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Coordination chemistry of an asymmetric P,N,O tridentate ligand containing primary phosphine, amine and alcohol donors

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ABSTRACT

The asymmetric, heterodonor tridentate ligand 2(*S*)-amino-4-phosphinobutan-1-ol, *S*-PNO, has been prepared from (*S*)-aspartic acid and some aspects of its coordination chemistry with a number of metal complexes investigated. Reaction of *S*-PNO with appropriate metal precursors led to the isolation of the complexes *fac*-$Cr(CO)_3(\kappa^3$-*S*-PNO), **1**, *fac*-$[Mn(CO)_3(\kappa^3$-*S*-PNO)$]PF_6$, **2**, and *fac*-$[Re(CO)_3(\kappa^3$-*S*-PNO)$]BF_4$, **3**. The alcohol and amine donors in *fac*-$Cr(CO)_3(\kappa^3$-*S*-PNO) were substituted upon addition of trivinylphosphine to **1** to give the complex *fac*-$Cr(CO)_3(\kappa^1$-P-*S*-PNO$\{P(C_2H_3)_3\}_2$, **4**. Addition of base to **4** gave a coordinated linear tridentate P_3 ligand through the formation of two new chelate rings via hydrophosphination of one vinyl group on each coordinated $P(C_2H_3)_3$ with the P–H bonds of the complexed *S*-PNO. The alcohol donor in *fac*-$[Re(CO)_3(\kappa^3$-*S*-PNO$)]BF_4$ is labile and can be substituted with *tris*(2-fluorophenyl)phosphine, PAr^F_3, to give *fac*-$[Re(CO)_3(\kappa^2$-P,N-*S*-PNO$)(PAr^F_3)]BF_4$, **5**. Attempts to form a macrocyclic ligand through addition of base to *fac*-$[Re(CO)_3(\kappa^2$-P,N-*S*-PNO$)(PAr^F_3)]BF_4$ were unsuccessful due to loss of PAr^F_3 prior to any ring-closure. All the complexes have been fully characterised by spectroscopic and analytical techniques including a single-crystal X-ray structure analysis of **2**.

1. Introduction

Fac-$[M(CO)_3]^{n+}$ fragments are useful structural units for the template-assisted synthesis of small-ring P_3, P_2C and PN_2 macrocycles [1]. The success of these systems relies on a number of features including the facility to add, in a sequential manner, different donors at preferred positions in the coordination sphere prior to the cyclisation event. As part of a continued interest in small, facially capping macrocycles we are seeking new ligands bearing primary phosphine functions in addition to other potential donor types with the two-fold aim of making mixed-donor macrocycles and/or to access P_3 macrocycles bearing functionalised pendant arms. The inclusion of secondary donors *exo*- to the main macrocyclic ring is an attractive one as it is conceivable that such donors can be used to bind other metals to give hetero-bimetallic compounds. To this end we have synthesised the P,N,O containing ligand 2(*S*)-amino-4-phosphinobutan-1-ol (*S*-PNO) as a potential precursor to one or other of the aforementioned coordination systems. *S*-PNO is part of an under-represented ligand class that combine classically soft donors (P) with harder donors of two different types (in this case N and O). The availability of three different donor types should enable access to a range of coordination compounds showing metal ion dependent denticity and selectivity in the lower dentate modes. The current paper examines some aspects of the chemistry of *S*-PNO with low-valent middle transition metals in an attempt to explore the possibility of selective coordination of one or more donors and also highlights some preliminary efforts to synthesise P_2N macrocycles from the *S*-PNO complexes.

2. Experimental

The complexes were synthesised under dinitrogen using standard Schlenk line techniques. All solvents were freshly distilled from sodium (toluene, 40/60 petroleum ether), sodium/benzophenone (diethyl ether, tetrahydrofuran) or calcium hydride (acetonitrile, ethanol) under dinitrogen before use. The ^{31}P NMR spectra were recorded on a Jeol Eclipse 300 spectrometer operating at 121.7 MHz and referenced to 85% H_3PO_4 ($\delta = 0$ ppm). ^1H (500 or 300 MHz) and ^{13}C (125.8 or 75.6 MHz) NMR spectra were obtained on Bruker 500 and Jeol Eclipse 300 spectrometers and are referenced to tetramethylsilane ($\delta = 0$ ppm). Mass spectra were obtained on a Waters LCT Premier XE mass spectrometer. All other chemicals were of reagent grade and were used as supplied unless otherwise stated. The precursors to *S*-PNO and *R,S*-*S*-$P^{iPr}NO$ were prepared as described by Burgess et al. [2]. *Fac*-$[Cr(CO)_3(MeCN)_3]$

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[3], *fac*-$[Mn(CO)_3(MeCN)_3]PF_6$ [4] and $LiP(SiMe_3)_2$ [5] were prepared by literature methods.

2.1. 2(S)-amino-4-phosphinobutan-1-ol, S-PNO

To a solution of propan-2-yl 5-(2-hydroxyethyl)-2,2-dimethyl-1,3-oxazolidine-3-carboxylate tosylate (12 g, 0.03 mol) in Et_2O (250 ml) at −78 °C was added slowly a solution of $LiP(SiMe_3)_2$ (6.25 g, 0.034 mol) in THF (100 ml) over a period of 1 h. The mixture was stirred at −78 °C for 2 h then allowed to warm slowly to room temperature and stirred overnight. The mixture was filtered, methanol added (20 ml) and the volatiles removed *in vacuo* to give a sticky residue. The residue was dissolved in 5% aq. MeOH (100 ml) and stirred with Dowex-X8 cation exchange resin in the H^+-form (5 g) for 24 h. The solution was filtered and taken to dryness before repeating with fresh resin and solvent. After filtering again the volatiles were removed *in vacuo* and the residue stirred with 1.5 M HCl in MeOH (100 ml) for 24 h. The volatiles were removed, the residue dissolved in H_2O (10 ml) and made slightly basic by the addition of aq. NaOH. The solution was taken to dryness *in vacuo* and the residue extracted into THF (2 × 150 ml), dried over $MgSO_4$, filtered and the volatiles removed to give *S*-PNO as a white solid. Yield = 2.7 g (74%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz) δ −135.3 ppm ^1H NMR ($CDCl_3$, 500 MHz) δ 3.52 (1H, dd, J = 10.5, 4.0 Hz, C*H*$_2$OH), 3.23 (1H, dd, J = 10.5, 7.7 Hz, C*H*$_2$OH), 2.80 (1H, m, R$_2$C*H*NH$_2$), 2.65 (2H, dm, $^1J_{H-P}$ = 198 Hz, PH_2), 1.88 (3H, m br, NH_2, OH), 1.56 (2H, m, CH_2), 1.43 (2H, m, C*H*$_2$) ppm. ^{13}C DEPT NMR ($CDCl_3$, 125 MHz) δ 66.4 (s, *C*H$_2$OH), 53.3 (s, *C*HNH$_2$), 37.8 (s br, CH_2), 10.3 (d, J = 8.1 Hz, *C*H$_2$PH$_2$) ppm.

