

Mono- and Di-nuclear Rhodium and Palladium Complexes of Macrocyclic Ligands containing the 2,6-Di(thiomethyl)pyridine Sub-unit†

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The synthesis of three macrocyclic ligands containing the 2,6-di(thiomethyl)pyridine sub-unit is reported. 25,26-Diaza-3,7,15,19-tetrathiatricyclo[19.3.1.1^{9,13}]hexacosa-1(25),9(26),10,12,21,23-hexene is a ditopic macrocycle which forms dinuclear rhodium and palladium complexes while 13-aza-3,7-dithiabicyclo[7.3.1]trideca-1(13),9,11-triene yields an unusual dimeric rhodium carbonyl complex exhibiting fluxional behaviour in solution, which has been monitored by ¹H and ¹³C n.m.r. spectroscopy.

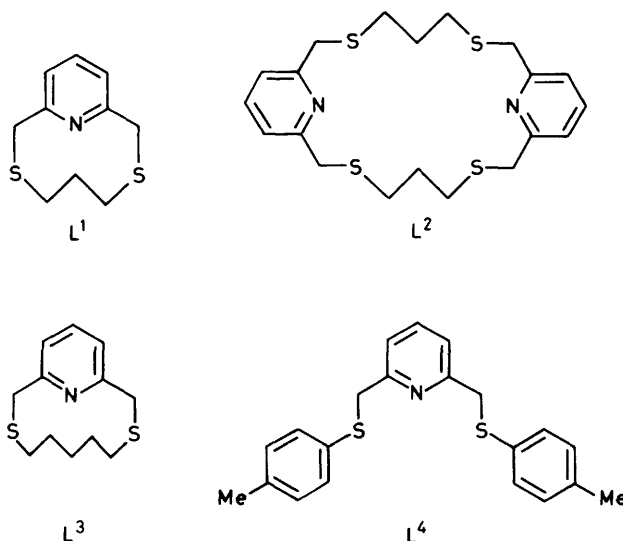
Numerous macrocyclic¹⁻³ as well as macropolycyclic³ ligands containing pyridine^{1,3} or sulphur^{2,3} binding sites have been synthesised in recent years and have been shown to complex various transition-metal cations. These sites markedly influence the properties of the bound cation, for example stabilising low oxidation states,⁴ which play a role in reactions catalysed by many metal complexes. Ligands containing pyridine and sulphur sites in the same framework should take advantage of the effect of both on bound metal ions.

We report here the synthesis and some complexation properties of three macrocyclic ligands L¹–L³ and of an acyclic one, L⁴, containing these sites combined in a 2,6-di(thiomethyl)pyridine sub-unit. Since L² contains two such units, it should in addition be able to bind two metal ions forming dinuclear macrocyclic complexes in which the ions would be bound in proximity and could bring together (and perhaps into reaction) small substrate molecules co-ordinated to them.

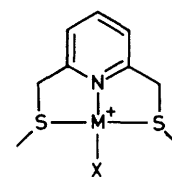
Results and Discussion

Synthesis of the Ligands.—Sulphur-containing macrocycles² are accessible in particular by cyclisation reactions involving the formation of two carbon–sulphur bonds. Condensation of propane-1,3-dithiol with 2,6-di(bromomethyl)pyridine yields a mixture of compounds from which the bicyclic and tricyclic macrocycles L¹ and L² respectively may be isolated in moderate yield. Similarly, using pentane-1,5-dithiol, bicyclic L³ is obtained but the corresponding tricyclic ligand was not isolated. Separations of L¹ and L² and purification of L³ were effected by chromatography on alumina. For purposes of comparison, the acyclic chelating ligand L⁴ has been prepared by reacting *p*-thiocresol with 2,6-di(bromomethyl)pyridine. Ligand L¹ has already been described in the literature.⁵

Mononuclear Complexes.—Reaction of equimolar amounts of [Rh₂Cl₂(CO)₄] with L³ and L⁴ in methanol gave an orange solution (with rapid evolution of one equivalent of CO) from which the air-stable cationic complexes [RhL³(CO)]PF₆ (1) and [RhL⁴(CO)]PF₆ (2) may be isolated by addition of ammonium hexafluorophosphate. The complexes are characterised by single terminal carbonyl bands in the i.r. spectrum at 2 000 and 2 015 cm⁻¹ for (1) and (2) respectively. Co-ordination of rhodium to the pyridine nitrogen atom is indicated by the splitting and shifting of ring vibrations (Table) as observed for



many pyridine–metal complexes.⁶⁻⁸ In their ¹³C n.m.r. spectra a single rhodium-coupled doublet is observed for the co-ordinated carbonyl (δ_C 183 p.p.m., *J*_{RhC} 64 Hz).⁹ Such data suggest the common structure (I) shown below, in which the



