; N, 6.5. $C_9H_{26}Cl_3N_2P_2Rh$ requires C, 24.95; H, 6.05; N, 6.45%); δ_H(CD$_3$OD) 1.54 (3 H, filled-in d, *J* 10.1, PCH$_3$), 1.76 (3 H, filled-in d, *J* 11.3, PCH$_3$), 2.14 (2 H, m, PCH$_2$), 3.09 (2 H, m, NCH$_2$), 3.89 [2 H, td, ^2J(RhH) 2.2, ^3J(PH) 4.1, RhCH$_2$Cl] and 4.29 [2 H, s(br), NH$_2$]; δ_C(CD$_3$OD) 9.49 (filled-in d, *J* 36.6, PCH$_3$), 12.77 (filled-in d, *J* 36.6, PCH$_3$), 33.56 (filled-in d, *J* 33.6, PCH$_2$), 40.25 [dt, ^1J(RhC) 29.0, ^2J(PC) 9.2, RhCH$_2$Cl] and 41.38 (s, NCH$_2$); δ_P(CD$_3$OD) 41.76 [d, ^1J(RhP) 117.4 Hz]. The complex is soluble in methanol, acetonitrile or dichloromethane.

***trans*(*Cl,C*)*cis*(*P,P′*)-[RhCl(CH$_2$Cl)(edmp)$_2$]PF$_6$.** To a dichloromethane solution (45 cm^3) of [{RhCl(cod)}$_2$] (0.49 g, 1.0 mmol) was added a methanol solution (7 cm^3) of edmp (0.42 g, 4.0 mmol) with stirring. The resulting pale yellow solution was stirred for 3 h before being mixed with a methanol solution (15 cm^3) of $NaPF_6$ (2.02 g, 12.0 mmol). The pale yellow precipitate obtained was filtered off, washed with diethyl ether (5 cm^3 × 2) and dried *in vacuo*. The crude product was recrystallized from acetone as pale yellow *crystals* (0.48 g, 44%) (Found: C, 20.35; H, 4.85; N, 5.10. $C_9H_{26}Cl_2F_6N_2P_3Rh$ requires C, 19.9; H, 4.85; N, 5.15%). The NMR spectra were almost identical with those for the chloride salt. The complex is soluble in methanol, acetonitrile or acetone.

***trans*(*Cl,C*)*cis*(*P,P′*)-[RhCl(CH$_2$Cl)(edpp)$_2$]Cl 2.** To a dichloromethane solution (40 cm^3) of [{RhCl(cod)}$_2$] (0.49 g, 1.0 mmol) was added a methanol solution (7 cm^3) of edpp (0.92 g, 4.0 mmol) with stirring. The resulting pale yellow solution was stirred overnight, concentrated under reduced pressure to *ca.* 5 cm^3 and mixed with diethyl ether (70 cm^3) to afford a pale yellow precipitate. The precipitate was filtered off, washed with diethyl ether (5 cm^3 × 2) and dried *in vacuo*. The crude product was recrystallized by a method similar to that for complex **1**, giving pale yellow *crystals* (0.97 g, 71%) (Found: C, 50.1; H, 5.05; N, 4.05. $C_{29}H_{34}Cl_3N_2P_2Rh$ requires C, 51.1; H, 5.05; N, 4.05%); δ_C(CD$_3$OD) 32.80 (virtual t, PCH$_2$), 41.91 (s, NCH$_2$), 44.42 [dt, ^1J(RhC) 29.0, ^2J(PC) 8.4, RhCH$_2$Cl], 129.48 (virtual t, *m*-C), 130.90 (filled-in d, *J* 51.9, *ipso*-C), 130.42 (virtual t, *m*-C), 132.51 (s, *p*-C), 132.84 (s, *p*-C), 133.54 (virtual t, *o*-C) and 135.14 (virtual t, *o*-C); δ_P(CD$_3$OD) 43.77 [d, ^1J(RhP) 120.1 Hz]. This complex is soluble in methanol, dichloromethane, acetonitrile or nitromethane.

***trans*(*P,N*)-[Rh(S$_n$)(edpp)$_2$]ClO$_4$ 3 (*n* = 4 or 5). CAUTION:** this perchlorate salt is potentially explosive and should be handled carefully.

To a methanol suspension (45 cm^3) of [{RhCl(cod)}$_2$] (0.49 g, 1.0 mmol) was added a methanol solution (7 cm^3) of edpp (0.92 g, 4.0 mmol) with stirring. The resulting pale yellow solution was stirred for 3 h and mixed with a toluene solution (80 cm^3) of S_8 (0.56 g, 2.2 mmol) to afford a deep red solution. The solution was stirred overnight and evaporated to dryness under reduced pressure. The red residue was stirred in toluene (100 cm^3) for 2 h to remove any unchanged S_8. The remaining red residue was dissolved in methanol (40 cm^3). The solution was applied to a column (5 × 45 cm) of Sephadex LH-20 in two 20 cm^3 portions. The adsorbed products were eluted with methanol, affording minor red and major orange bands in this order. The pooled eluates of the major orange band were concentrated under reduced pressure, mixed with a methanol solution of an excess of $NaClO_4$ and kept in a refrigerator overnight to deposit red-orange *crystals*. The crystals were recrystallized from acetone and diethyl ether (0.56 g, 35%) (Found: C, 41.75; H, 4.0; N, 3.35. $C_{28}H_{32}ClN_2O_4P_2RhS_{4.5}$ requires C, 41.6; H, 4.05; N, 3.45%). A single crystal was subjected to X-ray analysis and found to contain *trans*(*P,N*)-[Rh(S$_4$)(edpp)$_2$]ClO$_4$ **3a** and *trans*(*P,N*)-[Rh(S$_5$)(edpp)$_2$]ClO$_4$ **3b** in 1:1 ratio (see below). δ_P(CD$_3$CN) 25.04 [dd, ^1J(RhP) 101.2, ^2J(PP) 29.0], 34.42 [dd, ^1J(RhP) 115.0, ^2J(PP) 29.0], 35.15 [dd, ^1J(RhP) 116.9, ^2J(PP) 19.8] and 43.39 [dd, ^1J(RhP) 102.3, ^2J(PP) 19.8 Hz]. The complex is slightly soluble in acetone or acetonitrile.

