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1-1-1998

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Recommended Citation
Heard, P. J., & Alliev, A. E. (1998) '2,6-Bis(diphenylphosphinosulfide)pyridine (L) as a facial terdentate ligand: synthesis and characterisation of the tricarbonylrhenium(I) complexes fac-$[Re(CO)_3L]^+$ $[Re_2(CO)_6(\mu\text{-}X)_3]^-$ (X = Cl, Br or I) and fac-$[Re(CO)_3L]^+[SbF_6]^-$.'. Polyhedron, 17(23-24), 3981-3987

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2,6-Bis(diphenylphosphinosulfide)pyridine (L) as a facial terdentate ligand: synthesis and characterisation of the tricarbonylrhenium(I) complexes *fac*-$[Re(CO)_3L]^+$ $[Re_2(CO)_6(\mu\text{-}X)_3]^-$ (X = Cl, Br or I) and *fac*-$[Re(CO)_3L]^+$ $[SbF_6]^-$.

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Abstract.

The halogenopentacarbonylrhenium(I) compounds react with 2,6-bis-(diphenylphosphinosulfide)pyridine (L) under mild conditions to yield ionic complexes of general formulae, *fac*-$[Re(CO)_3L]^+$ $[Re_2(CO)_6(\mu\text{-}X)_3]^-$ (X = Cl, Br or I), in which the ligand adopts a facial terdentate bonding mode. A synthesis of $[Re(CO)_3L]^+$ $[SbF_6]^-$ was carried out to established the presence cation, *fac*-$[Re(CO)_3L]^+$, in the complexes. The character of the anions was confirmed by negative ion MALDI-TOF mass spectrometry. The cation is fluxional; the P-phenyl rings oriented towards the metal moiety exhibit restricted rotation at low temperature. The free energy of activation, $\Delta G^{\ddagger}$, for hindered rotation is *ca*. 47 kJ mol^{-1} for all complexes. Solid-state ^{31}P NMR data are reported for the free ligand and for the complexes, $[Re(CO)_3L][SbF_6]$ and $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}X)_3]$ (X = Cl, Br or I).

Introduction.

Metal complexes of ligands that have unco-ordinated donor atoms are now well established as fluxional species. The classical example of this type of fluxional behaviour is exhibited by transition metal complexes of 2,2':6',2"-terpyridine (terpy), in which terpyridine is restricted to a bidentate bonding mode [1,2]. Other potentially terdentate ligands, such as 2,6-bis(oxazolinyl)pyridines [3,4] and 2,6-bis(sulfanyl)pyridines [5,6], also display fluxional behaviour when co-ordinated to a metal in a bidentate fashion. As part of our on-going interest in the dynamic stereochemical behaviour exhibited by transition metal complexes of this type, we chose to investigate the tricarbonylrhenium(I) halide complexes of 2,6-bis(diphenyl-phosphinosulfide)pyridine (L). It was expected that, under mild conditions, the ligand would react with the halogenopentacarbonylrhenium(I) compounds, to form complexes of general formulae *fac*-[ReX(CO)$_3$L] (X = Cl, Br or I), with the ligand bound in a bidentate fashion via the N donor of the pyridine ring, and one of the sulfur donors. However, analytical and spectroscopic data indicate that ionic complexes of the type *fac*-[Re(CO)$_3$L]$^+$ A$^-$ (where A is the counter ion) are formed, with the ligand adopting a facial terdentate bonding mode. Accordingly, we report here on the synthesis and characterisation of the complexes *fac*-[Re(CO)$_3$L]$^+$ [Re$_2$(CO)$_6$(μ-X)$_3$]$^-$ (X = Cl, Br or I) and *fac*-[Re(CO)$_3$L]$^+$ [SbF$_6$]$^-$.

Experimental.

