Metal complexes of chiral phosphorylalkoxides: crystal structure of dichlorobis[(1*S*)-2-(diphenylphosphoryl)-1-methylethanolato]titanium(IV)

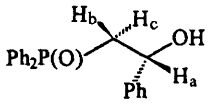
Ronald J. Cross, Louis J. Farrugia, Paul D. Newman, Robert D. Peacock and Diane Stirling

Chemistry Department, University of Glasgow, Glasgow G12 8QQ, UK

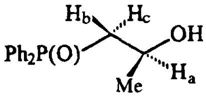
The chiral alcohols, (1*S*)-2-(diphenylphosphoryl)-1-methylethanol (*S*-Hdpomeo) and (1*R*)-2-(diphenylphosphoryl)-1-phenylethanol (*R*-Hdpopeo), have been synthesised in optically pure form by a simple two-step procedure. They can be readily deprotonated and the monoanions L so formed co-ordinate readily to Ti^{IV} or Mo^{VI} to give complexes of the type $[TiCl_2L_2]$, *cis*-$[MoO_2(acac)L]$ or *cis*-$[MoO_2L_2]$. The complex $[TiCl_2(S\text{-dpomeo})_2]$ crystallised in the orthorhombic space group $P2_12_12_1$, with $a = 11.572(1)$, $b = 13.209(1)$, and $c = 20.452(1)$ Å. It is octahedral, with *trans* chlorides, and *cis* phosphoryl and alkoxide donors. The six-membered chelate rings adopt asymmetric boat conformations, with equatorially projecting methyl groups. This is the first structurally characterised complex containing a phosphorylalkoxide ligand. The NMR spectroscopic evidence suggests retention of the solid-state structure upon dissolution, and considerable rigidity in the chelate rings.

Interest in the co-ordination chemistry of phosphoryl (P=O) donor ligands has largely been fuelled by the discovery of their utility as selective extractants for economically important metals. Most systems studied have involved monodentate donors, although several examples of homoleptic multidentate phosphoryl compounds and their metal complexes have been documented.[1,2] There is a surprising dearth of published material concerning heterodonor compounds containing one or more P=O functions, and only in recent years a number of compounds of this type have been reported.[2–4] Phosphoryl oxygens are moderately basic, and although tolerant of a whole range of metal oxidation states are most suited to high-valent metals.

Our interest in P=O donors stems from a desire to synthesise anionic chiral heterobidentate compounds capable of forming stable complexes with the hard acid metal centres in high oxidation levels commonly used as oxidation catalysts. We describe here the syntheses of (1*R*)-2-(diphenylphosphoryl)-1-phenylethanol (*R*-Hdpopeo) and (1*S*)-2-(diphenylphosphoryl)-1-methylethanol (*S*-Hdpomeo), and an examination of the co-ordination chemistry of their anions with Ti^{IV} and Mo^{VI}. β-Hydroxyphosphoryl compounds have been employed extensively in organic chemistry, as they provide access to synthetically useful alkene synthons *via* Wittig–Horner type transformations.[1] Part of the appeal of these compounds has been their ease of preparation and purification, as they tend to be easily crystallisable solids.



R-Hdpopeo



S-Hdpomeo

Experimental

The NMR spectra were recorded on a Bruker AM 200 spectrometer operating in the Fourier-transform mode, IR spectra on a Philips PU 9800 spectrometer as KBr discs. Microanalyses were performed by Glasgow University Chemistry Department microanalytical service. Melting points were determined on a Gallenkamp apparatus in air and are uncorrected.

All solvents were dried and deoxygenated by distillation from sodium diphenylketyl [tetrahydrofuran (thf), diethyl ether, toluene, light petroleum (b.p. 40–60 °C)] or CaH_2 (acetonitrile, dichloromethane) under oxygen-free nitrogen. (*R*)-Styrene oxide and (*S*)-propylene oxide were obtained from Aldrich Chemical Company and used as supplied. The precaution of working under oxygen-free nitrogen was taken for the preparation of the metal complexes using standard Schlenk-line techniques, although the titanium(IV) species proved air- and moisture-stable.

Preparations

(1*R*)-2-(Diphenylphosphoryl)-1-phenylethanol. To a stirred solution of diphenylphosphine (5.38 g, 2.89×10^{-2} mol) in dimethyl sulfoxide (dmso, 40 cm^3) under N_2 was added 56% aqueous KOH (3.41 cm^3, 3.45×10^{-2} mol) dropwise to generate the red Ph_2P^- anion. To this mixture was added (*R*)-styrene oxide (3.41 g, 2.89×10^{-2} mol) in dmso (10 cm^3) *via* a syringe. The mixture was stirred at 50 °C for 3 h, poured into water (500 cm^3), and extracted with $CHCl_3$ (2 × 250 cm^3). The organic phase was stirred vigorously with 15% H_2O_2 (60 cm^3) for 3 h, then with an aqueous solution of Na_2SO_3 for 30 min. After separating and drying (anhydrous Na_2SO_4), the solvent was removed from the organic phase *in vacuo* to give a white solid. This was boiled in acetone (200 cm^3) for 5 min, cooled to room temperature, and the insoluble white solid, the known compound 1,2-bis(diphenylphosphoryl)-1-phenylethane,[5] was filtered off, washed with acetone and air-dried. Yield 0.75 g, m.p. 276–277°. NMR ($CDCl_3$): ^1H, δ 2.70 (m, 1 H, CH_2), 3.10 (m, 1 H, CH_2), 4.20 (m, 1 H, CH) and 6.7–8.10 (m, 25 H, aromatic hydrogen); ^{31}P, δ 32.3 (d, $J = 56$) and 37.0 (d, $J = 56$); ^{13}C, δ 30.3 (d, $J = 67$), 39.1 (d, $J = 65$ Hz) and 126–135 (aromatics). IR (KBr): 3076w, 3055w, 3042w, 2959w, 2934w, 2916w, 2901w, 2847w, 1967w, 1898w, 1496w, 1483w, 1456w, 1439vs, 1417w, 1182vs, 1143m, 1118s, 1101s, 1070m, 1028w, 997w, 800w, 771m, 763m, 752m, 742vs, 729m, 721s, 715m, 692vs, 594m, 559m, 547s, 526vs, 509m, 495s, 455w and 445w cm^{-1}. The dd pattern in the ^{31}P NMR spectrum is split into two components of equal intensity on addition of a chiral shift reagent [(*S*)-*N*-(3,5-dinitrobenzoyl)-α-methylbenzylamine] indicating a racemic mixture.