2.2. 2(S)-amino-4-(2-propylphosphino)butan-1-ol, R,S-S-P^{iPr}NO

The reaction was performed as detailed for *S*-PNO above except using 6 g (0.015 mol) of tosylate and the appropriate amount of $LiP(SiMe_3)_2$. The hemiaminal primary phosphine was dissolved in 1.6 M HCl in MeOH (100 ml) and the solution refluxed for 18 h. The volatiles were removed *in vacuo*, and the residue dissolved in THF (200 ml) to which was added $LiAlH_4$ (1 g) portionwise with stirring. The mixture was stirred overnight and then hydrolysed by the dropwise addition of O_2-free water (1 ml) then degassed 12% NaOH solution (1 ml) and finally O_2-free water (3 ml). The mixture was filtered, the THF solution dried over $MgSO_4$, filtered once more and the volatiles removed *in vacuo* to give a colourless oil which was distilled under dynamic vacuum (bp = 90-5°, 0.05 mm Hg). Yield = 1.2 g (49%). $^{31}P\{^1H\}$ NMR (C_7D_8, 121.7 MHz) δ −29.3, −29.4 ppm ^1H NMR (C_6D_6, 400 MHz) δ 3.26 (1H, dd, J = 10.4, 4.0 Hz, C*H*$_2$OH), 2.96 (1H, dd, J = 10.4, 7.5 Hz, C*H*$_2$OH), 2.90 (1H, dm, $^1J_{H-P}$ = 193 Hz, P*H*), 2.41 (1H, m, *CH*NH$_2$), 1.63 (1H, m, *CH*Me$_2$), 1.48 (3H, s br, N*H*$_2$, O*H*), 1.4–1.0 (4H, m, 2 × *CH*$_2$), 0.96 (1.5H, d, J = 7.0 Hz, *CH*$_3$), 0.93 (3H, d, J = 7.0 Hz, *CH*$_3$), 0.89 (1.5H, d, J = 7.0 Hz) ppm. ^{13}C DEPT NMR (C_6D_6, 125.8 MHz) δ 66.2 (s, CH_2), 54.0 (d, J = 8.1 Hz, CH), 53.9 (d, J = 7.9 Hz, CH), 33.1 (d, J = 10.0 Hz, CH_2), 22.2 (d, J = 8.9 Hz, CH), 21.4 (d, J = 3.2 Hz, CH_3), 21.3 (d, J = 3.2 Hz, CH_3), 21.2 (d, J = 6.7 Hz, CH_3), 21.1 (d, J = 7.0 Hz, CH_3), 15.8 (d, J = 2.5 Hz, CH_2), 15.7 (d, J = 2.6 Hz, CH_2) ppm.

2.3. fac-Cr(CO)$_3$(κ^3-S-PNO), 1

To a stirred solution of *fac*-$[Cr(CO)_3(MeCN)_3]$ (0.39 g, 1.50×10^{-3} mol) in CH_2Cl_2 (20 ml) was added *S*-PNO (1.9 ml of a 10% solution in THF, 1.05 mol equiv.) and the solution stirred overnight. The solution was filtered to remove some unwanted green precipitate and all volatiles removed *in vacuo* to give a sticky orange solid that crystallised upon continued application of dynamic vacuum. Yield = 0.37 g (88%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.7 MHz) δ −56.3 ppm ^1H NMR (CD_2Cl_2, 500 MHz) δ 4.41 (1H, d br, $^1J_{H-P}$ = 330 Hz, P*H*), 4.35 (1H, dm, $^1J_{H-P}$ = 310 Hz, PH), 3.46 (1H, d br, C*H*$_2$OH), 3.12 (1H, br, C*H*$_2$OH), 2.82 (1H, br, OH), 2.42 (1H, m br, C*H*$_2$PH$_2$), 2.39 (1H, m br, R$_2$C*H*NH$_2$), 1.88 (1H, m br, C*H*$_2$), 1.65 (2H, m br, C*H*$_2$PH$_2$, N*H*$_2$), 1.08 (2H, m br, C*H*$_2$, N*H*$_2$) ppm. ^{13}C DEPT NMR (CD_2Cl_2, 125.8 MHz) δ 224.0 (d, J = 12.6 Hz, CO), 217.8 (d, J = 15.0 Hz, CO), 217.5 (d, J = 15.0 Hz, CO), 67.2 (s, *C*H$_2$OH), 58.2 (s, R$_2$*C*HNH$_2$), 28.0 (s, CH_2), 13.7 (d, J = 18.8 Hz, *C*H$_2$PH$_2$) ppm. IR: υCO (CH_2Cl_2) 1942 s, 1887 vs, 1846 s; υOH (KBr) 3572 m; υNH$_2$ (KBr) 3334 m, 3265 m; υPH (KBr) 2354 m, 2336 m cm^{-1}. *Anal.*: Calc. for $C_7H_{12}NO_4PCr$: C, 32.69; H, 4.71; N, 5.45%. Found: C, 32.3; H, 4.9; N, 5.3%. MS: 258 ([M + H$^+$], 20%), 230 ([M + H$^+$ − CO], 35%).

2.4. fac-[Mn(CO)$_3$(κ^3-S-PNO)]PF$_6$, 2

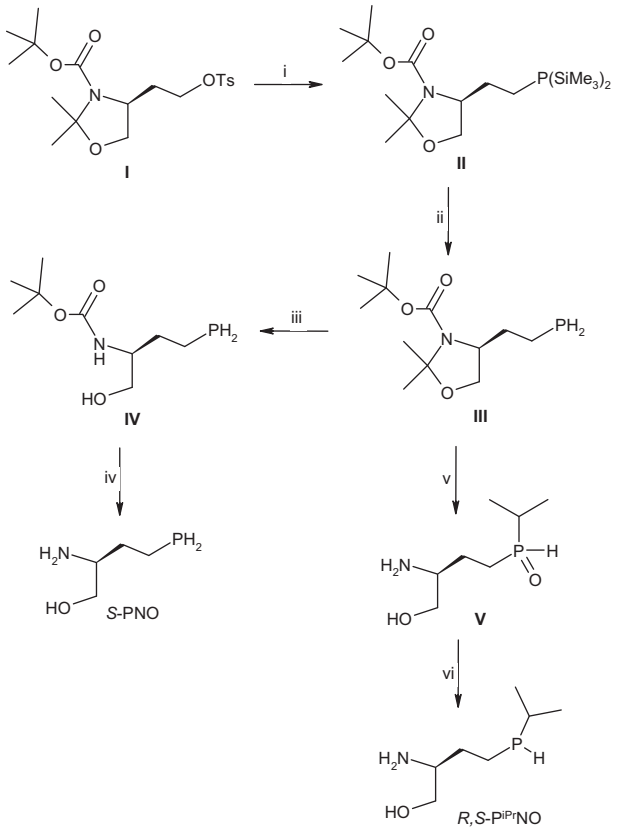
To a stirred solution of *fac*-$[Mn(CO)_3(MeCN)_3]PF_6$ (120 mg, 2.95×10^{-4} mol) in CH_2Cl_2 (10 ml) was added *S*-PNO (0.8 ml of a 5% solution in THF, 1.1 mol equiv.) and the solution stirred overnight. The solution was taken to dryness and the solid residue treated with CH_2Cl_2 (15 ml), filtered and the filtrate allowed to stand at 4 °C overnight. The precipitated crystals of **2** were isolated by filtration. A second crop was obtained upon leaving the filtrate to stand. Yield = 62 mg (52%). $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121.7 MHz) δ −58.4 ppm ^1H NMR (CD_3NO_2, 500 MHz) δ 4.65 (1H, br, N*H*$_2$/O*H*), 4.60 (1H, d br, $^1J_{H-P}$ = 365 Hz, P*H*), 4.45 (1H, dd, $^1J_{H-P}$ = 345 Hz, J = 11.5 Hz, P*H*), 4.02 (1H, d, J = 10.3 Hz, C*H*$_2$OH), 3.65 (1H, d, J = 10.3 Hz, C*H*$_2$OH), 3.61 (1H, s br, R$_2$C*H*NH$_2$), 3.30 (1H, br, N*H*$_2$/O*H*), 2.42 (1H, m, C*H*$_2$PH$_2$), 2.10 (3H, m, C*H*$_2$PH$_2$, C*H*$_2$, N*H*$_2$/O*H*), 1.82 (1H, m, C*H*$_2$) ppm. ^{13}C DEPT NMR (CD_3NO_2, 125.8 MHz) δ 210.3 (br, CO), 206.9 (br, CO), 200.0 (br, CO), 68.5 (s, *C*H$_2$OH), 51.4 (s, R$_2$CHNH$_2$), 32.6 (s, CH_2), 12.2 (d, J = 20.0 Hz, *C*H$_2$PH$_2$) ppm. IR (KBr): υCO 2039 vs, 1945 vs, 1915 sh; υOH 3509 m; υNH$_2$ 3350 m, 3312 m; υPH 2380 w, 2351 w cm^{-1}. *Anal.*: Calc. for $C_7H_{12}NP_2O_4F_6Mn$: C, 20.75; H, 2.99; N, 3.46%. Found: C, 20.2; H, 2.9; N, 3.3%. MS: 301 ([M$^+$] + MeCN, 60%), 260 ([M$^+$], 15%).