Syntheses

All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen, using standard Schlenk techniques [7]. Solvents were dried [8] and degassed before use. The pentacarbonylrhenium(I) halides [9] were prepared using previously published procedures and the ligand, 2,6-bis(diphenylphosphinosulfide)pyridine (L) was prepared by Professor W. McFarlane [10]. The three complexes [Re(CO)$_3$L]$^+$[Re$_2$(CO)$_6$(μ-X)$_3$]$^-$ (X = Cl, Br or I) were prepared similarly, as illustrated by the procedure for [Re(CO)$_3$L]$^+$[Re$_2$(CO)$_6$(μ-Br)$_3$]$^-$. The hexafluoroantimonate complex was prepared by treatment of [Re(CO)$_4$(thf)]$^+$ [SbF$_6$]$^-$ with 2,6-bis(diphenylphosphinosulfide)pyridine, and from [Re(CO)$_3$L]$^+$[Re$_2$(CO)$_6$(μ-Br)$_3$]$^-$, by treatment with AgSbF$_6$, as described.

$[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}Br)_3]$.— Pentacarbonylrhenium(I) bromide (120 mg, 0.295 mmol) and 2,6-bis(diphenylphosphinosulfide)pyridine (150 mg, 0.293 mmol) were heated under reflux in 20 cm^3 of a 50:50 (v/v) mixture of benzene-petroleum ether (b.pt. 60 - 80 ^oC) for *ca*. 18 h. The resulting orange solid was isolated by filtration, and recrystallised from dichloromethane. Yield: 77 mg, 50%.

$[Re(CO)_3L][SbF_6]$

Method A. $[ReBr(CO)_5]$ (50 mg, 0.123 mmol) and $AgSbF_6$ (30 mg, 0.127 mmol) were refluxed in 15 cm^3 of tetrahydrofuran (thf) for *ca*. 2 h. The resulting solution was filtered (to remove AgBr) and then added to a stirred solution of 2,6-bis(diphenylphosphinosulfide)pyridine (70 mg, 0.137 mmol in 5 cm^3 of thf). The reaction mixture was refluxed for *ca*. 18 h, then the solvent removed *in vacuo*, to yield a yellow-orange solid. Recrystallisation from dichloromethane-pentane yielded 60 mg (48%) of yellow $[Re(CO)_3L][SbF_6]$.

Method B. $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}Br)_3]$ (100 mg, 0.06 mmol) and $AgSbF_6$ (25 mg, 0.106 mmol) were stirred at ambient temperature for *ca*. 24 h., in 20 cm^3 of CH_2Cl_2. The resulting yellow solution was filtered (to remove AgBr), and evaporated to dryness *in vacuo*. The crude yellow product was crystallised from dichloromethane-pentane. Yield: 64 mg, 98%.

Physical methods

Infrared spectra were recorded in CH_2Cl_2, using matched CaF_2 solution cells on a Nicolet 205 FT-IR spectrometer operating in the region 4000 - 400 cm^{-1}. Elemental analyses were carried out at University College London. Mass spectra were obtained at the London School of Pharmacy. Fast atom bombardment (FAB) mass spectra were carried out on a VG Analytical ZAB-SE instrument, using Xe^+ ion bombardment at 8 kV energy. Matrix assisted laser desorption/ionisation time of flight (MALDI-TOF) mass spectra were obtained on a Fisons TofSpec instrument, with a linear flight path of 0.9 m, operating in the negative ion mode. The laser was fired fifty times at minimal energy, to produced the averaged spectra. The matrix used was 5-chloro-2-mercaptobenzothioazole. X-Ray powder patterns were obtained by Dr. I. P. Parkin,

University College London, on a Siemens D5000 X-ray powder diffractometer, using Ge monochromated Cu-K_α radiation (λ = 1.5406 Å).

Solution-state ^{1}H, ^{19}F and ^{31}P NMR spectra were recorded in CD_2Cl_2 or $CDCl_3$ on a Bruker AMX400 Fourier transform spectrometer, operating at 400.13, 376.45 and 161.98 MHz, respectively. Chemical shifts are reported relative to tetramethylsilane (^{1}H), $CFCl_3$ (^{19}F) and 85% aqueous H_3PO_4 (^{31}P). NMR probe temperatures were controlled by a standard B-VT 2000 unit; probe temperatures were periodically checked (100% MeOH) and are considered accurate to within ± 1 ^{o}C.