Removal of the acetone from the filtrate gave the desired product which was recrystallised from hot EtOH–water. The crystals were filtered off, washed with cold aqueous ethanol (1:1) and air-dried. Yield 6.2 g (67%), m.p. 136–137 °C (Found: C, 74.3; H, 6.0. Calc. for $C_{20}H_{19}O_2P$: C, 74.5; H, 5.95%). NMR ($CDCl_3$): ^1H, δ 2.61 (m, 2 H, CH_2), 4.93 (s, 1 H, OH), 5.08 (t, 1 H, CH) and 7.15–7.75 (m, 15 H, aromatics); ^{31}P, δ 33.9; ^{13}C, δ 39.0 (d, J = 68, CH_2), 69.0 (d, J = 4, CH), 125.5, 127.6, 128.4, 128.6 (d, J = 12), 128.9 (d, J = 11), 130.3 (d, J = 10), 130.5 (d, J = 10), 132.0, 133.0 (d, J = 70) and 144.0 (d, J = 13 Hz). Addition of the chiral shift reagent produced no change in the NMR spectra. IR (KBr): 3268m, 3072w, 3035w, 2954w, 2912w, 1589w, 1499w, 1483w, 1457s, 1439m, 1395m, 1354w, 1322m, 1264m, 1223m, 1159vs, 1119s, 1099s, 1072m, 1026vs, 1010m, 996m, 917m, 873s, 782s, 764s, 749s, 741s, 719s, 701vs, 691vs, 596w, 558m, 532vs, 512vs, 487m, 451m and 431m cm^{-1}.

(1*S*)-2-(Diphenylphosphoryl)-1-methylethanol. The procedure detailed above was repeated using (*S*)-propylene oxide instead of (*R*)-styrene oxide. The mixture was stirred at 20 °C for 2 h, then worked up as before. No complications arose due to the formation of 1,2-bis(diphenylphosphoryl)-1-methylethane, and the compound was obtained as a clear oil which crystallised on standing after removing the solvent from the original $CHCl_3$ extract. Yield 5.5 g (73%), m.p. 83–84 °C (Found: C, 69.1; H, 6.5. Calc. for $C_{15}H_{17}O_2P$: C, 69.2; H, 6.6%). NMR ($CDCl_3$): ^1H, δ 1.23 (dd, 3 H, CH_3), 2.38 (m, 2 H, CH_2), 4.23 (m, 1 H, CH) and 7.35–7.77 (m, 10 H, aromatics); ^{31}P, δ 34.0; ^{13}C, δ 24.8 (d, J = 13, CH_3), 38.0 (d, J = 70, CH_2), 63.0 (d, J = 3, CH), 128.6 (d, J = 12), 130.3 (d, J = 11), 130.7 (d, J = 10) and 131.9, 133.8 (d, J = 51 Hz). Addition of the chiral shift reagent produced no change in the NMR spectra. IR (KBr): 3371s, 3072w, 3055w, 3034w, 2996w, 2977w, 2933w, 2889w, 1967w, 1897w, 1590m, 1482m, 1453m, 1436vs, 1396m, 1369m, 1354m, 1319m, 1302m, 1228s, 1197s, 1162vs, 1119vs, 1097vs, 1076s, 1068s, 1033m, 1026m, 997m, 931s, 866m, 814s, 752vs, 745vs, 739vs, 718vs, 695vs, 668m, 649m, 618m, 545vs, 515vs, 485m, 464m, 435m, 410w and 406w cm^{-1}.

Dichlorobis[(1*R*)-2-(diphenylphosphoryl)-1-phenylethanolato]titanium(IV)–toluene (1/1). To a stirred solution of $TiCl_4\cdot 2thf$ (283 mg, 8.46 × 10^{-4} mol) in thf (20 cm^3) was added solid *R*-Hdpopeo (545 mg, 1.69 × 10^{-3} mol). Dissolution of the latter resulted in change from green to very pale yellow. The solution was stirred for 12 h, then pumped dry to leave a colourless solid. This was triturated with diethyl ether under N_2, the ether washings removed *via* a cannula, and the solid dried under vacuum. Crystallisation was achieved by slow evaporation of a toluene–dichloromethane–pentane (3:1:3, 50 cm^3) solution under N_2. The air- and moisture-stable yellow crystalline solid was filtered off, washed with toluene–pentane (1:2) and air-dried. Yield 600 mg (83%) (Found: C, 65.8; H, 5.3; Cl, 8.7. Calc. for $C_{47}H_{44}Cl_2O_4P_4Ti$: C, 66.15; H, 5.2; Cl, 8.3%). NMR ($CDCl_3$): H, δ 2.75 (dt, 1 H, CH_2), 3.72 (ddd, 1 H, CH_2), 5.92 (tt, 1 H, CH), 7.25 (m, 5 H), 7.47 (m, 4 H), 7.65 (m, 2 H), 7.95 (m, 2 H) and 8.18 (m, 2 H); ^{31}P, δ 45.1; ^{13}C, δ 39.0 (d, J = 68, CH_2), 81.2 (d, J = 5, CH), 125.5, 127.3, 128.2, 128.7 (d, J = 12), 129.1 (d, J = 11), 132.0 (d, J = 10), 132.7 (d, J = 10) and 143.5 (d, J = 12 Hz). IR (KBr): 3057m, 3026m, 2914m, 2855m, 2716m, 1967w, 1898w, 1819w, 1599m, 1589m, 1493m, 1485m, 1450m, 1439vs, 1385m, 1332m, 1309m, 1304m, 1280m, 1215s, 1194m, 1154s, 1129vs, 1078vs, 1046vs, 1026vs, 997s, 972vs, 924m, 857vs, 835s, 783s, 743vs, 731vs, 725vs, 706vs, 698vs, 664vs, 617m, 604vs, 545s, 523vs, 469vs, 436s and 413s cm^{-1}.

Dichlorobis[(1*S*)-2-(diphenylphosphoryl)-1-methylethanolato]-titanium(IV). The procedure detailed above was repeated using *S*-Hdpomeo instead of *R*-Hdpopeo. The solid obtained after the ether washing was recrystallised from acetonitrile in air to give air- and moisture-stable colourless crystals suitable for X-ray analysis. Yield 80% (Found: C, 56.3; H, 5.0; Cl, 11.2. Calc. for $C_{30}H_{32}Cl_2O_4P_2Ti$: C, 56.55; H, 5.05; Cl, 11.1%). NMR ($CDCl_3$): ^1H, δ 1.27 (dd, 3 H, CH_3), 2.54 (ddd, 1 H, CH_2), 3.28 (ddd, 1 H, CH_2), 5.06 (m, 1 H, CH), 7.17 (m, 1 H), 7.55 (m, 5 H) and 8.08 (m, 4 H); ^{31}P, δ 44.3; ^{13}C, δ 24.6 (d, J = 13, CH_3), 37.0 (d, J = 70, CH_2), 76.0 (d, J = 6, CH), 128.7(d, J = 13), 132.0 (d, J = 11), 132.6 (d, J = 11 Hz), 132.8 and 133.4 (d, J = 55 Hz). IR (KBr): 3055m, 3024m, 2968m, 2912m, 2862m, 2716m, 2610m, 2249w, 1973w, 1909w, 1822w, 1589m, 1485m, 1437s, 1386m, 1371m, 1344w, 1313m, 1230m, 1176m, 1151s, 1128vs, 1109vs, 1084vs, 1068vs, 1020vs, 997m, 947vs, 873s, 854m, 831s, 821s, 787s, 756s, 746s, 721s, 694s, 623vs, 557vs, 513s, 491s, 470s, 447m and 416m cm^{-1}.