2.5. fac-[Re(CO)$_3$(κ^3-S-PNO)]BF$_4$, 3

To a stirred solution of $Re(CO)_5Cl$ (186 mg, 5.14×10^{-4} mol) in MeCN (20 ml) was added $AgBF_4$ and the solution stirred for 10 min in the absence of light. Subsequent addition of *S*-PNO (0.68 ml of a 10% solution in THF, 1.1 mol equiv.) caused an immediate darkening of the solution with precipitation of a black solid. The mixture was filtered and the very pale yellow solution taken to dryness. The solid residue was triturated with MeOH (20 ml), filtered to remove a small amount of $Re(CO)_5Cl$ and the filtrate taken to dryness to give **3** as a white solid. Yield = 62 mg (52%). $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121.7 MHz) δ −88.8 ppm ^1H NMR (CD_3NO_2, 500 MHz) δ 6.60 (2H, br, N*H*$_2$/O*H*), 4.75 (2H, d m, $^1J_{H-P}$ = 369 Hz, P*H*$_2$), 4.00 (1H, dd, J = 10.3, 4.1 Hz, C*H*$_2$OH), 3.75 (1H, dd, J = 10.4, 7.9 Hz, C*H*$_2$OH), 3.61 (1H, s br, R$_2$C*H*NH$_2$), 3.23 (1H, br, N*H*$_2$/O*H*), 2.25 (1H, m, C*H*$_2$PH$_2$), 2.18 (2H, m, C*H*$_2$) ppm. ^{13}C DEPT NMR (CD_3NO_2, 75.6 MHz) δ 185.7 (d, J = 10.4 Hz, CO), 185.6 (d, J = 58.9 Hz, CO), 183.9 (d, J = 6.9 Hz, CO), 66.6 (s, *C*H$_2$OH), 56.2 (br, R$_2$*C*HNH$_2$), 30.6 (d, J = 6.9 Hz, CH_2), 14.5 (d, J = 33.5 Hz, *C*H$_2$PH$_2$) ppm. IR (KBr): υCO 2000 vs, 1940 vs; υOH 3559 m, 3463 m; υNH$_2$ 3259 m, 3199 m; υPH 2379 w cm^{-1}. *Anal.*: Calc. for $C_7H_{12}NPO_4BF_4Re$: C, 17.58; H, 2.53; N, 2.93%. Found: C, 17.9; H, 2.7; N, 2.9%. MS: 452 ([M$^+$] + CH_3NO_2, 100%), 391 ([M$^+$], 20%).

2.6. fac-Cr(CO)$_3$(κ^3-P,P,P-S-P$_3$NO), 4

To a stirred solution of *fac*-$[Cr(CO)_3(MeCN)_3]$ (0.09 g, 3.47×10^{-4} mol) in CH_2Cl_2 (40 ml) was added *S*-PNO (0.84 ml of a 5% solution in THF, 1.0 mol equiv.) and the solution stirred for 20 min whereupon a solution of trivinylphosphine (0.78 ml of a 10%



Scheme 1. i) $LiP(SiMe_3)_2$, THF, −78 °C; ii) MeOH; iii) Dowex-X50 (H^+); iv) 1.5 M HCl in MeOH, RT; v) 1.5 M HCl in MeOH, reflux; vi) $LiAlH_4$, THF.

solution in THF, 2 mol equivs.) was added and the whole stirred overnight. The solution was concentrated to one third volume and stirred for a further 3 days at RT. The solution was taken to dryness *in vacuo* and the solid residue dissolved in THF (25 ml) to which was added 2 mol equivalents of K^tOBu causing an immediate precipitation. The mixture was stirred overnight, filtered and the volatiles removed to leave a bright yellow solid which was washed with water (1 × 5 ml) then dry diethyl ether and dried under vacuum. Yield = 0.57 g (34%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz) δ 114.2 (t, $^2J_{P-P}$ = 17.9 Hz), 68.7 (d, $^2J_{P-P}$ = 17.9 Hz) ppm. ^1H NMR ($CDCl_3$, 500 MHz) δ 6.3–5.4 (12H, m), 3.50 (3H, br), 2.90 (1H, br), 2.1–1.1 (12H, br) ppm. ^{13}C DEPT NMR (CD_2Cl_2, 125.8 MHz) δ 234.0 (br, CO), 229.9 (br, CO), 135.2 (m, CH), 134.8 (d, J = 20.4 Hz, CH), 134.5 (d, J = 20.5 Hz, CH), 128.0 (s, CH_2), 127.2 (s, CH_2), 125.4 (s, CH_2), 125.1 (s, CH_2), 65.3 (br, CH_2OH), 53.0 (br, R_2CHNH_2), 28.2 (br, CH_2), 26.4 (br, CH_2), 24.9 (br, CH_2), 10.5 (br, CH_2PH_2) ppm. IR (KBr): υCO 1940 s, 1860 vs br cm^{-1}. MS: 482 ([M + H^+], 25%), 454 ([M + H^+ − CO], 55%).