(I)
M = Rh, X = CO
M = Pd, X = Cl

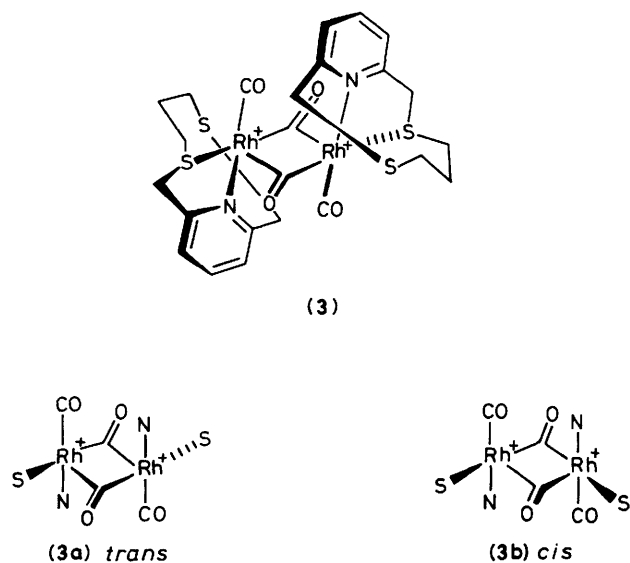
ligand structure imposes *trans* dithioether co-ordination to the pyridine bound rhodium.

Reaction of L¹ with [Rh₂Cl₂(CO)₄] in methanol gave no CO evolution and addition of ammonium hexafluorophosphate yielded the orange-red complex [(RhL¹(CO))₂][PF₆]₂ (3). This complex showed two carbonyl bands in the i.r. spectrum at 2 036 and 1 798 cm⁻¹ corresponding to terminal and bridging carbonyl groups respectively.¹⁰ Complex (3) exhibits interesting

† Non-S.I. unit employed: mmHg ≈ 13.6 × 9.8 Pa.

fluxional behaviour in solution which has been monitored by ^1H and ^{13}C n.m.r. spectroscopy. At 320 K in $[\text{D}_6]\text{acetone}$, the ^1H n.m.r. spectrum shows a sharp triplet for the *para* ring proton but a broadened doublet for the *meta* protons. As the temperature is lowered the signal for the *meta* protons coalesces ($T_c \sim 300$ K) and at 280 K appears as two doublets. Around 250 K the resonances for all of the aromatic protons broaden and below 240 K eight distinct doublets may be discerned for the *meta* protons [Figure 1(b)]. The benzylic protons resonate at 320 K as a distinct doublet ($J = 17$ Hz) and a broad band centred around 5.3 p.p.m. The low-field doublet broadens as the temperature is lowered to reveal a complex multiplet below 240 K. The higher-field multiplet sharpens to a doublet at 280 K ($J = 17$ Hz) but broadens again around 250 K and below 240 K is a complex multiplet. The ^1H n.m.r. spectra are shown in Figure 1. It is clear there are at least two dynamic processes occurring, one with a coalescence temperature around 300 K ($\Delta G_c^\ddagger \sim 65$ kJ mol $^{-1}$), and a second process with T_c of about 250 K ($\Delta G_c^\ddagger \sim 55$ kJ mol $^{-1}$). In order to investigate these processes further, the ^{13}CO -labelled complex was prepared using $[\text{Rh}_2\text{Cl}_2(^{13}\text{CO})_4]$ (85% enriched) and its behaviour monitored by ^{13}C n.m.r. Figure 2 illustrates the ^{13}C spectrum of ^{13}CO -enriched (3) in the carbonyl region as a function of temperature. Below 240 K the spectrum is static and shows two doublets at 186 p.p.m. corresponding to two distinct terminal carbonyl groups ($J_{\text{RhC}} 61$ Hz) and three overlapping triplets at 229 p.p.m. in ratio 1:2:1 corresponding to bridging carbonyls ($J_{\text{RhC}} 41$ Hz).⁹ At 253 K the pair of doublets coalesces and appears as a doublet above 260 K ($J_{\text{RhC}} 61$ Hz) before broadening again at 320 K. The bridging carbonyl signals similarly coalesce around 250 K ($\Delta G_c^\ddagger \sim 55$ kJ mol $^{-1}$) and appear as a rather indistinct signal thereafter. Thus the ^{13}C n.m.r. gives added information about the lower energy exchange phenomenon.