[(1*R*)-2-(Diphenylphosphoryl)-1-phenylethanolato]dioxo-(pentane-2,4-dionato)molybdenum. To a stirred solution of $[MoO_2(acac)_2]$ (acac = acetylacetonate) (506 mg, 1.55 mmol) in toluene–dichloromethane (1:1, 30 cm^3) was added *R*-Hdpopeo (500 mg, 1.55 mmol) as a solid. The mixture was stirred at room temperature for 1 h, filtered in air, the filtrate concentrated *in vacuo* to *ca.* 10 cm^3 and diluted with diethyl ether (10 cm^3). After storing at −20 °C for 1 h the crystalline very pale green solid was filtered off, washed with ether and air-dried. Yield 700 mg (82%) (Found: C, 54.9; H, 4.7. Calc. for $C_{25}H_{25}MoO_6P$: C, 54.75; H, 4.60%). NMR ($CDCl_3$): ^1H, δ 1.71 (s, 3 H, CH_3), 2.10 (s, 3 H, CH_3), 2.70 (dd, 1 H, CH_2), 3.00 (br m, 1 H, CH_2), 5.60 (s, 1 H, CH), 5.91 (br t, 1 H, CH) and 7.18–8.0 (m, 15 H); ^{31}P, δ 39.0; ^{13}C, δ 26.4 (CH_3), 27.1 (CH_3), 36.5 (d, J = 67, CH_2), 80.06 (br, CH), 103.2 (CH), 125.5, 127.6, 128.4, 128.9 (d, J = 12), 129.2 (d, J = 11), 130.4 (d, J = 10), 131.3 (d, J = 10), 133.0 (d, J = 3), 143.9 (d, J = 12 Hz), 186.9 and 193.5. IR (KBr): 3055w, 3030w, 2922w, 2862w, 1589s, 1566m, 1560m, 1527s, 1495w, 1456w, 1439s, 1365s, 1315m, 1280m, 1213w, 1159m, 1145vs, 1118s, 1099m, 1018s, 1001w, 974m, 929vs, 904vs, 854m, 825w, 790m, 763w, 750m, 723m, 702s, 652m, 598m, 536w, 522s, 493w, 453m, 412w and 408w cm^{-1}.

[(1*S*)-2-(Diphenylphosphoryl)-1-methylethanolato]dioxo-(pentan-2,4-dionato)molybdenum. This compound was made by an analogous procedure to that detailed for *R*-Hdpopeo, but using *S*-Hdpomeo. A light green powder was obtained after triturating thoroughly with dry ether. Yield 75%. IR (KBr): 3443w, 3059w, 2972w, 2924w, 1591m, 1560w, 1554w, 1523m, 1485w, 1458w, 1439s, 1381m, 1325w, 1277w, 1236w, 1124vs, 1080m, 1068m, 1020m, 997w, 954vs, 935vs, 914vs, 864m, 800s, 748s, 723s, 692s, 613w, 553m, 511m, 464w and 441w cm^{-1}. No analytical or NMR data are available for this compound as it readily decomposed upon dissolution giving a blue precipitate.

Bis[(1*R*)-2-(Diphenylphosphoryl)-1-phenylethanolato]dioxo-molybdenum monohydrate. To a stirred solution of MoO_2Cl_2 (308 mg, 1.55 mmol) in dichloromethane (50 cm^3) was added *R*-Hdpopeo (1 g, 3.1 mmol). The mixture was stirred for 10 min at room temperature, and thallium(I) ethoxide (773 mg, 3.1 mmol) added *via* a syringe. The mixture was stirred for 1 h, and the precipitated TlCl removed by filtering through a Celite pad in air. The colourless filtrate was pumped dry to give a slightly gummy solid, which was triturated thoroughly with dry diethyl ether until a free-flowing white solid was obtained, which was filtered off, washed with Et_2O, and air-dried. Yield 750 mg (63%) (Found: C, 61.4; H, 4.9. Calc. for $C_{40}H_{38}MoO_7P_2$: C, 60.9; H, 4.85%). NMR ($CDCl_3$): ^1H, δ 2.66 (dd, 1 H, CH_2), 2.98 (q, 1 H, CH_2), 5.82 (t, 1 H, CH) and 7.15–8.10 (15 H); ^{31}P, δ 39.3; ^{13}C, δ 36.2 (d, J = 67, CH_2), 79.0 (d, J = 3, CH), 125.5, 127.0, 128.1, 128.3 (d, J = 12), 128.7 (d, J = 11), 130.2 (d, J = 10), 131.8 (d, J = 10) and 146.3 (d, J = 12 Hz). IR (KBr): 3416w, 3057w, 3028w, 2914w, 2835w, 1971w, 1900w, 1589w, 1491w, 1485w, 1450w, 1437s, 1385w, 1334w, 1313w, 1284w, 1213w, 1159s, 1140vs, 1120s, 1097m, 1070m, 1041m, 1028m, 999w, 968m, 925s, 898vs, 858m, 825w, 787w, 742s, 723m, 696vs, 653w, 596m, 542w, 520m, 451w and 420w cm^{-1}.

Bis[(1*S*)-2-(diphenylphosphoryl)-1-methylethanolato]dioxomolybdenum. The procedure detailed for *R*-Hdpopeo above was repeated with *S*-Hdpomeo. The product was obtained as a pale green solid. Yield 70%. NMR ($CDCl_3$): ^1H, δ 1.38 (dd, 3 H, CH_3), 2.31 (dd, 1 H, CH_2), 2.65 (m, 1 H, CH_2), 4.92 (m, 1 H, CH) and 7.15–8.00 (10 H); ^{31}P, δ 38.8; ^{13}C, δ 27.0 (d, J = 15, CH_3), 35.7 (d, J = 71, CH_2), 74.3 (d, J = 4 Hz, CH) and 128.0–132.0 (aromatics). IR (KBr): 3379w, 3055w, 2968w, 2922w, 2858w, 1971w, 1907w, 1591w, 1485w, 1437s, 1385w, 1369w, 1342w, 1323w, 1230w, 1165s, 1142vs, 1122vs, 1091s, 1070m, 1022s, 997w, 920vs, 897vs, 871m, 829m, 804m, 785w, 748s, 721s, 694vs, 596m, 551s, 515s and 464w cm^{-1}.