The pooled eluates from the first minor red band were evaporated to dryness under reduced pressure and washed with diethyl ether. The red product (0.57 g) which was soluble in methanol, acetonitrile or nitromethane was determined by ^{31}P-{^{1}H} NMR spectroscopy to be a mixture of unspecifiable compounds. Attempts further to separate these products were unsuccessful.

***trans*(*N,N′*)-[Rh(S$_n$)(edmp)$_2$]BPh$_4$ and *trans*(*N,N′*)-[Rh(S$_n$)(edmp)$_2$]PF$_6$ 4 (*n* = 4 or 5).** To a methanol suspension (45 cm^3) of [{RhCl(cod)}$_2$] (0.49 g, 1.0 mmol) was added a methanol solution (7 cm^3) of edmp (0.42 g, 4.0 mmol) with stirring. A pale yellow solution was obtained immediately. The solution was stirred for 3 h and mixed with a toluene solution (80 cm^3) of S_8 (0.56 g, 2.2 mmol) yielding a dark red solution. It was stirred overnight and evaporated to dryness under reduced pressure. The red residue was washed with toluene (100 cm^3) to remove any unchanged S_8 before being dissolved in methanol (40 cm^3). The methanol solution was applied to a column (5 × 45 cm) of Sephadex LH-20 in two 20 cm^3 portions. The adsorbed products were eluted with methanol, affording minor red and major orange bands in this order. The pooled eluates of the major orange bands were concentrated under reduced pressure and mixed with a methanol solution of an excess of $NaBPh_4$ to give an orange precipitate. The precipitate was recrystallized from a mixture of acetone and ethanol to give an orange *crystalline solid* (0.62 g, 40%). The FAB mass spectrum of the product indicated the presence of [Rh(S$_4$)(edmp)$_2$]$^+$ **4a** (*m/z* 441) and [Rh(S$_5$)(edmp)$_2$]$^+$ **4b** (*m/z* 473), while the ^{31}P-{^{1}H} NMR spectrum also suggests a mixture in the ratio *ca.* 2:1. The hexafluorophosphate analogue was also prepared using NH_4PF_6 instead of $NaBPh_4$ and found to contain a small amount of the S$_5$ complex (*ca.* 20%) which was difficult to remove (Found: C, 16.45; H, 4.3; N, 4.75. $C_8H_{24}F_6N_2P_3RhS_{4.2}$ requires C, 16.2; H, 4.1; N, 4.75%); δ_P(CD$_3$NO$_2$) 40.06 [d, ^1J(RhP) 107.9, S$_4$ complex] and 38.38 [d, ^1J(RhP) 109.0 Hz, S$_5$ complex].

The pooled eluate of the first minor red band was evaporated under reduced pressure to dryness and the residue washed with diethyl ether and dried *in vacuo* (0.38 g). The product was found by ^{31}P-{^{1}H} NMR spectroscopy to be a mixture of many unspecifiable compounds which could not be further separated by column chromatography.

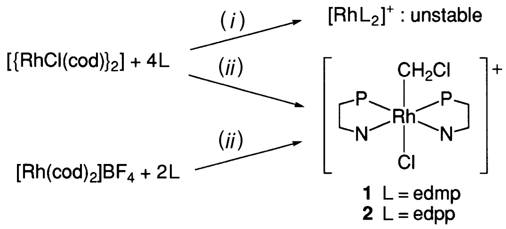
***trans*(*N,N′*)-[Rh(O$_2$)(edmp)$_2$]Cl 5.** To a methanol suspension (45 cm^3) of [{RhCl(cod)}$_2$] (0.25 g, 2.0 mmol) was added a methanol solution (7 cm^3) of edmp (0.21 g, 2.0 mmol) with stirring. The mixture was stirred for 4 h and air was bubbled into the solution overnight, changing from pale yellow to yellow-orange. It was evaporated to dryness under reduced pressure. The brown residue was dissolved in methanol–ethanol (1:1, 7 cm^3). The solution was applied to a column (2.5 × 50 cm) of Sephadex LH-20. The adsorbed products were eluted with methanol–ethanol (1:1), affording yellow and then green bands. The eluate of the yellow band was evaporated to dryness under reduced pressure and the residue recrystallized from ethanol and diethyl ether by a method similar to that for complex **1** (0.13 g, 30%) (Found: C, 25.35; H, 6.55; N, 7.5. $C_8H_{24}ClN_2O_2P_2Rh$ requires C, 25.25; H, 6.35; N, 7.35%); δ_H(CD_3OD) 2.00 [d(br), *J* 8.97, PCH_3], ≈2.5 [m(br), PCH_2], ≈3.0 [m(br), NCH_2] and 4.78 (s, NH_2); δ_P(CD_3OD) 38.25 [d, ^1J(RhP) 100.1 Hz].