2.7. *fac*-[Re(CO)$_3$(κ^2-*P,N*-*S*-PNO)(PAr^F_3)]BF_4, 5

To a stirred solution of **3** (80 mg, 1.67 × 10^{-4} mol) in CH_3NO_2 (5 ml) was added one mol equivalent of *tris*(2-fluorophenyl)phosphine (53 mg, 1.67 × 10^{-4} mol) and the solution heated at 80 °C for 30 min. The solution was concentrated to small volume and diethyl ether slowly added through vapour diffusion. The initial precipitate was filtered off and discarded. The filtrate was removed *in vacuo* to give a pale yellow solid which was triturated in toluene, isolated by filtration and dried *in vacuo*. Yield = 70 mg (53%). $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121.7 MHz) δ −10.4 (d, J = 26.8 Hz), −72.3 (d, J = 26.8 Hz) ppm. ^1H NMR (CD_3NO_2, 500 MHz) δ 6.9–6.1 (12H, m, Ar*H*), 4.25 (1H, d br, $^1J_{H-P}$ = 359 Hz, PH_2), 3.98 (1H, d br, $^1J_{H-P}$ = 364 Hz, PH_2), 3.93 (1H, d br, J = 10.4 Hz, CH_2OH), 3.72 (1H, br, CH_2OH), 3.62 (1H, s br, R_2CHNH_2), 3.21 (1H, br, NH_2/O*H*), 2.30 (1H, m, CH_2PH_2), 2.08 (2H, m, CH_2) ppm. ^{13}C DEPT NMR (CD_3NO_2, 75.6 MHz) δ 164.6 (d, J = 248.2 Hz, *C*F), 136.5 (d, J = 10.4 Hz, CH), 135.8 (s, CH), 129.9 (d, J = 54.3 Hz, C), 126.0 (d, J = 9.2 Hz, CH), 117.7 (d, J = 21.9 Hz, CH), 60.1 (s, CH_2OH), 56.6 (d, J = 10.4 Hz, R_2CHNH_2), 30.8 (d, J = 7.5 Hz, CH_2), 14.7 (dd, J = 31.2, 10.1 Hz, CH_2PH_2) ppm. IR (KBr): υCO 2036 vs, 1955 vs, 1911 vs; υPH 2360 w cm^{-1}. *Anal.*: Calc. for $C_{25}H_{24}NP_2O_4BF_7Re$: C, 37.80; H, 3.05; N, 1.76%. Found: C, 37.2; H, 2.9; N, 1.7%. MS: 740 ([M^+] − CO + CH_3NO_2, 100%), 707 ([M^+], 10%).

3. Crystallography

Single crystal X-ray diffraction data were collected at 150 K on a Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) and an Oxford Cryostream cooling apparatus. The data was corrected for Lorentz and polarization effects and for absorption using SORTAV [6]. Structure solution was achieved by Patterson methods (Dirdiff-99 program system) [7]. Structure solution and full-matrix least-squares refinement on F^2 were performed using SHELX-97 [8] with all non hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in idealised positions and a riding model used during subsequent refinement.

4. Results and discussion

4.1. Ligand syntheses

The preparation of the ligand is highlighted in Scheme 1. The starting point of the synthesis, namely the protected tosylate **I** was prepared by the method of Burgess [2]. Subsequent reaction of **I** with $LiP(SiMe_3)_2$ at low temperature gives the N,O-protected species **II** which is desilylated quantitatively in MeOH to the primary phosphine compound **III**. The dimethylmethyl hemiaminal protecting group is selectively removed upon treatment of **III** with cation exchange resin (H^+ - form) in methanol at room temperature to give the N-Boc protected phosphino alcohol **IV**. Subsequent treatment of **IV** with 1.5 M HCl in MeOH leads to removal of the Boc group and isolation of the primary phosphine derivative *S*-PNO as a low-melting solid.[1] Efforts to remove both protecting groups simultaneously by refluxing a solution of **III** in methanolic HCl led only to the 2-propylphosphine oxide derivative **V**; this occurs even when air has been vigorously excluded suggesting that the source of the oxygen in the product comes from the methanol or from traces of water in the methanolic HCl. Water is more than likely present in the methanolic HCl hence the generation of acetone after cleavage of the hemiaminal protecting group is expected. The acetone could react with the primary phosphine to give an α-hydroxyphosphine species which rearranges by a 1,2 migration of the hydroxyl function to give the observed product [9]. The resultant P(V) species is readily reduced back to the potential ligand 2 (*S*)-amino-4-(*R,S*-2-propyl-phosphino)butan-1-ol, *R,S*-*S*-$P^{iPr}NO$, by $LiAlH_4$ reduction and the secondary phosphine obtained by high-vacuum distillation.

Compound *S*-PNO is very soluble in water and alcohols, moderately soluble in CH_2Cl_2 and $CHCl_3$ and poorly soluble in diethyl ether and acetonitrile. The $^{31}P\{^1H\}$ NMR spectrum of *S*-PNO consists of a singlet at δ_P = −135.3 ppm and the ^1H NMR spectrum

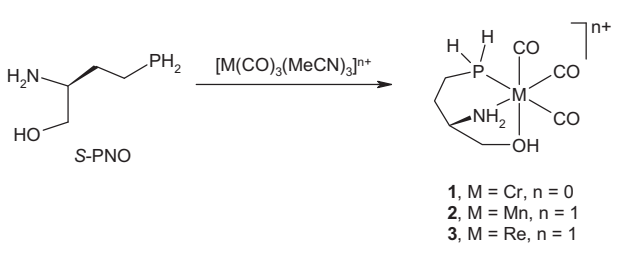
[1] On occasion some contamination (<10%) with the oxide of *R,S*-*S*-$P^{iPr}NO$ was observed.

shows the expected pattern of peaks with the diastereotopic hydrogens α to the alcohol group being observed as two doublets of doublets at 3.52 and 3.23 ppm respectively, the P*H*$_2$ hydrogens as a doublet of multiplets at 2.65 ppm with a large $^1J_{H-P}$ of 198 Hz, the amine and alcohol protons as a broad composite peak at 1.88 ppm and the remaining methylene hydrogens as multiplets at 1.56 and 1.43 ppm. The $^{13}C\{^1H\}$ NMR spectrum has the anticipated four signals, two of which show clear coupling with the ^{31}P nucleus and one of which is broadened. The relative simplicity of the NMR spectra of *S*-PNO contrast with those for *R,S-S*-P^{iPr}NO which clearly show the presence of two diastereomers namely P$_{(R)}$-P^{iPr}NO and P$_{(S)}$-P^{iPr}NO. This is evident from the $^{31}P\{^1H\}$ NMR spectrum which shows two singlets at $\delta_P = -29.3$ and -29.4 ppm and the ^1H NMR spectrum which is complex in the region of the 2-propyl methyls. The $^{13}C\{^1H\}$ NMR spectrum of *R,S-S*-P^{iPr}NO shows a number of duplicated peaks particularly for those carbons in closer proximity to the phosphorus centre (see experimental) confirming the diastereomeric nature of the product.