Crystallography

Details of data collection procedures and structure refinement are given in Table 3. Crystals of the complex [$TiCl_2$(*S*-dpomeo)$_2$] were obtained as colourless prisms. A single crystal of suitable size was attached to a glass fibre using acrylic resin, and mounted on a goniometer head in a general position. Data were collected on an Enraf-Nonius Turbo CAD4 diffractometer, running under CAD4-Express software, and using graphite-monochromated X-radiation (λ = 0.710 73 Å). An ω–2θ scan mode was used. Unit-cell dimensions were determined by refinement of the setting angles of 25 reflections. Standard reflections were measured every 2 h during data collection, and no significant variations were noted. Lorentz-polarization and absorption (by semiempirical ψ scans using nine reflections with χ > 80.3° and 3.5 < θ < 12.4°) corrections were then applied to the reflection data. The structure was solved by direct methods (SIR 92).[6] All non-H atoms were allowed anisotropic thermal motion. Hydrogen atoms were included at calculated positions, with C–H 0.96 Å. Refinement (SHELXL 93)[7] was by full-matrix least squares on F^2, using the weighting scheme $w = [\sigma^2(F_o)^2 + (0.0387P)^2 + 0.5773P]^{-1}$ where $P = [F_o^2/3 + 2F_c^2/3]$; $\sigma(F_o)^2$ was estimated from counting statistics. The neutral atom scattering factors embedded in the program SHELXL 93 were used, with corrections applied for anomalous dispersion. Fractional atomic coordinates are presented in Table 4.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Synthesis

The reaction of Ph_2P^- with the readily available chiral epoxides *R*-styrene oxide and *S*-propene oxide, followed by H_2O_2 oxidation, gave the chiral diphenylphosphoryl alcohols in good yields. Their NMR spectra were unchanged on addition of a chiral shift reagent, indicating the production of essentially pure single enantiomers. The chiral integrity of the oxiranes remains intact since the asymmetric centre is not the one attacked by the diphenylphosphine anion. The styrene oxide reaction also produced small amounts of a by-product, 1,2-bis(diphenylphosphoryl)-1-phenylethane.[5] This diphosphine oxide is insoluble in acetone, and was readily separated from the more soluble product, *R*-Hdpopeo.

Similar compounds to the disphosphine oxide have been made by Wife *et al.*[8] from the reaction of $R_2P(O)^-$ (R = aryl) and oxiranes, the balance between products of type *R*-Hdpopeo and the diphosphine oxide being determined by the oxirane substituents and the solvent polarity. The action of Ph_2P^- on oxiranes is presumably similar, forming the diphosphine oxide in our case from the H_2O_2 oxidation of intermediate 1,2-bis(diphenylphosphino)-1-phenylethane. Single enantiomers of this diphosphine ligand have been used in asymmetric hydrogenation reactions,[9] but the product from our reaction was racemic. The formation of diphosphine oxides from the action of $R_2P(O)^-$ on oxiranes is believed to proceed through a planar, aldehydic intermediate which would result in loss of stereochemistry at carbon.[8] Our Ph_2P^- reaction presumably proceeds in the same manner.

Addition of 2 mole equivalents of *R*-Hdpopeo or *S*-Hdpomeo to $TiCl_4$ in dichloromethane gave the ternary complexes [$TiCl_2L_2$] (L = *R*-dpopeo or *S*-dpomeo) as colourless, crystalline solids. Although the precaution of working under nitrogen was adopted for their syntheses, the compounds were remarkably air- and moisture-stable, and could be readily recrystallised from hot solvents on the bench. The complex [$TiCl_2$(*S*-dpomeo)$_2$] was soluble in chlorinated solvents, but only sparingly so in toluene, diethyl ether and acetonitrile; [$TiCl_2$(*R*-dpopeo)$_2$]·C_6H_5Me was soluble in chlorinated solvents, toluene and acetonitrile. The reaction of 2 mole equivalents of *R*-Hdpopeo or *S*-Hdpomeo with MoO_2Cl_2 in the absence of base did not give [MoO_2L_2], but produced the adducts [$MoO_2(HL)_2Cl_2$] instead. These were not isolated, but could be observed in solution by NMR methods. When the reactions were repeated with the addition of 2 mole equivalents of thallium(I) ethoxide as base the complexes [MoO_2L_2] were obtained. Unlike the titanium(IV) compounds, these were produced as hydrates in air, and decomposed fairly rapidly on treatment with solvents to give blue solutions [presumably consisting of molybdenum(V) dimers] followed by deposition of dark blue solids.

Mixing [$MoO_2(acac)_2$] and the phosphoryl alcohols HL in a 1 : 1 ratio in organic solvents gave the quaternary complexes [MoO_2(acac)L]. These syntheses had no requirement for the addition of base, although the reaction of [$MoO_2(acac)_2$] with 2 mole equivalents of HL did not proceed as cleanly as the reactions between MoO_2Cl_2 and HL in the presence of base. The complex [MoO_2(acac)(*R*-dpopeo)] was obtained as an air-stable crystalline solid which decomposed only slowly when dissolved, its colourless solution in chloroform becoming blue overnight. In contrast, [MoO_2(acac)(*S*-dpomeo)] did not crystallise readily, proved difficult to obtain as a manageable solid, and decomposed rapidly upon dissolution. The NMR spectroscopic details for this complex could not be obtained.

Crystal and molecular structure of [$TiCl_2$(*S*-dpomeo)$_2$]

A view of the molecular complex is shown in Fig. 1, and selected bond lengths and angles are given in Table 1. The complex has the expected octahedral geometry, but with the chloride donors in the *trans* positions. This is quite uncommon, with compounds such as [$Ti(acac)_2Cl_2$] having *cis*-chlorides in the solid state and most probably in solution;[10–14] [$Ti(acac)_2I_2$] is a rare example where the halides lie *trans* in solution,[15] probably due to steric constraints. The phosphoryl donors (and, by necessity, the alkoxide oxygens) are mutually *cis*.