High-resolution solid-state ^{31}P NMR spectra were recorded at 121.5 and 242.9 MHz on Bruker MSL300 and AMX600 Fourier transform spectrometers, respectively, equipped with standard Bruker magic angle spinning probes. Spectra were measured at ambient temperature (298 K), on polycrystalline powders in zirconia rotors with a 4 mm external diameter. Chemical shifts are quoted relative to 85% aqueous H_3PO_4. Spectra were recorded using a 'single-pulse' sequence with magic angle spinning and high-power ^{1}H decoupling. The isotropic peaks were identified by varying the MAS frequencies (3 - 11 kHz), and the principal components of the ^{31}P CSA tensor (δ_{11}, δ_{22} and δ_{33}) were determined using the Herzfeld-Berger method [11] [prior to the spinning side-band analyses, the overlapping resonances were deconvoluted using the NUTS (Acorn NMR) line fitting subroutine]. The chemical shielding anisotropy, $\Delta\sigma$, and the asymmetry parameter, η, are defined as [12]: $\Delta\sigma = [(\delta_{11} + \delta_{22})/2]-\delta_{33}$ and $\eta = (\delta_{11} - \delta_{22})/(\delta_{iso} - \delta_{33})$, where $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.

Results and Discussion.

Treatment of the halogenopentacarbonylrhenium(I) compounds with a stoichiometric quantity of 2,6-bis(diphenylphoshinosulfide)pyridine (L) (Figure 1) under moderate conditions was expected to yield complexes of general formulae *fac*-[$ReX(CO)_3L$] (X = Cl, Br or I), with the ligand bound to the metal in a bidentate fashion [structure (**II**) Fig. 1]. However, micro analytical data indicated the formation of complexes of molecular formulae $Re_3(CO)_9X_3L$. The fast atom bombardment (FAB) mass spectra of all three complexes displayed a molecular ion at m/z^+ = 782, which corresponds to the species

$[Re(CO)_3L]^+$ [structure (**I**) Fig. 1] (the observed and calculated isotope patterns are consistent). Since rhenium-halide bonds in halogenotricarbonylrhenium(I) complexes usually remain intact on ionisation [13], FAB mass spectral data indicate the formation of a cationic species, in which the ligand acts in a terdentate bonding mode. As the cation stoichiometry is $Re(CO)_3L$, the counter ions must have the molecular formulae (from the C, H and N analyses) $Re_2(CO)_6X_3$ (X = Cl, Br or I). Complex anions of this stoichiometry are know; namely the triply halide-bridged dirhenium anions, $[Re_2(CO)_6(\mu\text{-}X)_3]^-$ (X = Cl, Br or I) [14,15]. Negative ion mass spectrometry (using the MALDI-TOF technique) was carried out on the complexes to confirm the nature of the anions; molecular ions were observed for the three complexes at $m/z^- = 645$ (X = Cl), 779 (X = Br) and 920 (X = I), due to the proposed anions. Analytical data are reported in Table 1.

Attempts to prepare the desired complexes, $[ReX(CO)_3L]$, by treatment of the rheniumpentacarbonyl halides with 2,6-bis(diphenylphoshinosulfide)pyridine under milder conditions (CH_2Cl_2; ambient temperature) were unsuccessful; the ionic species, $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}X)_3]$ (X = Cl, Br or I), were again isolated (although reaction times were significantly longer).