4.2. Complexes of S-PNO

As stated above, *S*-PNO has the potential to bind through one, two or three donors at a single-metal centre and it is anticipated that all three modes will be accessible through appropriate choice of metal ion. Further metal-dependent isomerism is possible as the ligand has the option of binding solely though the phosphine, amine or alcohol donor in the monodentate mode and via P/N, P/O or N/O combinations when coordinated through two donors. We were interested in incorporating the phosphorus centre into a P-containing macrocycle and thus chose metal precursors that favour P-coordination and also have accessible sites *cis* to the phosphine ligand; it was envisaged that the ideal systems would be those that possessed tridentate κ^3-*S*-PNO with relatively weak (easily substituted) M-NH$_2$R and M-OHR bonds. To this end the complexes *fac*-Cr(CO)$_3$(κ^3-*S*-PNO), *fac*-[Mn(CO)$_3$(κ^3-*S*-PNO)]BF$_4$ and *fac*-[Re(CO)$_3$(κ^3-*S*-PNO)]BF$_4$ were sought through displacement of labile acetonitrile ligands from the familiar *fac*-[M(CO)$_3$(MeCN)$_3$]$^{n+}$ starting materials.

The synthesis of the complexes is shown in Scheme 2. In all cases, complete substitution of the poorly bound MeCN ligands occurred giving the desired complexes. *Fac*-Cr(CO)$_3$(κ^3-*S*-PNO), **1**, could be crystallised as orange prisms from CH_2Cl_2 at low temperature. The $^{31}P\{^1H\}$ NMR spectrum of **1** consists of a singlet at $\delta_P = -56.3$ ppm which splits into a triplet of multiplets in the proton-coupled spectrum with an absolute $^1J_{P-H}$ coupling constant of 320 Hz. The coordination shift ($\Delta^{31}P = \delta_{coord\ P} - \delta_{uncoord\ P}$) is smaller than that observed in related *fac*-Cr(CO)$_3$(PRH$_2$)$_3$ systems but the magnitude of the $^1J_{P-H}$ coupling is comparable [1f]. The relatively small $\Delta^{31}P$ is unexpected as phosphine donors which are part of a chelate ring(s) tend to show enhanced coordination shifts compared to monodentate analogues. However triphosphorus ligands with the same carbon skeleton as *S*-PNO also show similar reduced coordination shifts for the phosphorus in the 6-membered



Scheme 2. Synthesis of the metal complexes.

ring especially when bound as a tridentate ligand [10] and it may be that there is some strain within the ligand framework when bound through all three donors as indicated in the molecular structure of the manganese complex (see below). The ^1H NMR spectrum of **1** is broadened, but all the peaks are identifiable and assignable through a combination of 1D and 2D techniques. The outstanding feature of the ^1H NMR spectrum is the presence of two separate resonances for the two hydrogens directly bonded to the phosphorus atom, one of which is observed as a slightly broadened doublet at $\delta_P = 4.33$ ppm ($^1J_{H-P} = 330$ Hz) and the other as a doublet of multiplets at $\delta_P = 4.31$ ppm ($^1J_{H-P} = 310$ Hz). Both these signals are shifted downfield of their position in the ^1H NMR spectrum of the free ligand. The remaining resonances show smaller coordination shifts as noted in the experimental section. The $^{13}C\{^1H\}$ NMR spectrum of **1** does not suffer from broadening and all the pertinent C–P coupling constants are readily obtained. There are the expected three signals at low field assignable to the three distinct carbonyls at 224.0, 217.9 and 217.5 ppm with $^2J_{C-P}$ coupling constants of 12.6, 15.0 and 15.0 Hz respectively. The signal showing the greatest downfield shift and smallest absolute value of $^2J_{C-P}$ is assigned to the CO group trans to the P-donor in accord with previous observations on Cr(CO)$_5$(PR$_3$) systems [11]. Of the four aliphatic signals in the $^{13}C\{^1H\}$ NMR spectrum of **1** only the methylene carbon ($\delta_C = 13.7$ ppm) directly bonded to the P-atom shows any coupling to the phosphorus: $^1J_{C-P} = 18.8$ Hz. The solution (CH_2Cl_2) infrared spectrum of complex **1** shows three bands in the region of CO absorption at 1942s, 1887vs and 1846 s cm^{-1}. The lower energy bands are less well resolved in the solid-state IR spectrum recorded as a KBr disk where peaks are seen at 1877vs, 1835vs and 1821 cm^{-1}. The observation of three bands reflects the low symmetry of the complex. Other observable bands in the solid-state spectrum are assigned to P–H stretching (2354 and 2336 cm^{-1}), the O–H stretch (3572 cm^{-1}) and N–H stretching (3334 and 3265 cm^{-1}).

The cationic complexes *fac*-[Mn(CO)$_3$(κ^3-*S*-PNO)]PF$_6$, **2**, and *fac*-[Re(CO)$_3$(κ^3-*S*-PNO)]BF$_4$, **3**, are made in an analogous manner to the chromium species by displacement of three acetonitrile ligands from the *fac*-[M(CO)$_3$(MeCN)$_3$]X precursors. *Fac*-[Mn(CO)$_3$(κ^3-*S*-PNO)]PF$_6$, **2**, can be crystallised from CH_2Cl_2 at low temperature to give yellow crystals suitable for analysis by single-crystal X-ray methods. The molecular structure of the cation is shown in Fig. 1. As expected, the complex adopts a distorted octahedral geometry with the carbonyl groups and the *S*-PNO ligand occupying opposing faces of the octahedron. The tridentate ligand consists of two fused rings, a six-membered C$_3$PMnO cycle and a five-membered C$_2$NMnO ring. The former adopts a chair conformation while the latter is an asymmetric envelope with the λ conformation. The Mn-P bond length of 2.3121 (12) Å is slightly shorter than that of 2.3419(6) Å observed in the related mixed N,O,P-donor complex (κ^2-*P,N*-(2-NMe$_2$-3-P^{i}Pr$_2$-indene)Mn(CO)$_3$(OTf) [12]. The Mn-O {2.089(3) Å} and Mn-N {2.091(3) Å} bond lengths are close to those observed in (κ^2-*P,N*-(2-NMe$_2$-3-P^{i}Pr$_2$-indene)Mn(CO)$_3$(OTf) where Mn–N is 2.209(2) Å and Mn-O 2.094(2) Å [12]. The largest angular distortion about the metal occurs for the N–Mn–O angle which is compressed to 78.92(11)°, the two remaining chelate rings have angles of 85.64(9) (P–Mn–N) and 83.68 (8)° (P–Mn–O) respectively. All of these angles are smaller than in related systems such as [Mn(dppe)(CO)$_3$(H$_2$O)]$^+$ [13] Mn(dppp)(CO)$_3$X [14] and Re(dppb)(CO)$_3$(H) [15] where bite angles of 84.24(4)°, 90 ± 2° and 92.99° are observed for the 5-, 6- and 7-membered chelates respectively. Tripodal phosphines do show some angular contraction compared to those forming single chelates. For example *fac*-[Mn(CO)$_3${MeC(CH$_2$PPh$_2$)$_3$}]$^+$ has P–Mn–P angles ranging from 85.89(6) to 89.14(6) [16]. The P–Mn–O angle in **2** is particularly constrained for a seven-membered chelate which may explain in part the unusual chemical shift of the compound (and indeed the other