Crystallography

A colourless prismatic crystal of complex **1** as its PF_6 salt grown from an acetone solution and a red-orange prismatic crystal of **3** obtained by diffusion of diethyl ether vapour into an acetone solution were glued on the top of glass fibres with epoxy resin. A pale yellow crystal of **2** obtained by diffusion of diethyl ether vapour into a methanol solution was sealed in a glass capillary to prevent possible deliquescence. The X-ray intensities were measured at 23 °C with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) on a Rigaku automated four-circle diffractometer AFC-5R (for **1** and **3**) or AFC-5 (for **2**). Final lattice constants were determined by least-squares refinements of the orientation angles of 25 centred reflections in the range $20 \leqslant 2\theta \leqslant 30°$. Three standard reflections were monitored every 150 and showed no serious decomposition $[|F_o|/(|F_o|)_{initial} > 96\%]$. The intensities collected for a (+*h*, +*k*, +*l*) octant (for **1**) or (+*h*, +*k*, ±*l*) octants (for **2** and **3**) at $2\theta \leqslant 60°$ were corrected for Lorentz-polarization factors, and absorption corrections were made either by the numerical Gauss-integration method (for **1** and **3**)[20] or by an empirical method based on a set of ψ scans (for **2**).[21] The structures were solved by the standard heavy-atom method and refined on *F* by full-matrix least squares using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located at the positions generated by Fourier-difference syntheses or by calculations. Complex neutral-atom scattering factors[22] were used. All calculations were carried out on a Fujitsu S-4/IX workstation using the XTAL 3.2 software.[23] The X-ray data collections and structural calculations were performed at Institute for Molecular Science (Okazaki, Japan). Some experimental details of each analysis are given below.

Systematic absences for complex **1** (0*kl*, *k* = odd; *h*0*l*, *h* + *l* = odd) indicated the space group was either *Pbnm* or *Pbn*2_1. The centrosymmetric *Pbnm* was chosen and the structure successfully refined based on this assumption, indicating that both the complex cation and the PF_6^- counter ion have a plane of symmetry. The space group of **2** was uniquely determined by systematic absences to be *P*2_1/*n*.

For complex **3** a Laue symmetry check and systematic absences (*hkl*, *h* + *k* = odd; *h*0*l*, *l* = odd) indicated the space group was either *Cc* or *C*2/*c*. Initially the structure was refined based on the centrosymmetric *C*2/*c*. A series of Fourier syntheses showed seven peaks assignable to sulfur atoms, two of which [S(1) and S(2)] were bound to Rh and were fully occupied. The remaining sulfur positions could be grouped into five- and six-membered chelates when they were combined with S(1) and S(2). The five- and six-membered chelate rings have typical *gauche* and chair conformations, respectively. Thus, $[Rh(S_4)(edpp)_2]^+$ and $[Rh(S_5)(edpp)_2]^+$ were cocrystallized with disorder observed at the sulfur atoms of S(3)–S(7). When the space group was deduced to be non-centrosymmetric *Cc* (and the subgroup *C*2) the disorder between the S_4 and S_5 chelates could not be resolved and the *R* values did not improve. Consequently, the space group *C*2/*c* was adopted, and random cocrystallization of two complex cations was assumed. The occupancy factors of atoms S(3)–S(7) were fixed at 0.5 in the subsequent Fourier syntheses. Although the present structure refinement has not yet given a satisfactory solution (*R* = 0.073), the structure of the complex with positional disorder for S(3)–S(7) is basically correct and consistent with the elemental analysis and the ^{31}P NMR spectrum.



Scheme 1 Oxidative addition of dichloromethane. L = edmp or edpp. (*i*) MeOH; (*ii*) CH_2Cl_2

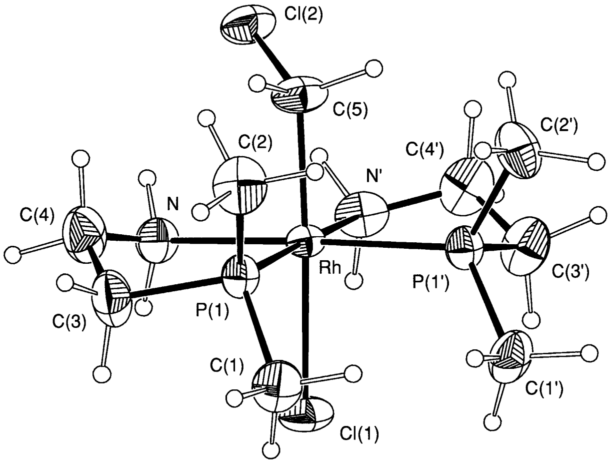


Fig. 1 Perspective drawing of the complex cation in *trans*(*Cl*,*C*)-*cis*(*P*,*P*′)-$[RhCl(CH_2Cl)(edmp)_2]PF_6$ **1** (PF_6 salt)

Crystal data are summarized in Table 1, selected bond lengths and angles in Tables 2 and 3.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/387.

Results and Discussion

Oxidative addition of dichloromethane

Reaction of $[\{RhCl(cod)\}_2]$ with either edmp or edpp in methanol yields a pale yellow solution; however initial attempts to isolate $[Rh^I(edmp)_2]^+$ and $[Rh^I(edpp)_2]^+$ complexes were unsuccessful due to their instabilities. On the other hand, when the reactions were carried out in dichloromethane air-stable complexes were isolated. The reaction of an orange dichloromethane solution of $[\{RhCl(cod)\}_2]$ with a methanol solution of edmp or edpp in a 1:4 molar ratio immediately produced a pale yellow solution. Addition of diethyl ether afforded pale yellow crystalline precipitates. The products were identified by NMR and X-ray analyses to have *trans*(*Cl*,*C*)*cis*(*P*,*P*′)-$[RhCl(CH_2Cl)(edmp)_2]^+$ **1** and *trans*(*Cl*,*C*)*cis*(*P*,*P*′)-$[RhCl(CH_2Cl)(edpp)_2]^+$ **2** cations. When chloride-free $[Rh(cod)_2]BF_4$ was used as a starting material instead of $[\{RhCl(cod)\}_2]$ in the reaction with edmp, *trans*(*Cl*,*C*)*cis*(*P*,*P*′)-$[RhCl(CH_2Cl)(edmp)_2]BF_4$ **1** (BF_4 salt) was generated in a 66% yield. The ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra of **1** (BF_4 salt) coincide with those observed for the chloride. These results suggest that the chlor-