To confirm the presence of the $[Re(CO)_3L]^+$ cation in the complexes isolated (see above), an explicit synthesis of the hexafluoroantimonate salt, $[Re(CO)_3L]^+[SbF_6]^-$ was carried out. Reaction of $[ReBr(CO)_5]$ with $AgSbF_6$ in tetrahydrofuran (thf), followed by treatment of the $[Re(CO)_5(thf)]^+$ cation with a stoichiometric quantity of 2,6-bis(diphenylphoshinosulfide)pyridine (L), yielded $[Re(CO)_3L][SbF_6]$ as a yellow solid (see above). Treatment of $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}Br)_3]$ with $AgSbF_6$ also yielded $[Re(CO)_3L][SbF_6]$. Data (FAB-MS, IR and NMR) for the cation in $[Re(CO)_3L][SbF_6]$ were the same as for the proposed cation in the complexes, $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}X)_3]$ (X = Cl, Br or I). Attempts were made to grow single crystals for X-ray crystallographic studies in order to confirm unambiguously the terdentate bonding mode of the ligand; suitable crystals could not be obtained.

All four complexes, $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}X)_3]$ (X = Cl, Br or I) and $[Re(CO)_3L][SbF_6]$, are stable in the solid-state under ambient conditions, and are soluble in moderately polar solvents (*e.g*. CH_2Cl_2). In co-ordinating solvents, such as acetone and methanol, the complexes quickly decompose; infrared spectroscopy indicates the formation of the $[Re(CO)_3(solvent)_3]^+$ cation, and a quantitative yield of the free ligand is recovered.

The infrared spectrum of $[Re(CO)_3L][SbF_6]$ displayed three bands in the carbonyl stretching region, characteristic of a *fac*-octahedral co-ordination geometry, with local C_s symmetry, for the $Re(CO)_3$ moiety [16]. The free ligand displays a strong band 647 cm^{-1} due to the P=S stretching mode [10]. Although no band assignable unambiguously to the P=S stretch in the cation, $[Re(CO)_3L]^+$, was observed, the band at 647 cm^{-1} is absent in the IR spectrum of the complex; infrared data therefore clearly indicate that the ligand, 2,6-bis(diphenylphoshinosulfide)pyridine, is acting in a *fac*-terdentate bonding mode with the S atoms co-ordinated to the metal. The IR spectra of the complexes $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}X)_3]$ (X = Cl, Br or I) each displayed three bands due to the CO stretching modes of the cation (these were in identical positions to those observed for the SbF_6 salt), plus additional bands due to the counter ions, $[Re_2(CO)_6(\mu\text{-}X)_3]^-$ (X = Cl, Br or I). No band assignable to the free P=S stretching mode (see above) was observed. The isolated $[Re_2(CO)_6(\mu\text{-}X)_3]^-$ anions have local D_{3h} symmetry, and are therefore expected to exhibit two IR active carbonyl stretching modes (A_2" and E'). The sharp A_2" bands are clearly observed to slightly lower frequency of the A_1 band of the cation. The E' bands tend to overlap with the cation band at 1920 cm^{-1}; however, the E' bands of the bromo- and iodo-species are observable. The CO stretching frequencies for the anions are close to those reported previously for the complexes $[Et_4N][Re_2(CO)_6(\mu\text{-}X)_3]$ (X = Cl, Br or I), in the same solvent (CH_2Cl_2) [14]. Infrared data are reported in Table 1.

NMR studies

The ambient temperature (298 K) $^{31}P\{^1H\}$ NMR spectra of the complexes $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}X)_3]$ (X = Cl, Br or I) and $[Re(CO)_3L][SbF_6]$ in CD_2Cl_2 are, as

expected, identical. The spectra display a single resonance at $\delta \approx 67.0$ [*cf.* $\delta = 38.4$ for the free ligand (in $CDCl_3$)], indicating that either (i) both P are equivalent, as a result of the ligand adopting a symmetrical bonding mode, or (ii) the ligand is undergoing some rapid fluxional process that leads to the averaging of different P environments. To try to distinguish between these two possibilities spectra were recorded at low temperature (190 K), in an attempt to 'freeze-out' any dynamic stereochemical processes. No spectral changes were observed, indicating a stereochemically rigid molecule, with the two P atoms in identical chemical positions. Solution ^{31}P NMR data therefore indicate the formation of complex, in which both $S(=PPh_2)$ atoms of the ligand are bound to the metal centre. This was confirmed by solid-state ^{31}P NMR spectroscopy (see below).