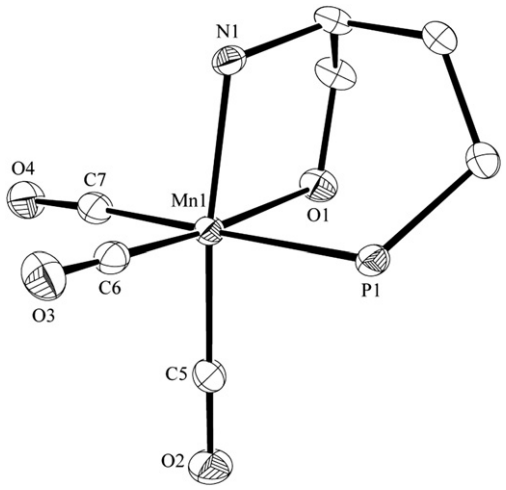


Fig. 1. Ortep view of the molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. Selected bond lengths (Å) and angles(°) for **2**: Mn1-P1 2.3121(12), Mn1-N1 2.091(3), Mn1-O1 2.089(3), Mn1-C5 1.843(4), Mn1-C6 1.815(4), Mn1-C5 1.789(4), N1-Mn1-P1 85.64(9), O1-Mn1-P1 83.68(8), N1-Mn1-O1 78.92(11).

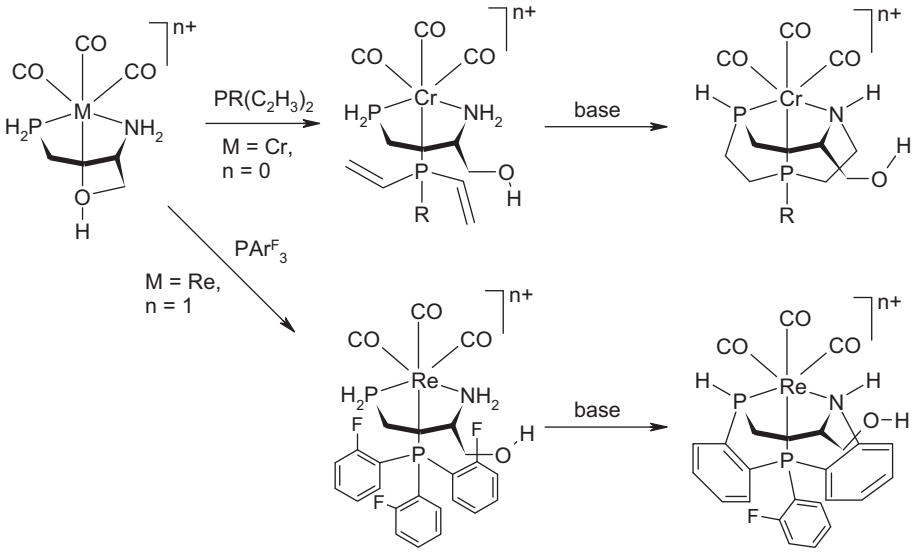
complexes containing κ^3-*S*-PNO) observed in the ^{31}P NMR spectrum. It is notable that the Mn—CO bond length to the carbonyl group *trans* to the phosphine donor is somewhat longer at 1.843(4) Å than those *trans* to the amine and alcohol donors which have values of 1.815(4) and 1.789(4) Å respectively. However, this pattern resembles closely that seen in (κ^2-*P,N*-(2-NMe$_2$-3-P^{i}Pr$_2$-indene)Mn(CO)$_3$(OTf) where the appropriate Mn—C bond lengths are 1.859(2), 1.806(2) and 1.779 (3) Å [12].

The IR spectrum of **2** recorded as a KBr disk shows a strong υ(CO) stretch at 2040 cm^{-1} and a very strong carbonyl stretch at 1945 cm^{-1} with a low-energy shoulder at approximately 1915 cm^{-1}. These compare to values of 2052, 1956 and 1919 cm^{-1} in *fac*-{Mn(CH$_3$CN)(CO)$_3$[H(pzAn^{Me})]}(PF$_6$) where H(pzAn^{Me}) is 2-(pyrazolyl)-4-toluidine [17], 2031s, 1961s, and 1915s cm^{-1} in *fac*-[(CO)$_3$Mn{(Ph^F)$_2$PC$_6$H$_4$P(Ph^F)$_2$}(CH$_3$CN)]PF$_6$ [18], and those of 2036, 1957 and 1916 cm^{-1} in (κ^2-*P,N*-(2-NMe$_2$-3-P^{i}Pr$_2$-indene)Mn(CO)$_3$(OTf) [12], but differ somewhat from the values of 2049, 1980 and 1944 cm^{-1} reported for *fac*-[Mn(PPh$_3$)(CO)$_3$(pyC(H) = O)][OTf] [19]. In addition to the carbonyl stretches, the IR spectrum of **2** shows three peaks at 3509, 3350 and 3312 cm^{-1} assignable to the O—H and N—H stretches and two weak peaks at 2380 and 2351 cm^{-1} for the P—H stretches. The ^{31}P{^{1}H} NMR spectrum of **2** consists of a singlet at −58.4 ppm in addition to the septet for the PF_6^- anion at −143.6 ppm. The resonance for the coordinated phosphine splits into a triplet of multiplets ($^1J_{P-H}$ = 375 Hz) in the ^{31}P NMR spectrum. The ^{1}H NMR spectrum recorded in CD_3NO_2 shows the anticipated number of signals but all are broadened to a varying degree. The two chemically inequivalent PH hydrogens are seen as two distinct doublets with large $^1J_{H-P}$ coupling constants of 365 and 345 Hz; both are ~1.7 ppm downfield of their position in the ^{1}H NMR spectrum of *S*-PNO and the upfield resonance shows a $^2J_{H-H}$ coupling of small magnitude (11.5 Hz). The resonances for the methylene hydrogens α to the alcohol function also show downfield coordination shifts and are observed at 4.02 and 3.65 ppm, respectively. The ^{13}C{^{1}H} NMR spectrum of **2** is also broadened in the region of the CO resonances where three peaks with no resolved ^{31}P coupling are seen at 210.3, 206.9 and 200.0 ppm. The remaining resonances in the ^{13}C{^{1}H} NMR spectrum are sharp singlets with the exception of the RCH$_2$PH$_2$ carbon which is a doublet at 12.2 ppm with an absolute $^1J_{C-P}$ of 20.0 Hz.

The colourless complex *fac*-[Re(CO)$_3$(κ^3-PNO)]BF$_4$, **3**, shares many of the features already discussed for the analogous manganese compound, although the coordination shift in the ^{31}P{^{1}H} NMR spectrum is less with a signal being observed 46.5 ppm downfield of the uncoordinated ligand at −88.8 ppm. The ^{1}H NMR spectrum of **3** is also better resolved with all the resonances bar that for the NH$_2$ and OH hydrogens showing appropriate coupling. The CO resonances in the ^{13}C{^{1}H} NMR spectrum of **3** are seen as three separate doublets at 185.7 ($^2J_{C-P}$ = 10.4 Hz), 185.6 ($^2J_{C-P}$ = 58.9 Hz) and 183.9 ($^2J_{C-P}$ = 6.9 Hz) ppm. The signal with the large coupling constant is assigned to the carbonyl *trans* to the P-donor in accordance with the similar system {2-(CH$_3$CO)-C$_4$H$_3$N}Re(PPh$_3$)(CO)$_3$ where a value of 55.5 Hz is observed for the *trans* $^2J_{C-P}$ coupling [20]. The IR spectrum of **3** recorded as a KBr disk shows two strong absorbances for the CO stretches at 2000 and 1940 cm^{-1} which compare with values of 2048, 1967 and 1933 cm^{-1} for *fac*-[Re(PPh$_3$)(CO)$_3$(pyC(H) = O)][OTf] [20], 2024, 1931 and 1875 cm^{-1} for *fac*-{κ^3-P,N,O-Ph$_2$PC$_6$H$_4$C(H)N(C$_6$H$_4$O}Re(CO)$_3$ [21] and 2022, 1923, 1892 cm^{-1} for {2-(CH$_3$CO)-C$_4$H$_3$N}Re(PPh$_3$)(CO)$_3$ [20].