This dynamic behaviour may be interpreted in terms of the dimeric structure shown for (3) in which the terminal carbonyls are *trans* to the pyridine nitrogens as in the related monomeric complexes described herein. The complex may exist as *cis* and *trans* stereoisomers, (3a) and (3b), and these are observed in a



53:47 ratio. In the *cis* isomer the bridging carbonyls are non-equivalent and may be expected to give rise to two rhodium-coupled triplets in the ^{13}C n.m.r. spectrum; in the *trans* isomer the bridging carbonyls are enantiotopic and equivalent. The two terminal carbonyls of each stereoisomer are related by a C_2 axis.

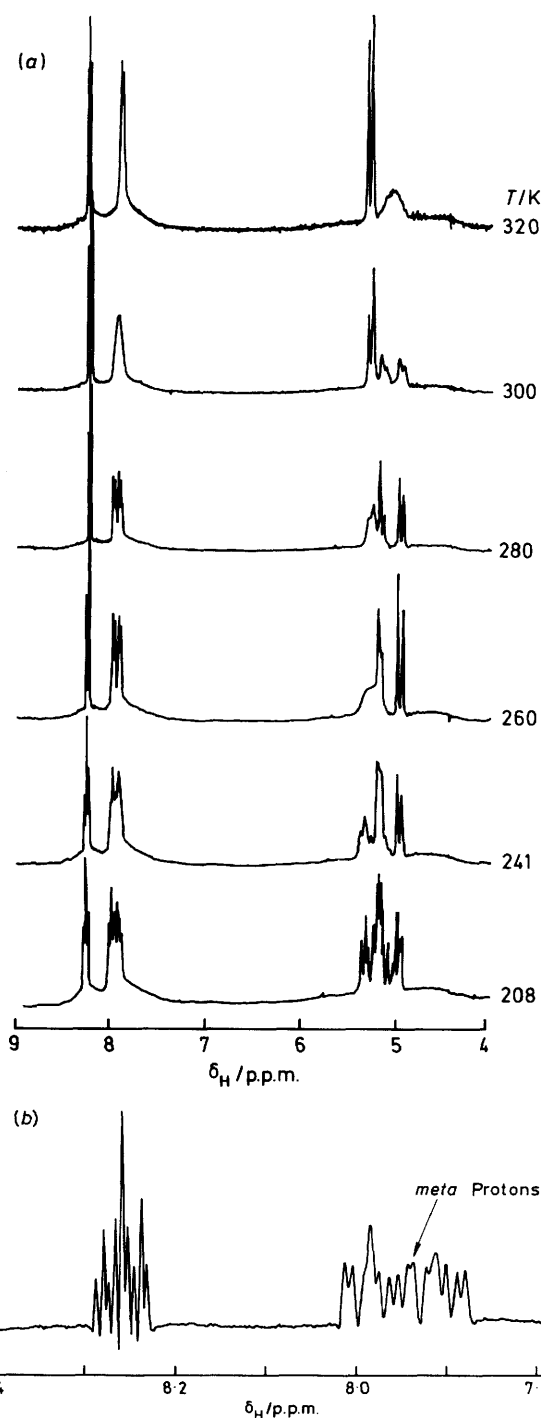


Figure 1. (a) ^1H N.m.r. spectra of $[\{\text{RhL}^1(\text{CO})_2\}_2][\text{PF}_6]_2$ (3) in $[\text{D}_6]\text{acetone}$ as a function of temperature; (b) shows an expansion of the aromatic region at 208 K

The exchange between *cis* and *trans* stereoisomers which probably occurs *via* an intramolecular on/off exchange between free and bound sulphurs is rapid above 250 K. Such a process ought also to render the *meta* aromatic protons equivalent in the ^1H n.m.r. spectrum. That it does not implies that there may be a second dynamic process occurring. This could involve a small degree of dissociation of the dimer into the corresponding monomer, (3c), in which the carbonyl group which was *trans* to the pyridine nitrogen in the dimer remains *trans* to nitrogen in