The solid-state ^{31}P spectrum of the free ligand, 2,6-bis(diphenylphoshinosulfide)-pyridine, displays two isotropic resonances, with spinning side-bands, in a 1:1 intensity ratio at $\delta = 41$ and 38, as a result of the two P atoms being crystallographically inequivalent. The spectra also indicate the presence of residual dipolar coupling between the nitrogen (^{14}N nuclide) of the pyridine ring and the phosphorus nuclides. We are currently undertaking a full analysis of the solid-state NMR spectra of 2,6-bis(diphenylphoshinosulfide)pyridine and the related oxide and selenide compounds, and will report the results of these studies shortly.

The solid-state ^{31}P NMR spectra of the complexes $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}X)_3]$ (X = Cl, Br or I) also display two isotropic resonances (with spinning side-bands), in a 1:1 (integral) intensity ratio at *ca.* $\delta = 65$ and 62. The small chemical shift differences between the signals indicate that they arise as a result of the P atoms being crystallographically inequivalent, rather than as a result of chemical inequivalence. This clearly supports the hypothesis of the ligand bonding in a symmetrical fashion, with both S atoms co-ordinated. The hexafluoroantimonate salt, $[Re(CO)_3L][SbF_6]$, displays two isotropic signals, in a 1:1 intensity ratio, at *ca.* $\delta = 71$ and 66. The different chemical shifts of the isotropic resonances of the $[SbF_6]^-$ complex compared to those of the other three complexes (see above) presumably arise because of different packing in the solid-state. This interpretation is supported by the results of X-ray powder diffraction studies on the four complexes. The powder patterns obtained for the

complexes $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}X)_3]$ (X = Cl, Br or Br) are essentially identical, but are different from that obtained for $[Re(CO)_3L][SbF_6]$. The solid-state ^{31}P NMR spectrum of $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}Br)_3]$ is shown in Figure 2, and ^{31}P NMR data for the ligand, 2,6-bis(diphenylphosphinosulfide)pyridine, and the four complexes, $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}X)_3]$ (X = Cl, Br or I) and $[Re(CO)_3L][SbF_6]$ are reported in Table 2.

The ambient temperature (298 K) ^1H NMR spectra of the complexes $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}X)_3]$ (X = Cl, Br or I) and $[Re(CO)_3L][SbF_6]$ [L = 2,6-bis(diphenylphosphinosulfide)pyridine] in CD_2Cl_2 are essentially identical. The spectra displayed eight distinct chemical shifts in the region δ = 7.2 - 8.2, and are indicative of the ligand bonding in a symmetrical fashion. The signals of the pyridine-H nuclides, H_J, H_K and $H_{K'}$ (Fig. 1), show the characteristic pattern of an ABB' sub-set of an ABB'XX' spin system (the P atoms being the XX' sub-set). The signal from H_J is readily assigned because the $^4J_{PH}$ coupling (≈ 3.8 Hz) is approximately half that of the $^3J_{HH}$ coupling (≈ 7.8 Hz); thus H_J gives rise to a pseudo septet. The signal from $H_K/H_{K'}$ is then readily identified from a ^1H-^1H COSY experiment (see below).

If rotation about the P-C(phenyl) bonds is assumed to be rapid at ambient temperature (298 K), as appears apparent from the ^1H NMR spectra, the hydrogen nuclides of the P-phenyl rings would be expected to give rise to three resonances, characteristic of an AA'BB'C spin system. Thus the six remaining chemical shifts (see above) must result from inequivalence of pairs of phenyl rings. This inequivalence arises because two phenyl rings point towards the metal moiety and two away from it (Fig. 1). If the inequivalence arose as a result of an unsymmetrical mode of co-ordination, then all four P-phenyl rings would be expected to be inequivalent (see Figure 1), and twelve distinct chemical shifts would result. Ambient temperature ^1H NMR data are therefore consistent with either (i) a symmetrical bonding mode for the ligand or (ii) the presence of rapid fluxional process that leads to a time-averaging of pairs of phenyl rings. The latter possibility can be excluded to the basis of the ^{31}P NMR data (see above) and the results of a low temperature ^1H NMR study (see below). The resonances of the *ortho*-hydrogens of the phenyl rings are readily identified by their couplings to the phosphorus