The Ti–O bond lengths to the anionic alkoxide donors are strikingly shorter (*ca.* 1.80 Å) than to the phosphoryl oxygens (*ca.* 2.06 Å). These Ti–O_{alc} lengths are in the range expected from previous X-ray studies on alkoxotitanium(IV) complexes.[16–21] Also, from the few titanium(IV) compounds containing phosphoryl donors that have been structurally characterised, we note that the Ti–OP(NMe_2)$_3$ bond lengths in [$Ti(O_2)${OP(NMe_2)$_3$}(acac)L] and [$Ti(O_2)${OP(NMe_2)$_3$}L_2] (L = pyrazine-2,3-dicarboxylate or pyridine-2-carboxylate) of 2.002(4) and 2.042(4) Å, respectively, are comparable to our values.[22,23] Both the alkoxy and phosphoryl oxygen atoms are expected to behave as π-electron donors to Ti^{IV}. The extended

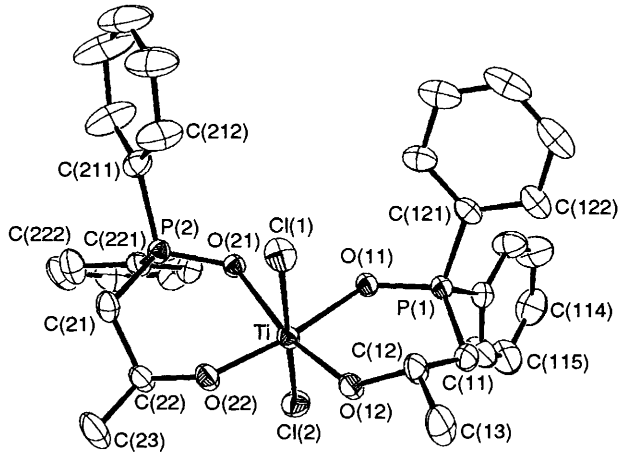


Fig. 1 Molecular structure and atomic labelling scheme of [TiCl$_2$(*S*-dpomeo)$_2$] with thermal ellipsoids shown at the 20% probability level

Table 1 Selected bond lengths (Å) and angles (°) for [TiCl$_2$(*S*-dpomeo)$_2$]

Ti–O(22)	1.800(2)	P(2)–O(21)	1.508(2)
Ti–O(12)	1.809(2)	P(2)–C(21)	1.790(3)
Ti–O(21)	2.061(2)	P(2)–C(221)	1.792(3)
Ti–O(11)	2.062(2)	P(2)–C(211)	1.795(3)
Ti–Cl(2)	2.4050(9)	O(12)–C(12)	1.423(3)
Ti–Cl(1)	2.4054(9)	O(22)–C(22)	1.420(3)
P(1)–O(11)	1.509(2)	C(11)–C(12)	1.521(4)
P(1)–C(11)	1.791(3)	C(12)–C(13)	1.510(4)
P(1)–C(121)	1.801(3)	C(21)–C(22)	1.528(4)
P(1)–C(111)	1.805(3)	C(22)–C(23)	1.511(4)
O(22)–Ti–O(12)	102.87(9)	C(121)–P(1)–C(111)	108.51(14)
O(22)–Ti–O(21)	89.20(8)	O(21)–P(2)–C(21)	110.38(12)
O(12)–Ti–O(21)	166.63(8)	O(21)–P(2)–C(221)	110.06(12)
O(22)–Ti–O(11)	167.99(8)	C(21)–P(2)–C(221)	108.87(14)
O(12)–Ti–O(11)	88.65(8)	O(21)–P(2)–C(211)	109.72(13)
O(21)–Ti–O(11)	79.72(7)	C(21)–P(2)–C(211)	110.02(14)
O(22)–Ti–Cl(2)	89.15(7)	C(221)–P(2)–C(211)	107.74(14)
O(12)–Ti–Cl(2)	96.84(7)	P(1)–O(11)–Ti	131.93(11)
O(21)–Ti–Cl(2)	88.96(5)	C(12)–O(12)–Ti	132.4(2)
O(11)–Ti–Cl(2)	86.08(6)	P(2)–O(21)–Ti	131.83(11)
O(22)–Ti–Cl(1)	94.14(7)	C(22)–O(22)–Ti	134.3(2)
O(12)–Ti–Cl(1)	87.79(7)	C(12)–C(11)–P(1)	111.4(2)
O(21)–Ti–Cl(1)	85.60(5)	O(12)–C(12)–C(13)	109.9(3)
O(11)–Ti–Cl(1)	89.62(6)	O(12)–C(12)–C(11)	109.1(2)
Cl(2)–Ti–Cl(1)	173.60(4)	C(13)–C(12)–C(11)	112.5(3)
O(11)–P(1)–C(11)	110.63(12)	C(22)–C(21)–P(2)	111.3(2)
O(11)–P(1)–C(121)	108.95(13)	O(22)–C(22)–C(23)	108.7(2)
C(11)–P(1)–C(121)	108.6(2)	O(22)–C(22)–C(21)	109.7(2)
O(11)–P(1)–C(111)	110.80(12)	C(23)–C(22)–C(21)	111.9(3)
C(11)–P(1)–C(111)	109.3(2)		

P=O bonds in the OP(NMe$_2$)$_3$ compounds above [1.482(2) and 1.479(4), compared to 1.461(7) Å for the unco-ordinated phosphine][24] result from π donation from O to Ti, as do the P=O values of 1.51 Å in [TiCl$_2$(dpomeo)$_2$]. It should be noted, however, that the P=O bond lengths in Ti^{IV}-co-ordinated and unco-ordinated POCl$_3$ are very similar.[25]

The P=O and (P)O–Ti lengths of 1.51 and 2.06 Å in [TiCl$_2$(dpomeo)$_2$] are very similar (1.51 and 2.02 Å, respectively) to those reported by us[26] for the complex [V{OCOCHMeP(O)Ph$_2$}$_3$], which has ligands of similar geometry. The V–O bonds to the carboxylate oxygens in the latter complex are comparable in length to the V–O(P) links to those phosphorylcarboxylate ligands, however, and we note that Ti^{IV}–O bond lengths to the oxygens of carboxylate or acetylacetonate ligands are also about 2.00 Å,[22,23] much longer than the Ti–O (alkoxide) bonds found here and elsewhere.[16–21] Clearly these strikingly short Ti–O (alkoxide) bonds are a common feature of titanium(IV) chemistry, and are most probably due to enhanced π donation from the non-delocalised sp^3 oxygen. The main reason for the adoption of the *cis* geometry found in [TiCl$_2$(dpomeo)$_2$] would then be the reluctance of the alkoxides to adopt a geometry where they are competing for the same metal orbitals for π donation.