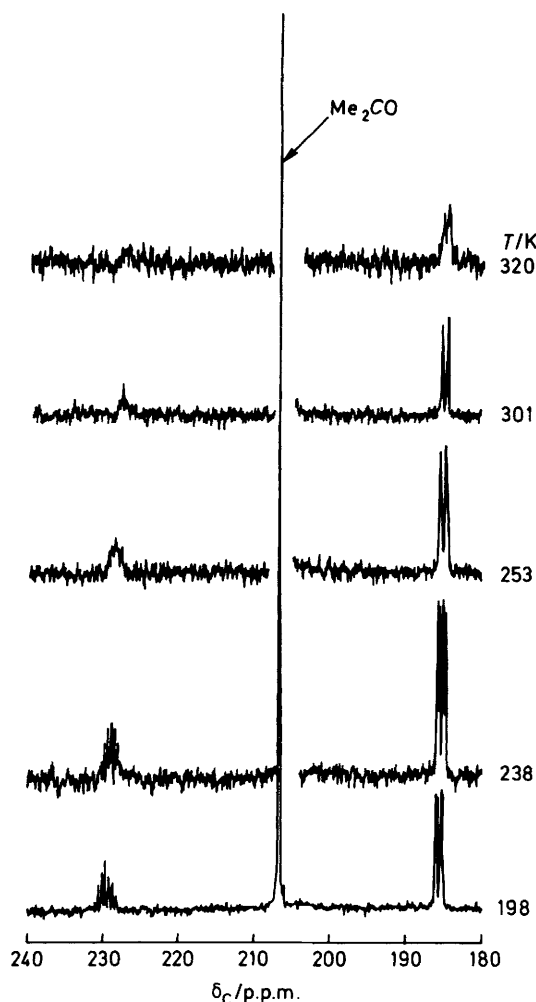
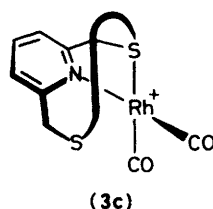


Figure 2. ^{13}C N.m.r. spectra of ^{13}C -labelled $[\{\text{RhL}^1(\text{CO})_2\}_2][\text{PF}_6]_2$ (3) in $[\text{D}_6]\text{acetone}$ as a function of temperature



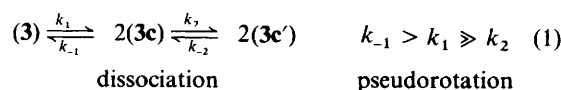
the monomer. In the monomer (3c) the *meta* hydrogens are non-equivalent and remain so provided that recombination to form the dimer is fast with respect to a pseudorotation of (3c) (by which the *meta* protons will become equivalent). This behaviour is observed in the temperature region 250–290 K.

The benzylic hydrogens will also remain non-identical in the monomer (3c) as long as pseudorotation is not occurring. When the temperature is raised the proportion of monomer (in which both the carbonyl groups are terminal) increases and the bridging carbonyl resonances broaden and disappear in the ^{13}C spectrum accordingly. Above 300 K the terminal carbonyl doublet of the dimer also broadens and the *meta* protons collapse to a single doublet as pseudorotation of (3c) occurs. This complex spectral behaviour is in agreement with the exchange reactions represented by equation (1).

Table. Infrared absorptions of the ligands and their complexes^a

Compound	Pyridine ring vibration	Carbonyl stretch	P–F stretch
L^1	1 587, 1 570		
L^2	1 591, 1 572		
L^3	1 590, 1 571		
L^4	1 596, 1 579		
(3) $[\{\text{RhL}^1(\text{CO})_2\}_2][\text{PF}_6]_2$	1 600, 1 577	2 036, 1 798	840
(9) $[\text{Rh}_2\text{L}^2(\text{CO})_2][\text{PF}_6]_2$	1 596, 1 562	2 013	845
(1) $[\text{RhL}^3(\text{CO})]\text{PF}_6$	1 599, 1 576	2 000	830
(2) $[\text{RhL}^4(\text{CO})]\text{PF}_6$	1 603, 1 566	2 015	847
(6) $[\text{PdL}^1\text{Cl}_2]$	1 585, 1 572		
(10) $[\text{Pd}_2\text{L}^2\text{Cl}_2]\text{Cl}_2$	1 596, 1 562		
(5) $[\text{PdL}^4\text{Cl}]\text{Cl}$	1 603, 1 569		
(7) $[\text{CuL}^2][\text{ClO}_4]_2$	1 601, 1 592, 1 566		

^a Measured as Nujol mulls; values are given in cm^{-1} .