nuclides ($^3J_{PH} \approx 14$ - 15 Hz). The remaining signals (Table 3) can then be assigned on the basis of a single ^{1}H-^{1}H COSY experiment. The assignment of the two sets of phenyl-H signals to the two pairs of phenyl rings was based on the low temperature ^{1}H NMR spectra (see below). The ^{1}H NMR spectrum of $[Re(CO)_3L][Re_2(CO)_6(\mu\text{-}Cl)_3]$ at 298 K is shown in Figure 3, and data are reported in Table 3.

A variable temperature ^{1}H NMR study of the complexes was undertaken, between ambient temperature (298 K) and *ca*. 200 K, to help confirm the stereochemical rigidity of the complexes, and thence the symmetrical bonding mode of the ligand, 2,6-bis(diphenylphosphinosulfide)pyridine. Although the ^{1}H NMR spectra are temperature dependent (see below), there was no evidence to indicate the slowing of an oscillatory rearrangement, that would be expected if the ligand were bound in a bidentate fashion [1-6]. The low temperature ^{1}H NMR spectra are therefore consistent with a stereochemically rigid symmetrical bonding mode for the ligand. Band shape changes indicative of restricted rotation about the P-C(phenyl) bonds of *one pair* of phenyl rings were observed on cooling. If it is assumed that the phenyl rings oriented towards the metal moiety have the higher magnitude for the free energy of activation ($\Delta G^{\ddagger}$) for the P-C(phenyl) bond rotation, as a consequence of steric interactions with the metal moiety, a full assignment of the phenyl-H resonances to the two pairs of rings can be made. Assignments were made on this basis (Table 3). A full analysis of the variable temperature spectra was not undertaken. Approximate values for the free energies of activation were determined [17] at the temperature of initial line broadening ($T_i \approx 203$ K), and from band coalescence ($T_c \approx 243$ K); $\Delta G^{\ddagger}$, ≈ 47 kJ mol^{-1} at both T_i and T_c. The apparent temperature independence of $\Delta G^{\ddagger}$ indicates that the entropy of activation, $\Delta S^{\ddagger}$, is approximately zero, as expected for an intramolecular process. The activation energies measured were the same for all four complexes, consistent with the presence of the same cation in each case.

Although the ^{1}H and ^{31}P NMR data clearly show that the ligand is co-ordinated to the metal centre in a symmetrical fashion, via both S atoms, data do not exclude the possibility that the ligand is bound in a bidentate fashion, with the N donor of the pyridine ring uninvolved in bonding. This is considered highly unlikely on chemical

grounds, and is inconsistent with the mass spectral and IR data (see above). The orange/yellow colour of the complexes (which is indicative of tricarbonylrhenium(I)-pyridine complexes [3,13]) is also consistent with the pyridine ring being bound.

The ^{19}F NMR spectrum of the hexafluoroantimonate complex, $[Re(CO)_3L][SbF_6]$, was obtained to confirm the presence of the $[SbF_6]^-$ anion. The ambient temperature ^{19}F spectrum (in CD_2Cl_2) comprises two overlapping sub-spectra (at δ = -123.4), due to coupling to ^{121}Sb (I = 5/2, 57.25%) and ^{123}Sb (I = 7/2, 42.75%); $^1J[^{121}Sb\text{-}F]$ = 1945 Hz, $^1J[^{123}Sb\text{-}F]$ = 1050 Hz. Data are consistent with those reported previously for the $[SbF_6]^-$ anion [18].

Acknowledgements.

We are grateful to Birkbeck College for financial support, to Professor W. McFarlane for the synthesis of the ligand, and to the University of London for access to the solid-sate NMR facilities at University College London and Queen Mary and Westfield College, and the 400 MHz solution NMR service at Kings College. Drs B. C. Smith and G. Hogarth are acknowledged for helpful discussions.

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