4.3. Further reactions of 1, 2 and 3

The coordinated primary phosphine group in the metal complexes of *S*-PNO was susceptible to chlorination when solutions of the complexes in CHCl$_3$ were left to stand. This observation, along with more typical reactivity such as the ready methylation of the phosphine with MeI, suggested that the coordinated phosphine is reactive and that the amino group when unbound may be assisting the generation of a metal-bound phosphido group. This is the type of reactivity we wished to exploit for the formation of mixed-donor macrocycles containing two P-donors and one other (N or O) donor. As a first step, we were interested in examining whether complex **1**, **2** or **3** would undergo selective replacement of one donor of *S*-PNO by another phosphine ligand that possessed substituents capable of undergoing further reaction to enable access to macrocyclic systems. The two approaches we hoped to exploit are summarised in Scheme 3. The alcohol is believed to be the most weakly bound of the donors for two reasons; firstly the nature of the metal ions is such that they prefer softer donors and secondly, if the phosphine is most strongly bound the resulting 6-membered P,N chelate should be more stable than the 7-membered P,O chelate. Initial studies focussed on the neutral *fac*-Cr(CO)$_3$(κ^3-*S*-PNO), **1**, system. Attempted introduction of the poorly donating *tris* (2-fluorophenyl)phosphine ligand was unsuccessful as only complex **1** and uncoordinated PAr$^F_3$ were observed by ^{31}P{^{1}H} NMR under the reaction conditions. Thus, the nature of the incoming phosphine was changed to the more strongly donating divinylbenzylphosphine. ^{31}P{^{1}H} NMR analysis of a solution prepared by adding one mol equivalent of P(CH$_2$Ph)(C$_2$H$_3$)$_2$ to a solution of **1** in CH$_2$Cl$_2$ showed, in addition to the singlets for free P(CH$_2$Ph)(C$_2$H$_3$)$_2$ and **1**, a triplet at − 29.4 ppm ($^2J_{P-P}$ = 38.7 Hz) and three doublets at 37.0 ($^2J_{P-P}$ = 35.7 Hz), 34.4 ($^2J_{P-P}$ = 38.7 Hz) and − 34.3 ($^2J_{P-P}$ = 35.7 Hz) ppm respectively. The two furthest upfield peaks gave large triplets in the ^{31}P NMR spectrum with $^1J_{P-H}$ coupling constants of around 310 Hz confirming their assignment as primary phosphines whereas the downfield peaks were tertiary phosphines. The $^2J_{P-P}$ coupling constants suggest that the peaks at 37.0 and −34.3 ppm belong to one species while the remaining peaks belong to a second species. The presence of a triplet for the primary phosphine for one of the complexes in the ^{31}P{^{1}H} NMR spectrum of the solution indicates coupling to two divinylbenzylphosphine ligands and hence this species must be *fac*-Cr(CO)$_3$(κ^1-P-*S*-PNO){P(CH$_2$Ph)(C$_2$H$_3$)$_2$}$_2$ while the second complex is most likely *fac*-Cr(CO)$_3$(κ^2-P,N-*S*-PNO){P(CH$_2$Ph)(C$_2$H$_3$)$_2$}. Thus it would appear that



Scheme 3. Proposed synthesis of chiral P_2N macrocycles.

selective introduction of one $P(CH_2Ph)(C_2H_3)_2$ ligand to **1** is not achieved under these conditions. When the reaction was performed in THF a similar outcome resulted. Addition of KO^{t}Bu to the THF solution gave a $^{31}P\{^1H\}$ NMR spectrum that consisted of four peaks: two triplets at 113.1 ($^2J_{P-P}$ = 20.8 Hz) and 112.3 ($^2J_{P-P}$ = 17.9 Hz) ppm, a multiplet at 73.9 ppm and a doublet at 72.7 ($^2J_{P-P}$ = 17.9 Hz) ppm all of which are tertiary phosphines as deduced upon inspection of the ^{31}P NMR spectrum. The chemical shift of these resonances would suggest that the low-field peaks at $\delta_P > 100$ ppm represent coordinated P-donors that are constituents of two chelate rings whereas the higher field signals at ~73 ppm are tertiary phosphines that are part of a single chelate [22]. The presence of more than one resonance around 113 ppm reflects an isomeric mixture of two closely similar species most likely resulting from isomerism at the terminal phosphine(s) as shown in Fig. 2.

The isomeric complication present in the reaction of **1** with divinylbenzylphosphine prompted an investigation of the same chemistry with trivinylphosphine where no such complexity is possible. Addition of one mol equivalent of $P(C_2H_3)_3$ to a solution of **1** in CH_2Cl_2 gave a mixture which, upon inspection by $^{31}P\{^1H\}$ NMR spectroscopy, showed a pattern closely similar to that observed with $P(CH_2Ph)(C_2H_3)_2$, i.e. three doublets at δ_P = 44.7 ($^2J_{P-P}$ = 38.7 Hz), 32.1 ($^2J_{P-P}$ = 35.7 Hz) and −27.9 ($^2J_{P-P}$ = 38.7 Hz) ppm and a triplet at −31.2 ppm ($^2J_{P-P}$ = 35.7 Hz) [in addition to peaks for **1** and some other minor signals]. It is clear from the distribution of species here and in the case of the same reaction with $P(CH_2Ph)(C_2H_3)_2$ that selective substitution of one of the donors of *S*-PNO by one tertiary phosphine ligand is not occurring and that a competitive binding of a second $P(CH_2Ph)(C_2H_3)_2$ or $P(C_2H_3)_3$ is frustrating attempts to get the desired *fac*-$Cr(CO)_3(\kappa^2$-P,N-*S*-PNO$)\{P(R)(C_2H_3)_2\}$ where R = CH_2Ph or C_2H_3. Addition of a second mol equivalent of trivinylphosphine led to the predominance of the species giving the doublet at 32.1 ppm and the triplet at −31.2 ppm which is assigned to the complex *fac*-$Cr(CO)_3(\kappa^1$-P-*S*-PNO$)\{P(C_2H_3)_3\}_2$. After removal of the solvent, the residue was dissolved in THF, 2 mol equivalents of KO^{t}Bu added thereto, and the reaction monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The peaks assigned to *fac*-$Cr(CO)_3(\kappa^1$-P-PNO$)\{P(C_2H_3)_3\}_2$ were lost after addition of the base and replaced by new peaks at 115.1 (t, $^2J_{P-P}$ = 17.9 Hz) and 70.7 (d, $^2J_{P-P}$ = 17.9 Hz) ppm both of which represent tertiary phosphines. The downfield shifts and decreased magnitude of $^2J_{P-P}$ is indicative of the formation of new chelate rings with the peak at 115.1 ppm being assigned to the central phosphine of a linear tridentate triphosphine and the doublet to the two equivalent terminal phosphines of the coordinated P_3 ligand. This suggests that the new complex is *fac*-$Cr(CO)_3(\kappa^3$-P,P,P-*S*-P_3NO), **4** as shown in Fig. 3. The complex was isolated as a yellow solid in modest yield. The ^1H NMR spectrum of the isolated complex was complex in the region of the alkenic protons as all 12 of the hydrogens are chemically inequivalent and was broad in the region of the aliphatic protons. The aliphatic signals in the $^{13}C\{^1H\}$ NMR spectrum were also broad but two new peaks for the CH_2 groups of the chelate backbones were evident at δ_C = 26.2 and 25.0 ppm. In addition, two broad carbonyl peaks were seen at 234.1 and 231.1 ppm, along with a multiplet at 135.2 for two of the alkenyl carbons α to the phosphorus atom and two doublets at 134.7 and 134.5 ppm for the other two α-carbons with $^1J_{C-P}$ values of 21.3 and 23.5 Hz respectively. Thus although hydrophosphination is observed in these systems the desired P_2N macrocycle highlighted in the upper part of Scheme 3 was not obtained.