The O–Ti–O angles of the six-membered chelate rings are both near 90°, but there is considerable distortion away from ideal octahedral geometry with the other (*cis*) angles lying between 103 and 80°. The Ti–Cl bonds are not collinear, the angle being slightly compressed to 173.1°. Neither are the four Ti–O bonds coplanar. Three of the bond vectors roughly define a plane, but the fourth then intersects at an angle of around 5° at the metal centre. The two *S*-dpomeo ligands are similar, but not exactly equivalent. The six-membered chelate rings adopt asymmetric boat conformations and are flattened in the Ti–O–P–CH$_2$ region, with torsion angles of 2.4 and 9.2° for the two distinct *S*-dpomeo ligands. Consequently, the conformation adopted by the chelates is that of a half-envelope, with the chiral carbon forming the apex of the 'flap' of the envelope and the methyls projecting equatorially. No unfavourable phenyl–phenyl contacts are observed even though the phosphoryl groups are *cis* and the (P)O–Ti–O(P) angle is compressed to 79.7°. This appears to be the first structurally characterised metal complex of a phosphorylalkoxide, although a phosphorylphenoxide complex of Ru^{II} has recently been reported.[2]

Infrared spectra

The infrared spectra of both the phosphorylalcohols and their complexes contain many sharp bands. The single most important for our discussion is that assigned to the P=O stretch, ν(P=O). In the solid state it is expected that *R*-Hdpopeo and *S*-Hdpomeo would possess intra- or inter-molecular hydrogen bonds involving the hydroxy functions and the phosphoryl groups. Such contacts would lower the frequency of ν(P=O) relative to those of simple monoalkylbiaryl phosphine oxides; this stretch is observed at 1159 and 1162 cm^{-1} for *R*-Hdpopeo and *S*-Hdpomeo, respectively. Upon co-ordination, further shifts to low frequency are to be expected, as the double-bond character of the P=O group is reduced. Such a progression is observed as detailed in Table 2. In general, the shifts are larger for the titanium(IV) complexes (≈ -32 cm^{-1}) than for the molybdenum(VI) species (≈ -20 cm^{-1}), and may reflect greater π donation to the metal for the former. The molybdenum complexes have the characteristic strong doublet of peaks at $\approx$930 and 900 cm^{-1}, such a pattern being consistent with *cis*-oxo groups.

NMR spectra

The most prominent details of the NMR spectra are listed in Table 2. The spectra of the titanium(IV) complexes are highly resolved at 298 K, reflecting the presence of a single, non-fluxional species in solution. The methine proton (H$_a$) adjacent to the hydroxy group shifts to low field upon co-ordination, typically by 0.8 ppm. In the ^{1}H NMR spectrum of [TiCl$_2$(*S*-dpomeo)$_2$] this resonance is observed at δ 5.06, and is a complex multiplet resembling that of the uncomplexed phosphorylalcohol. By way of contrast, the protons of the methylene group are separated in the complex, with the high-field resonance (H$_c$) occurring as a resolved doublet of doublets of doublets whereas the corresponding signals in the ^{1}H NMR spectrum of *S*-Hdpomeo overlap to give a complex multiplet. Similarly, the low-field methylene resonance (H$_b$) is seen as a doublet of doublets of doublets, albeit with two different coupling constants to H$_c$. The ^{1}H NMR spectrum of [TiCl$_2$(*R*-dpopeo)$_2$] is similar, except that the methine proton is now a simple triplet of triplets, and the high-field resonance of the methylenes is a doublet of triplets. Homonuclear decoupling experiments allowed all the relevant coupling constants to be

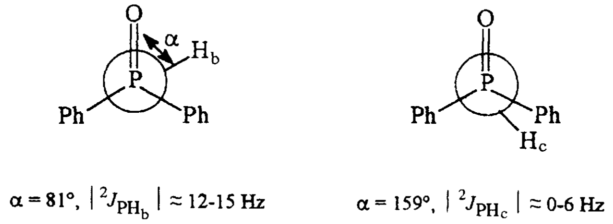
Table 2 Selected spectroscopic details for *S*-Hdpomeo, *R*-Hdpopeo and their metal complexes

	S-Hdpomeo	$[TiCl_2(S\text{-dpomeo})_2]$	$[MoO_2(S\text{-dpomeo})_2]$	$[MoO_2(acac)(S\text{-dpomeo})]$
$\tilde{\nu}(P{=}O)/cm^{-1}$	1162vs	1128vs	1142vs	1124vs
$\delta(^1H)$				
H_a	4.23 (m)	5.06 (m)	4.93 (m)	
H_b	2.38 (m)	3.28 (m)	2.65 (m)	
H_c	2.38 (m)	2.54 (ddd)	2.31 (dd)	
CH_3	1.23 (dd)	1.27 (dd)	1.38 (dd)	
$J_{H_a,Me}/Hz$		6.2		
J_{H_a,H_b}		10.5		
J_{H_a,H_c}		3.9		
$J_{H_a,P}$		7.2		
J_{H_b,H_c}		14.7		
$J_{H_b,P}$		14.2		
$J_{H_c,P}$		3.9		
$\delta(^{31}P)$	34.0	44.3	39.3	
	R-Hdpopeo	$[TiCl_2(R\text{-dpopeo})_2]$	$[MoO_2(R\text{-dpopeo})_2]$	$[MoO_2(acac)(R\text{-dpopeo})]$
$\tilde{\nu}(P{=}O)/cm^{-1}$	1159vs	1128vs	1140vs	1146vs
$\delta(^1H)$				
H_a	5.08 (t)	5.92 (tt)	5.82 (t)	5.91 (t)
H_b	2.61 (m)	3.72 (m)	2.98 (q)	3.00 (m)
H_c	2.61 (m)	2.75 (dt)	2.66 (dd)	2.70 (dd)
H_{acac}				5.60 (s)
CH_3				1.71 (s), 2.10 (s)
$J_{H_a,H_b}/Hz$		10.8		
J_{H_a,H_c}		2.7		
$J_{H_a,P}$		8.2		
J_{H_b,H_c}		14.7		
$J_{H_b,P}$		14.5		
$J_{H_c,P}$		2.7		
$\delta(^{31}P)$	33.9	45.1	39.3	39.0