Table 1 Crystallographic data for complexes **1** (PF_6 salt), **2** and **3**

	1 (PF_6 salt)	**2**	**3**
Formula	$C_9H_{26}Cl_2F_6N_2P_3Rh$	$C_{29}H_{34}Cl_3N_2P_2Rh$	$C_{28}H_{32}ClN_2O_4P_2RhS_{4.5}$
M	543.04	681.81	805.18
Crystal size/mm	0.60 × 0.45 × 0.25	0.55 × 0.25 × 0.25	0.40 × 0.30 × 0.10
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbnm* (alternative, *Pnma*, no. 62)	$P2_1/n$ (no. 14)	*C*2/*c* (no. 15)
a/Å	12.207(7)	17.105(7)	25.055(6)
b/Å	15.143(5)	10.103(3)	10.244(8)
c/Å	10.834(5)	17.741(4)	25.876(8)
β/°	—	100.65(3)	94.47(2)
U/Å^3	2003(2)	3013(2)	6621(6)
Z	4	4	8
D_c/Mg m^{-3}	1.80	1.50	1.62
μ(Mo-Kα)/mm^{-1}	1.41	0.952	1.01
F(000)	1099	1392	3280
No. reflections measured	3303	9530	10 372
Transmission factors	0.547–0.723	0.921–1.000	0.702–0.920
No. reflections used[a]	2319	4354	3217
R, *R′*[b]	0.052, 0.071	0.068, 0.063	0.073, 0.091

[a] $|F_o| > 3\sigma(|F_o|)$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$.

Table 2 Selected bond lengths (Å) and angles (°) for *trans*(*Cl*,*C*)-$[RhCl(CH_2Cl)L_2]^+$ (L = edmp **1**, edpp **2** or dmpe **6**) and *trans*(*Cl*,*Cl′*)-$[RhCl_2L_2]^+$ (L = edmp **7**, edpp **8** or dmpe **9**)[a]

	1	**2**	**6**[b]	**7**[c]	**8**[d]	**9**[c]
Rh–Cl	2.468(2)	2.438(2)	2.445(3)	2.340(1)[e]	2.337(2)[e]	2.358(2)[e]
Rh–C	2.050(7)	2.078(7)	2.161(2)	—	—	—
Rh–P	2.247(2)	2.309(2)[e]	2.344(1)	2.252(2)[e]	2.300(1)[e]	2.337(2)[e]
Rh–N	2.170(5)	2.147(7)[e]	—	2.165(4)[e]	2.125(4)[e]	—
P–Rh–N (P)[f]	84.3(1)	82.7(2)	*g*	84.1(1)[e]	83.8(1)[e]	84.2(1)[e]
P–Rh–P[h]	98.71(7)	106.97(8)	*g*	98.9(1)	105.4(1)	95.8(1)[e]
N–Rh–N	92.4(2)	87.3(3)	—	93.0(1)	87.3(2)	—
Cl–Rh–C (Cl)	174.4(2)	174.7(2)	168.5(3)	173.3(1)	172.1(1)	179.8(1)
Rh–C–Cl	115.3(4)	117.2(4)	119.9(7)	—	—	—

[a] All of the edmp and edpp complexes adopt a *cis*(*P*,*P′*) configuration. [b] Ref. 3. [c] Ref. 24. [d] Ref. 25. [e] Average. [f] Chelate bite angle. [g] Not reported. [h] Angles made by phosphorus atoms of adjacent ligands.

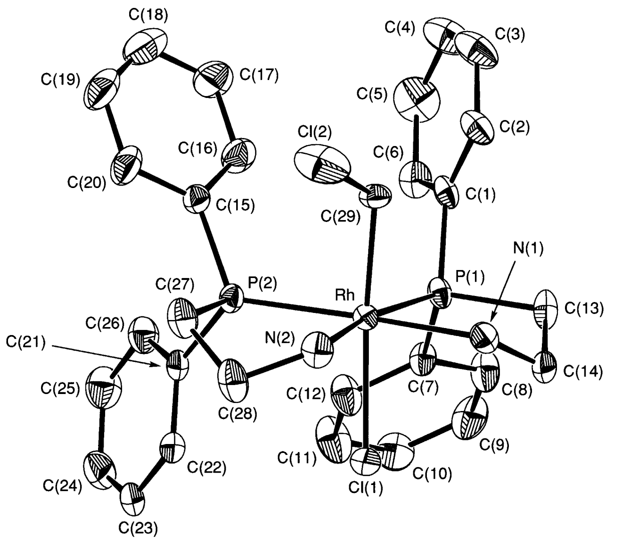


Fig. 2 Perspective drawing of the complex cation in *trans*(*Cl*,*C*)*cis*-(*P*,*P′*)-$[RhCl(CH_2Cl)(edpp)_2]Cl$ **2** (hydrogen atoms are omitted for clarity)

ide ligand in **1** and **2** comes from CH_2Cl_2 *via* oxidative addition (Scheme 1).