Although identified in solution, the desired complex of type $Cr(CO)_3(\kappa^2$-P,N-*S*-PNO$)\{P(R)(C_2H_3)_2\}$ was not isolable (or indeed

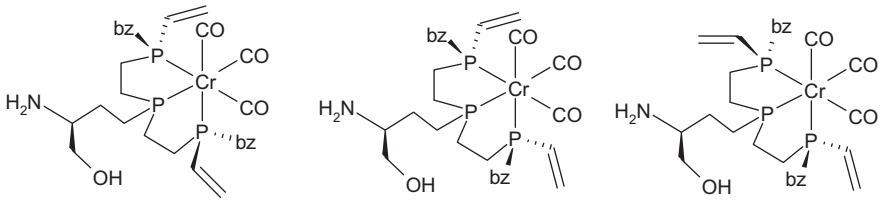


Fig. 2. Possible isomers from the base-induced cyclisation of *fac*-$Cr(CO)_3(\kappa^1$-P-*S*-PNO$)\{P(CH_2Ph)(C_2H_3)_2\}_2$.

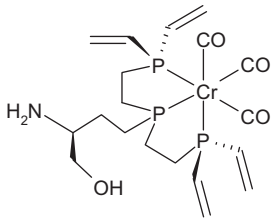


Fig. 3. Likely structure of the product from the intramolecular cyclisation of *fac*-Cr $(CO)_3(\kappa^1$-P-*S*-PNO$)\{P(C_2H_3)_3\}_2$.

useful for transformation into a P_2N macrocycle) due to the non-selectivity of the tertiary phosphine substitution. The extra bulk of tris-(2-fluorophenyl)phosphine should prevent coordination of a second PAr^F_3 ligand if a complex of type $[M(CO)_3(\kappa^2$-P,N-*S*-PNO$)(PAr^F_3)]^{n+}$ could be accessed. As noted above this proved to be difficult for the chromium system but we have shown previously that the ligand can be coordinated to both Mn(I) and Re(I) tricarbonyl fragments [18]. Several attempts at introducing the PAr^F_3 ligand by stirring 1:1 solutions of either $[Mn(CO)_3(\kappa^3$-*S*-PNO$)]^+$ or $[Re(CO)_3(\kappa^3$-*S*-PNO$)]^+$ with PAr^F_3 in various common organic solvents were frustrated by incomplete coordination with the desired complex being formed in less than 10% yield presumably because of competition with the displaced alcohol function of *S*-PNO. However, warming a solution of $[Re(CO)_3(\kappa^3$-*S*-PNO$)]BF_4$ with PAr^F_3 in CH_3NO_2 led to the desired complex $[Re(CO)_3(\kappa^2$-P,N-*S*-PNO$)(PAr^F_3)]BF_4$, **5**, which was isolated as a colourless solid in 53% yield after work-up. The IR spectrum of **5** recorded as a KBr disk showed three strong peaks in the region of C—O stretching at 2036, 1955 and 1911 cm^{-1} respectively. Comparison of the υCO stretching frequencies in the IR spectra of **3** and **5** shows a shift to high frequency for the highest energy band from 2000 cm^{-1} in **4** to 2036 cm^{-1} for **6** as might be expected when a good σ-donor is replaced by a π-acceptor. However, the highest energy absorbance in **3** is a composite band and the lowest energy maximum is to lower energy in **5** (1911 cm^{-1}) compared to **3** (1940 cm^{-1}). The mass spectrum of the complex showed a peak for the molecular ion at 708 amu and a peak at 741 amu for the complex plus one nitromethane minus a CO. The $^{31}P\{^1H\}$ NMR spectrum of **5** shows two doublets at $\delta_P = -10.4$ and -72.3 ppm with a $^2J_{P-P}$ coupling constant of 26.8 Hz. The high field peak is further split into a large triplet in the ^{31}P NMR spectrum with $^1J_{P-H}$ of 360 Hz. The position of this peak is downfield that of the κ^3-*S*-PNO as noted in the Mn(I) systems above. The ^{19}F NMR spectrum had two singlets at -95.4 ppm and -150.3 for the coordinated PAr^F_3 and the BF_4^- counterion respectively. The ^1H NMR spectrum of **5** is largely uninformative with the expected mass of peaks in the aromatic region and some broadening in the aliphatic, but the $^{13}C\{^1H\}$ NMR spectrum has some distinguishing features notably the large doublet for the *C*-F carbon at 164.6 ppm and the presence of a doublet of doublets for the CH_2PH_2 carbon of *S*-PNO at 14.7 ppm which shows, in addition to the expected $^1J_{C-P}$ coupling of 31.2 Hz, a $^3J_{C-P}$ coupling to the PAr^F_3 phosphorus of 10.1 Hz.

Efforts to form new chelate rings by nucleophilic substitution at one or two of the 2-fluoro carbons of the coordinated PAr^F_3 by metal-bound phosphido/amido nucleophiles were unsuccessful. Addition of base (Et_3N or KO^tBu) to a suspension of **5** in THF or in nitromethane generally led to a darkening of the solution (complete dissolution of **5** was not observed in THF) which, upon examination by $^{31}P\{^1H\}$ NMR, showed loss of the PAr^F_3 ligand from the metal centre. Other peaks were present in the $^{31}P\{^1H\}$ NMR spectrum of the reaction performed in CH_3NO_2, some of which were assignable to various *S*-NOP complexes of Re while others were not. Clearly if deprotonation had occurred the resultant complex(es) underwent loss of PAr^F_3 before any template cyclisation could result and the desired macrocyclic complex shown in the lower part of Scheme 3 was not obtained.

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