Table 3 Experimental details of the crystallographic study

Compound formula	$C_{30}H_{32}Cl_2O_4P_2Ti$
M_r	637.3
Space group	$P2_12_12_1$
Crystal system	Orthorhombic
a/Å	11.572(1)
b/Å	13.209(1)
c/Å	20.452(1)
U/Å^3	3126.3(4)
θ range for cell	17.6–20.9
Z	4
D_c/g cm^{-3}	1.354
F(000)	1320
μ(Mo-Kα)/cm^{-1}	5.8
ω-Scan angle/°	0.58 + 0.44 tan θ
θ Range/°	2.3–25.0
Crystal size/mm	0.6 × 0.5 × 0.40
Transmission coefficients/ corrections	0.999–0.965
No. data collected	4085
No. unique data	3830
hkl Ranges	−11 to 12, −13 to 0, −15 to 16
R_σ	0.0172
Standard reflections	(4,4,5), (−3, −1, 9), (−3, 6, 0)
No. data in refinement	3830
No. refined parameters	354
Final R (all data)	0.0268 (0.0297)
wR_2 (all data)	0.0653 (0.0666)
Goodness of fit, S	1.037
Largest remaining features in electron-density map/e Å^{-3}	0.19, −0.16
Shift/e.s.d. in last cycle	0.0005 (mean), 0.001 (maximum)

deduced for the titanium(IV) species, and these are given in Table 2. Correlations of $|^3J_{PCCH}|$ with torsion angle for rigid cyclic compounds have been shown to follow a Karplus-like curve.[27] From the crystal structure of $[TiCl_2(S\text{-dpomeo})_2]$, the PH_a torsion angle averages 53°, consistent with the observed



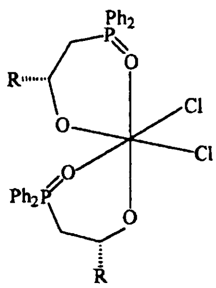
Scheme 1 Correlation of O–P–C–H torsion angle for *S*-dpomeo chelates in solid $[TiCl_2(S\text{-dpomeo})_2]$ with the expected $^2J_{PCH}$ coupling constants in solution. Data for couplings taken from ref. 28

coupling constant of 7 Hz. Additionally, $|^2J_{PCH}|$ values have been correlated in a similar way,[28] the angular dependence being defined by the torsion angle between the P=O bond and the C–H bond in question (Scheme 1). For $[TiCl_2(S\text{-dpomeo})_2]$, the $|^2J_{PH_b}|$ and $|^2J_{PH_c}|$ coupling constants are 14 and 4 Hz, respectively, in complete accord with the expected couplings for O–P–C–H torsion angles of 81 (H_b) and 159° (H_c) derived from the solid-state structure. This corroborative evidence suggests the adoption of a similar flattened-envelope chelate geometry in solution as is observed in the crystal. The analogous patterns seen for *R*-Hdpopeo in the NMR spectra of the titanium(IV) complex are indicative of the same conformation. In both cases the observation of fixed $|^2J_{PCH}|$ couplings is consistent with the formation of relatively rigid fixed chelates.

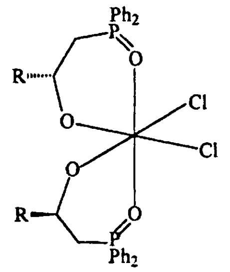
If *cis* forms of the complexes were present then three isomers **I**–**III** would be expected. The observation of the simple patterns alluded to above is indicative of a single *trans* form being present in solution. Of the two possible (**IV** and **V**), it seems logical to assign structure **IV** as this has been established in the solid state. No spectral change is observed on cooling to 223 K for either titanium(IV) complex, and it is proposed that in $[TiCl_2L_2]$ the *trans-cis-cis* isomer is formed stereospecifically,

Table 4 Atomic coordinates (× 10^4) for $[TiCl_2(S\text{-dpomeo})_2]$ **1**

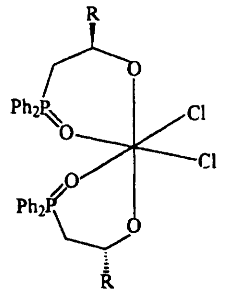
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ti	2 233(1)	8 898(1)	2 820(1)	C(116)	2 705(4)	5 266(3)	3 131(2)
Cl(1)	707(1)	9 800(1)	3 367(1)	C(121)	195(2)	6 980(2)	4 126(1)
Cl(2)	3 847(1)	7 962(1)	2 393(1)	C(122)	−714(3)	6 308(3)	4 207(2)
P(1)	1 233(1)	6 819(1)	3 478(1)	C(123)	−1 479(3)	6 451(4)	4 725(2)
P(2)	3 956(1)	10 355(1)	3 665(1)	C(124)	−1 321(4)	7 242(4)	5 145(2)
O(11)	2 037(2)	7 719(1)	3 472(1)	C(125)	−445(4)	7 912(4)	5 055(2)
O(12)	1 137(2)	8 321(2)	2 312(1)	C(126)	327(3)	7 792(3)	4 544(2)
O(21)	3 272(1)	9 394(1)	3 573(1)	C(211)	3 527(3)	10 965(2)	4 411(2)
O(22)	2 681(2)	9 973(1)	2 343(1)	C(212)	2 358(4)	11 116(4)	4 520(2)
C(11)	474(3)	6 720(2)	2 718(2)	C(213)	1 970(6)	11 468(5)	5 118(3)
C(12)	124(3)	7 756(3)	2 462(2)	C(214)	2 679(7)	11 644(4)	5 609(2)
C(13)	−642(4)	7 690(4)	1 865(2)	C(215)	3 807(7)	11 506(6)	5 505(3)
C(21)	3 736(3)	11 191(2)	2 987(1)	C(216)	4 243(5)	11 157(4)	4 914(2)
C(22)	3 672(2)	10 608(2)	2 343(1)	C(221)	5 466(2)	10 068(2)	3 726(1)
C(23)	3 605(4)	11 308(3)	1 760(2)	C(222)	6 310(3)	10 812(3)	3 693(2)
C(111)	2 024(3)	5 663(2)	3 623(2)	C(223)	7 465(3)	10 549(4)	3 774(2)
C(112)	2 036(4)	5 196(3)	4 222(2)	C(224)	7 766(3)	9 574(4)	3 893(2)
C(113)	2 719(4)	4 356(3)	4 325(2)	C(225)	6 946(3)	8 843(3)	3 932(2)
C(114)	3 383(4)	3 974(3)	3 835(2)	C(226)	5 785(3)	9 076(2)	3 841(2)
C(115)	3 379(4)	4 417(3)	3 235(2)				