Perspective drawings of the complex cations in **1** (PF_6 salt) and **2** are shown in Figs. 1 and 2, respectively. Both complexes assume octahedral co-ordination geometry with a *trans*(*Cl*,*C*)*cis*(*P*,*P′*) configuration. The chlorine atom of the chloromethyl group is oriented away from the dimethylphosphino or diphenylphosphino group. Selected bond lengths and angles for **1** and **2** are listed in Table 2, together with those for *trans*-$[RhCl(CH_2Cl)(dmpe)_2]^+$ **6**,[3] *trans*(*Cl*,*Cl′*)*cis*(*P*,*P′*)-$[RhCl_2(edmp)_2]^+$ **7**,[24] *trans*(*Cl*,*Cl′*)*cis*(*P*,*P′*)-$[RhCl_2(edpp)_2]^+$ **8**[25] and *trans*-$[RhCl_2(dmpe)_2]^+$ **9**[24] for comparison. The structural parameters of $[RhCl(CH_2Cl)L_2]^+$ (L = edmp, edpp or dmpe) are very similar to those of the corresponding $[RhCl_2L_2]^+$ complexes except for the Rh–Cl bond lengths. The Rh–Cl bond length in **1** is 0.128 Å longer than that in **7**, probably due to the stronger *trans* influence of the chloromethyl group. The elongation of the Rh–Cl bond in going from $[RhCl_2L_2]^+$ to $[RhCl(CH_2Cl)L_2]^+$ decreases in the order, **1** (Δ = 0.128) > **2** (0.101) > **6** (0.087 Å). This order correlates with the Rh–C bond lengths which increase in the order of **1** < **2** < **6**, as the *trans* influence of the CH_2Cl group becomes weaker with lengthening of the Rh–C bond. The long Rh–C bond length in **6** may be caused by the steric bulk of the four dimethylphosphino groups.

The *trans*(*Cl*,*C*)*cis*(*P*,*P′*) geometry of complexes **1** and **2** is retained in solution according to the NMR spectra. In the ^{31}P-{^1H} NMR spectra the two ^{31}P nuclei are equivalent and the ^1J(RhP) coupling constants (117.4 for **1** and 120.1 Hz for **2**) indicate that two P atoms in the complexes are mutually *cis*.[26,27] In the ^1H and ^{13}C-{^1H} NMR spectra the CH_2Cl signals appear as a doublet of triplets as a consequence of the couplings with ^{103}Rh and ^{31}P nuclei. Two sets of PCH_3 signals were observed in the ^1H and ^{13}C-{^1H} NMR spectra of **1** as were two sets of phenyl groups for **2**. The PCH_3 protons appear as a so-called filled-in doublet.[27,28] These NMR spectral features are consistent with the *trans*(*Cl*,*C*)*cis*(*P*,*P′*) geometry.

The reaction between $[\{RhCl(cod)\}_2]$ and dppe in dichloromethane was also carried out in a similar manner to that for the

Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

Rh–S(1)	2.349(4)	Rh–S(2)	2.404(5)
Rh–P(1)	2.295(4)	Rh–P(2)	2.360(4)
Rh–N(1)	2.15(1)	Rh–N(2)	2.15(1)
S(1)–S(3)	2.13(1)	S(1)–S(5)	1.98(1)
S(3)–S(4)	2.18(1)	S(5)–S(6)	2.10(1)
S(2)–S(4)	1.87(1)	S(6)–S(7)	1.98(1)
		S(2)–S(7)	2.10(1)
S(1)–Rh–S(2)	93.8(2)	P(1)–Rh–P(2)	100.9(1)
S(1)–Rh–P(1)	93.4(1)	S(1)–Rh–P(2)	93.8(1)
S(1)–Rh–N(1)	175.0(3)	S(1)–Rh–N(2)	92.0(3)
S(2)–Rh–P(1)	89.9(1)	S(2)–Rh–P(2)	166.4(1)
S(2)–Rh–N(1)	82.1(3)	S(2)–Rh–N(2)	86.4(3)
P(1)–Rh–N(1)	83.6(3)	P(1)–Rh–N(2)	173.6(3)
P(2)–Rh–N(1)	90.7(3)	P(2)–Rh–N(2)	82.1(3)
N(1)–Rh–N(2)	90.7(4)	Rh–S(1)–S(5)	115.4(3)
Rh–S(1)–S(3)	97.8(4)	S(1)–S(5)–S(6)	105.7(5)
S(1)–S(3)–S(4)	95.6(7)	S(5)–S(6)–S(7)	100.9(5)
S(2)–S(4)–S(3)	97.8(6)	S(2)–S(7)–S(6)	108.5(5)
Rh–S(2)–S(4)	107.4(4)	Rh–S(2)–S(7)	109.9(3)

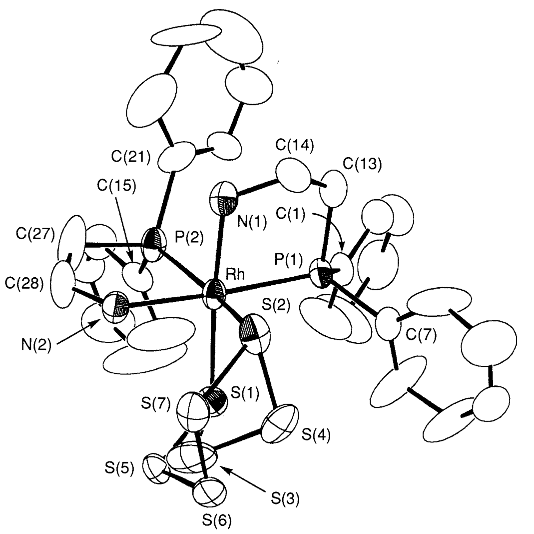
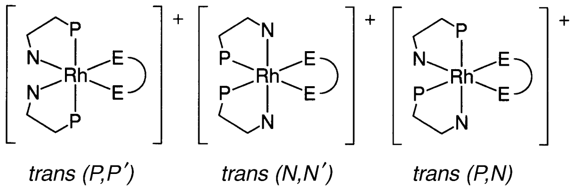


Fig. 3 Perspective drawing of the complex cation in *trans*(*P*,*N*)-$[Rh(S_n)(edpp)_2]ClO_4$ **3** (*n* = 4 or 5) (hydrogen atoms are omitted for clarity). Note that the population parameters of atoms S(3)–S(7) are 0.5

edmp or edpp complexes, yielding the known rhodium(I) complex $[Rh(dppe)_2]Cl$[29] in 88% yield. Interestingly, $[Rh(dppe)_2]Cl$ is inert toward oxidative addition of CH_2Cl_2. Thus, the dimethylphosphino and amino groups make the rhodium(I) centre more reactive toward oxidative addition than does the diphenylphosphino group. The steric congestion around the rhodium(I) centre in $[Rh(dppe)_2]^+$ may be a reason behind the different reactivity.

Oxidative addition of *cyclo*-octasulfur

A methanol solution of the rhodium(I) complex of edpp or edmp reacts readily with elemental sulfur in toluene to yield a red-orange compound as the major product (**3** or **4**). The perchlorate complex of edpp (**3**) was recrystallized from an acetone–diethyl ether solution to afford prismatic crystals, which were subjected to X-ray analysis. A perspective drawing of the complex cation is shown in Fig. 3. The central rhodium atom is surrounded octahedrally by two phosphorus, two nitrogen and two sulfur atoms in a *trans*(*P*,*N*) configuration, one of the three possible geometrical isomers, *trans*(*P*,*P*′), *trans*(*N*,*N*′) and *trans*(*P*,*N*) (Scheme 2). These red-orange crystals consist of $[Rh(S_4)(edpp)_2]ClO_4$ **3a** and $[Rh(S_5)(edpp)_2]ClO_4$ **3b** in a 1:1 ratio. The ring made by Rh, S(1), S(3), S(4) and S(2) forms a typical *gauche* conformation, while that of Rh, S(1), S(5), S(6), S(7) and S(2) adopts a typical chair conformation as shown in Fig. 4. The X-ray analysis is consistent with the elemental analysis and the ^{31}P-{^1H} NMR spectrum which exhibits two kinds of ABX octets (A, B = P; X = Rh) with equal intensity (see Experimental section).



trans (P,P′) *trans (N,N′)* *trans (P,N)*

Scheme 2 Possible geometrical isomers for $[Rh(E{-}E)L_2]^+$ ($E{-}E^{2-}$ = S_4^{2-}, S_5^{2-} or O_2^{2-}) complexes

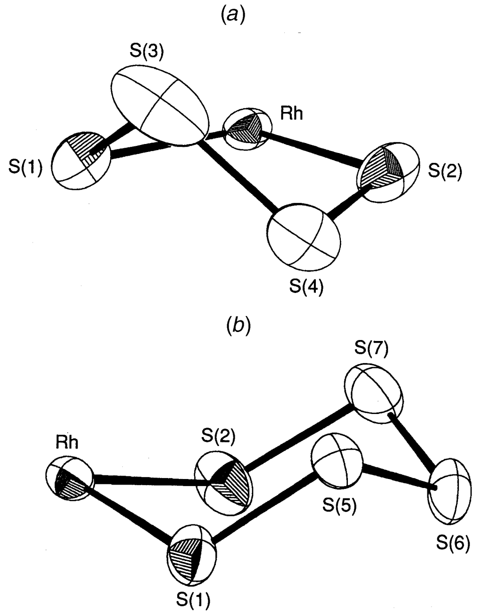
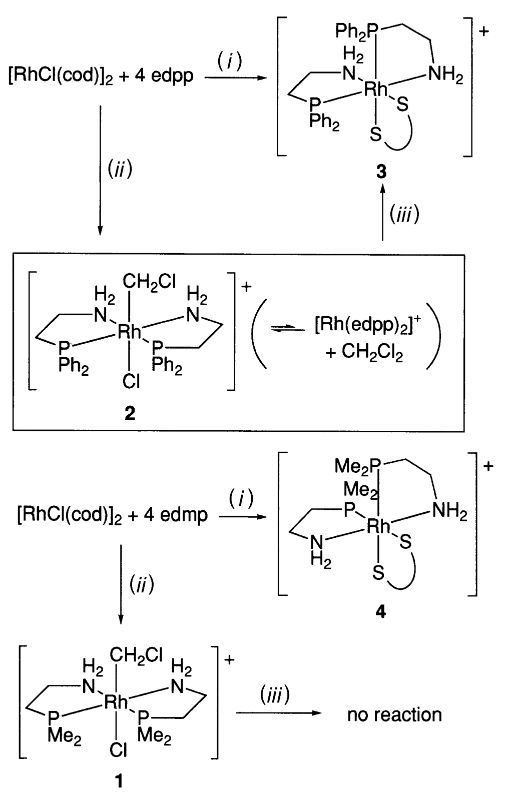


Fig. 4 Conformations of the five- and six-membered chelate rings in (*a*) *trans*(*P*,*N*)-$[Rh(S_4)(edpp)_2]^+$ **3a** and (*b*) *trans*(*P*,*N*)-$[Rh(S_5)(edpp)_2]^+$ **3b**, respectively