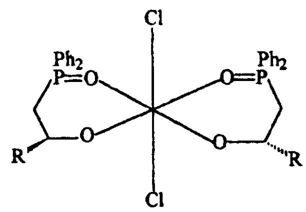
cis-cis-cis
I



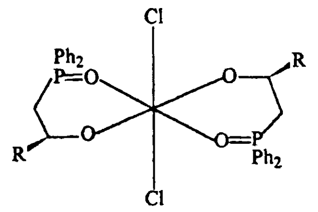
cis-trans-cis
II



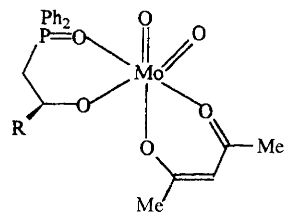
cis-cis-trans
III



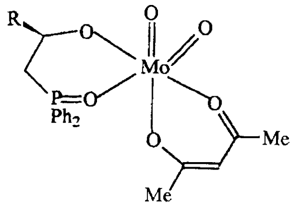
trans-cis-cis
IV



trans-trans-trans
V



VI



VII

and no conversion into other isomers occurs freely by fluxional processes. The only significant shift in the ^{13}C NMR spectra is that of the stereogenic carbon atom; this resonates 12–13 ppm downfield relative to the free phosphorylalcohol. For both these complexes significant low-field shifts are seen in the ^{31}P NMR spectra (Table 2), their magnitude being much greater than is seen for other titanium(IV) complexes of bidentate ligands with P=O donors.[4] This is further evidence of relatively strongly co-ordinated P=O functions in solution. The ^{31}P singlet remains unchanged on cooling to 223 K.

The ^1H NMR spectra of the $[MoO_2L_2]$ complexes are less well resolved than those of the titanium(IV) species, and may indicate a greater degree of conformational freedom in the chelates in these systems. Lack of free fluxionality is exemplified by the spectra of $[MoO_2(acac)(R\text{-dpopeo})]$. In the ^1H spectrum the typical features of co-ordinated *R*-dpopeo, as indicated above, are observed, although some broadening of the methine and low-field methylene resonances is observed. There are, however, two singlets assigned to the two chemically and magnetically distinct methyls of the acetylacetonate ligand. Such an observation is a result of the dpopeo ligand being a non-symmetric bidentate, hence the methyls are, by necessity, non-equivalent as shown in **VI** and **VII**. If the molecule were fluxional, the two forms would interconvert freely, and only a single averaged methyl resonance would be observed. This is not the case, and the complex is considered non-fluxional on the NMR time-scale. This inequivalence of methyls is mimicked in the ^{13}C NMR spectrum (see Experimental section). Unlike the titanium(IV) complexes, the geometry here is assigned as *cis*, by far the most prevalent arrangement for the dioxo groups in molybdenum(VI) chemistry. Similar, albeit smaller, low-field shifts are observed in the ^{31}P NMR spectra of the molybdenum complexes with respect to the titanium systems (Table 2). Again these are larger than reported for a similar complex.[4]

Acknowledgements

We gratefully acknowledge the support of the EPSRC (Process Engineering Separations Initiative; grant number GR/J 45190).

References

1 *The Chemistry of Functional Groups: The Chemistry of Organophosphorus Compounds*, ed. F. R. Hartley, series ed. S. Patai, Wiley, Chichester, 1992, vol. 2.

2 R. S. Tanke, E. M. Holt and R. H. Crabtree, *Inorg. Chem.*, 1991, **30**, 1714.

3 G. Borisov, S. G. Varbanov, L. M. Venanzi, A. Albinati and F. Demartin, *Inorg. Chem.*, 1994, **33**, 5430.

4 M. Gahagan, R. K. Mackie, D. J. Cole-Hamilton, M. Harman and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1990, 2195.

5 J. M. Brown and B. A. Murrer, *J. Chem. Soc., Perkin Trans. 2*, 1982, 489.

6 SIR 92, a program for automatic solution of crystal structures by direct methods, A. Altomare, G. Cascarno, C. Giacovazzo and A. Gualiardi, *J. Appl. Crystallogr.*, 1994, **27**, 435.

7 SHELXL 93, a program for crystal structure refinement, G. M. Sheldrick, University of Göttingen, 1993.

8 R. L. Wife, A. B. van Oort, J. A. van Doorn and P. W. N. M. van Leeuwen, *Phosphorus Sulfur*, 1983, **18**, 117.

9 D. P. Riley and R. E. Shumate, *J. Org. Chem.*, 1980, **45**, 5187.

10 D. W. Thompson, W. A. Somers and M. O. Workman, *Inorg. Chem.*, 1970, **9**, 1252.

11 R. C. Fay and R. N. Lowry, *Inorg. Chem.*, 1967, **6**, 1512.

12 N. Serpone and R. C. Fay, *Inorg. Chem.*, 1969, **8**, 2379.

13 N. Serpone and R. C. Fay, *Inorg. Chem.*, 1967, **6**, 1835.

14 H. Weingarten, M. G. Miles and N. K. Edelmann, *Inorg. Chem.*, 1968, **7**, 879.

15 R. C. Fay and R. N. Lowry, *Inorg. Chem.*, 1970, **9**, 2048.

16 A. Van der Linden, C. J. Schaverien, N. Meijboom, C. Ganter and A. G. Orpen, *J. Am. Chem. Soc.*, 1995, **117**, 3008.

17 T. J. Boyle, R. W. Schwartz, R. J. Doedens and J. W. Ziller, *Inorg. Chem.*, 1995, **34**, 1110.

18 J. A. van Doorn, H. van der Heijden and A. G. Orpen, *Organometallics*, 1994, **13**, 4271.

19 W. A. Nugent and R. L. Harlow, *J. Am. Chem. Soc.*, 1994, **116**, 6142.

20 D. M. Choquette, W. E. Buschmann, M. M. Olmstead and R. P. Planalp, *Inorg. Chem.*, 1993, **32**, 1062.

21 P. B. Hitchcock, M. F. Lappert and I. A. MacKinnon, *J. Chem. Soc., Chem. Commun.*, 1993, 1015.

22 H. Mimoun, M. Postel, F. Casabianca, J. Fischer and A. Mitschler, *Inorg. Chem.*, 1982, **21**, 1303.

23 M. Postel, F. Casabianca, Y. Gauffreteau and J. Fischer, *Inorg. Chim. Acta*, 1986, **113**, 173.

24 D. H. Brown, A. F. Cameron, R. J. Cross and M. McLaren, *J. Chem. Soc., Dalton Trans.*, 1981, 1459.

25 C.-I. Brändén and I. Lindqvist, *Acta Chem. Scand.*, 1960, **14**, 726.

26 R. J. Cross, L. J. Farrugia, P. D. Newman, R. D. Peacock and D. Stirling, *J. Chem. Soc., Dalton Trans.*, 1996, 1087.

27 C. Benezra, *J. Am. Chem. Soc.*, 1973, **95**, 6890.

28 W. G. Bentrude and W. N. Setzer, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*, eds. J. G. Verkade and L. D. Quin, VCH, Deerfield Beach, FL, 1987, pp. 380, 381.

Received 10*th October* 1995; *Paper* 5/06705G