Selected bond lengths and angles are listed in Table 3. The Rh–S(1) bond length [2.349(4) Å] is almost the same as the Rh–S distances in $[Rh(\eta^5\text{-}C_5H_5)(PPh_3)(S_5)]$ [2.359(2) and 2.351(2) Å] and $[Rh(\eta^5\text{-}C_5H_4CO_2Me)(PPh_3)(S_4)]$ [2.354(1) and 2.350(1) Å].[12] The Rh–S(2) bond length of 2.404(5) Å is 0.055 Å longer than Rh–S(1), probably due to the stronger *trans* influence of the PPh_2 relative to the NH_2 group. The Rh–P(1) bond length [2.295(4) Å] is similar to those in complexes **2** (average 2.309 Å) and **8**·Cl·2EtOH (average 2.300 Å).[25] The Rh–P(2) bond on the other hand is 0.065 Å longer than Rh–P(1) and more similar to those found in *cis*(*Cl*,*Cl*′)*trans*(*P*,*P*′)-$[RhCl_2(edpp)_2]Cl\cdot 4H_2O$ [2.334(3) and 2.337(3) Å].[25] Thus, the *trans* influence of the polysulfide ligand appears to be comparable in magnitude to that of the PPh_2 group. This trend is manifested in the almost identical Rh–N(1) and Rh–N(2) bond lengths. The bond angles in **3** are usual and similar to those in related complexes.[12,25,30]

The red-orange edmp complex obtained in a manner similar to that of the edpp complex is $[Rh(S_4)(edmp)_2]^+$ **4a**, based on the elemental analysis and the FAB mass spectrum. The $[Rh(S_5)(edmp)_2]^+$ **4b** complex is, however, always found in the product. The amount of the S_5 complex present (up to *ca.* 30%) was dependent on the solvents used as well as the counter anions. The ^{31}P-{^1H} NMR spectrum of the product with a mixture of the S_4 and S_5 moieties exhibits two doublets at δ 40.1 [^1J(RhP) 107.9] and 38.4 [109.0 Hz] with different peak intensities, the former being assigned to **4a** and the latter to **4b**. As



Scheme 3 Oxidative-addition reaction of S_8 to $[RhL_2]^+$ complexes. (*i*) S_8, toluene, MeOH; (*ii*) CH_2Cl_2; (*iii*) S_8, toluene, MeOH or CH_2Cl_2

each complex shows one kind of ^{31}P signal with comparable ^{1}J(RhP) values, two equivalent phosphorus atoms are mutually *cis* in the complexes[26,27] and they can be assigned to the *trans*-(*N*,*N*) isomer of the three possible geometrical isomers (Scheme 2). Unfortunately, crystals suitable for X-ray analysis were not obtained.

In contrast to the reaction of $[Rh(edmp)_2]^+$ with S_8 in methanol, a pale yellow dichloromethane solution containing $[\{RhCl(cod)\}_2]$ and edmp (1:4 molar ratio) did not react with S_8 in toluene; this is probably due to the formation of **1**. We observed that a methanol solution of **1** as its Cl^- salt also did not react with S_8 in toluene. On the other hand, both dichloromethane and methanol solutions of **2** react with S_8 in toluene to yield **3** in *ca.* 30% yield. This suggests a novel equilibrium between $[RhCl(CH_2Cl)(edpp)_2]^+$ and $[Rh(edpp)_2]^+$ in solution, the latter rhodium(I) complex reacting with S_8 to yield **3**. We could not however obtain any evidence for a reaction mechanism. The edmp complex **1** does not show such equilibrium in solution (Scheme 3).

It is worthwhile noting that the corresponding dmpe and dppe complexes $[RhL_2]^+$ react with S_8 to give η^2-S_2 adducts $[Rh(\eta^2\text{-}S_2)L_2]^+$,[10] while the main and isolable products are η^2-S_4 or -S_5 adducts for the present edmp and edpp complexes. Using chromatography to separate the products of reaction between an edmp or edpp complex with S_8 a minor red band was obtained. The products contained in this band may result from different fragmentations of S_8, however we were unable to isolate any pure product from this fraction. Further, it should be noted that the co-ordination geometries of the oxidative-addition products of S_8 with the edpp and edmp complexes (**3** and **4**) were different, *trans*(*P*,*N*) and *trans*(*N*,*N′*). These differences in these S_8 addition products are most likely caused by the different steric bulk of the ligands and the relative lability of the co-ordinated amino donor group of the edmp and edpp ligands.

Reaction with dioxygen

Various peroxo complexes of rhodium(III) have been prepared by treating the following rhodium(I) phosphine complexes with dioxygen; *e.g.* $[RhCl(PPh_3)_3]$,[31,32] $[Rh(PMe_2Ph)_4]BPh_4$,[33,34] $[Rh(dppe)_2]PF_6$,[35] $[Rh\{PhMeP(CH_2)_2PMePh\}_2]PF_6$,[10] $[Rh\{Ph_2P(CH_2)_2SR\}_2]BPh_4$,[36] $[Rh(o\text{-}Ph_2PC_6H_4NMe_2)_2]SbF_6$[14] and $[Rh(o\text{-}Ph_2PC_6H_4CH{=}NPr^i)_2]BPh_4$.[15] A pale yellow methanol solution of $[\{RhCl(cod)\}_2]$ containing edmp was air-sensitive and afforded the peroxo complex $[Rh(O_2)(edmp)_2]Cl$ **5** by bubbling air through it. The ^{31}P-{^{1}H} NMR spectrum in CD_3OD exhibits a doublet [^{1}J(RhP) 100.1 Hz] and the ^{1}H NMR resonance for the PCH_3 is a broad doublet. These features indicate a *trans*(*N*,*N′*) configuration. This geometry is the same as that of complex **4**, but different from the *trans*(*P*,*N*) configurations of **3**, $[Rh(O_2)(o\text{-}Ph_2PC_6H_4NMe_2)_2]SbF_6$[14] and $[Rh(O_2)(o\text{-}Ph_2PC_6H_4CH{=}NPr^i)_2]BPh_4$.[15] The sterically less demanding methyl substituents on the phosphorus of edmp may allow the complex to adopt a *trans*(*N*,*N′*) configuration.

Acknowledgements

The present work was in part supported by a Grant-in-Aid for Scientific Research No. 08640709, Developmental Scientific Research No. 07554061 and Scientific Research on Priority Areas No. 08220230 from the Ministry of Education, Science and Culture, Japan.

References

1 F. H. Jardine and P. S. Sheridan, *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 4, ch. 48. 6. 3.

2 For example, M. Kita, K. Kashiwabara, J. Fujita, H. Tanaka and S. Ohba, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2457 and refs. therein.

3 T. B. Marder, W. C. Fultz, J. C. Calabrese, R. L. Harlow and D. Milstein, *J. Chem. Soc., Chem. Commun.*, 1987, 1543.

4 P. J. Fennis, P. H. M. Budzelaar, J. H. G. Frijns and A. G. Orpen, *J. Organomet. Chem.*, 1990, **393**, 287.

5 G. E. Ball, W. R. Cullen, M. D. Fryzuk, B. R. James and S. J. Rettig, *Organometallics*, 1991, **10**, 3767.

6 H. Nishiyama, M. Horihata, T. Hirai, S. Wakamatsu and K. Itoh, *Organometallics*, 1991, **10**, 2706.

7 M. A. Ciriano, M. A. Tena and L. A. Oro, *J. Chem. Soc., Dalton Trans.*, 1992, 2123.

8 T. Yoshida, T. Ueda, T. Adachi, K. Yamamoto and T. Higuchi, *J. Chem. Soc., Chem. Commun.*, 1985, 1137.

9 E. G. Burns, S. S. C. Chu, P. de Meester and M. Lattman, *Organometallics*, 1986, **5**, 2383.

10 A. P. Ginsberg, W. E. Lindsell, C. R. Sprinkle, K. W. West and R. L. Cohen, *Inorg. Chem.*, 1982, **21**, 3666.

11 T. E. Nappier, jun., D. W. Meek, R. M. Kirchner and J. A. Ibers, *J. Am. Chem. Soc.*, 1973, **95**, 4194.

12 J. T. Mague and E. J. Davis, *Inorg. Chem.*, 1977, **16**, 131.

13 Y. Wakatsuki, H. Yamazaki and C. Cheng, *J. Organomet. Chem.*, 1989, **372**, 437.

14 T. B. Rauchfuss and D. M. Roundhill, *J. Am. Chem. Soc.*, 1974, **96**, 3098.

15 C. A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini and G. Scapacci, *J. Chem. Soc., Dalton Trans.*, 1992, 3371.

16 T. Suzuki, M. Rude, K. P. Simonsen, M. Morooka, S. Ohba, F. Galsbøl and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1013.

17 K. Kashiwabara, I. Kinoshita, T. Ito and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 725.

18 G. Giordano and R. H. Crabtree, *Inorg. Synth.*, 1979, **19**, 218.

19 T. G. Shenck, J. M. Downs, C. R. C. Milne, P. B. Mackenzie, H. Boucher, J. Whealan and B. Bosnich, *Inorg. Chem.*, 1985, **24**, 2334.

20 W. L. Busing and H. A. Levy, *Acta Crystallogr.*, 1957, **10**, 180.

21 K. Watenpaugh and J. Stewart, ABSCAL, Program for Scale Diffractometer Intensity Data in XTAL 3.2 Program Package, The Upjohn Company, Michegan, 1992.

22 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

23 S. R. Hall, H. D. Flanck and J. M. Stewart, XTAL 3.2, Program Package for Crystal Structure Determination, Universities of Western Australia, Geneva and Maryland, 1992.

24 K. P. Simonsen, N. Suzuki, M. Hamada, M. Kojima, S. Ohba, Y. Saito and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 3790.

25 F. Galsbøl, M. Kojima, T. Ishii, S. Ohba, Y. Saito and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1701.

26 T. Suzuki, K. Isobe and K. Kashiwabara, *J. Chem. Soc., Dalton Trans.*, 1995, 3609.

27 P. S. Pregosin and R. W. Kunz, ^{31}P *and* ^{13}C *NMR of Transition Metal Phosphine Complexes*, Springer, Berlin, Heidelberg, 1979.

28 D. A. Redfield, J. H. Nelson and L. W. Cary, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 727.

29 D. N. Lawson, J. A. Osborn and G. Wilkinson, *J. Chem. Soc. A*, 1966, 1733.

30 M. Draganjac and T. B. Rauchfuss, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 742.

31 M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn and G. Wilkinson, *Chem. Commun.*, 1966, 129.

32 M. J. Bennett and P. B. Donaldson, *Inorg. Chem.*, 1977, **16**, 1581.

33 L. M. Haines and E. Singleton, *J. Organomet. Chem.*, 1971, **30**, C81.

34 M. J. Nolte and E. Singleton, *Acta Crystallogr., Sect. B*, 1976, **32**, 1410.

35 J. A. McGinnety, N. C. Payne and J. A. Ibers, *J. Am. Chem. Soc.*, 1969, **91**, 6301.

36 M. Bressan, F. Morandini and P. Rigo, *Inorg. Chim. Acta*, 1983, **77**, L139.

Received 1st *October* 1996; *Paper* 6/06730A