Complex $[\text{RhL}^3(\text{CO})]\text{PF}_6$ (1) gives a slow-exchange ^1H n.m.r. spectrum at 298 K in which the benzylic protons appear as a sharp AB quartet centred at 5.1 p.p.m. The ^1H n.m.r. spectrum is shown in Figure 3 and proton assignments have been confirmed by selective decoupling experiments, irradiating each proton in turn. The anisochronous protons of the central methylene group lie close to the plane of symmetry along the N–Rh–CO vector, resonating at 4.17 and 2.25 p.p.m.

Reaction of L^3 or L^4 with $[\text{PdCl}_2(\text{PhCN})_2]$ ¹¹ in dichloromethane gives the water-soluble cationic organopalladium complexes $[\text{PdL}^3\text{Cl}]\text{Cl}$ (4) and $[\text{PdL}^4\text{Cl}]\text{Cl}$ (5) to which the general structure (I), analogous to the rhodium complexes, may be assigned. The complexes are 1:1 electrolytes with molar conductivities of 132 and 136 $\text{S cm}^2 \text{mol}^{-1}$ respectively and i.r. spectroscopy confirms that the pyridine nitrogen is bound to the metal (Table). Again the macrocycle L^1 behaves differently and in this case forms a water-insoluble yellow complex (6) in which the pyridine nitrogen is not bound, suggesting a neutral complex, $[\text{PdL}^1\text{Cl}_2]$ (possibly oligomeric), in which both sulphurs are co-ordinated as found for an external complex of palladium dichloride with a dithia-cryptand ligand.¹² It is clear that the C_3 chain in L^1 is too short to allow simultaneous binding of both sulphurs and the pyridine nitrogen, as evidenced by the complexation behaviour with rhodium and palladium.

Admixture of the ditopic macrocycle L^2 with copper(II) perchlorate in acetone gave dark green needles of a mononuclear copper(II) complex, $[\text{CuL}^2][\text{ClO}_4]_2$ (7), in which only one of the pyridine nitrogens appeared to be bound (Table). Reaction with $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ gave a yellow mononuclear copper(I) complex, $[\text{CuL}^2]\text{BF}_4$ (8). The three binding atoms (NS_2) of each sub-unit of L^2 define three corners of a fairly rigid square-planar environment which should favour formation of square-planar d^8 complexes.¹³ Copper(II) apparently binds to five of the available heteroatoms (S_4N) while copper(I) presumably co-ordinates to the four sulphur atoms in a favourable distorted-tetrahedral geometry.

Dinuclear Complexes of Macrocycle L^2 .—Reaction of equimolar amounts of L^2 and $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ in methanol gives a deep red solution from which a dicationic complex was isolated by addition of hexafluorophosphate anion. This compound showed only a single terminal carbonyl absorption in the i.r.

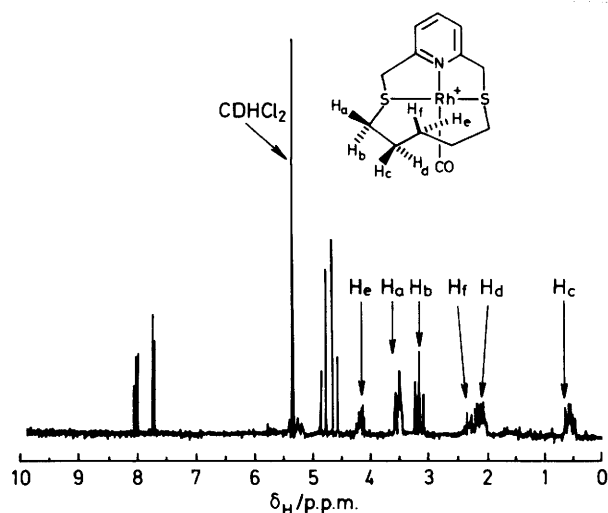
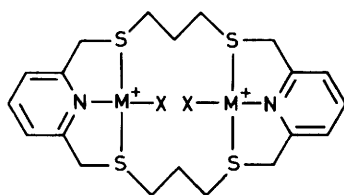


Figure 3. ^1H N.m.r. spectrum of $[\text{RhL}^3(\text{CO})]\text{PF}_6$ (1) in CD_2Cl_2 at 303 K



- (9) $\text{M} = \text{Rh}$, $\text{X} = \text{CO}$
 (10) $\text{M} = \text{Pd}$, $\text{X} = \text{Cl}$

(2013 cm^{-1}) and the absorptions due to the pyridine ring vibrations (1596 and 1562 cm^{-1}) indicated that both nitrogens are bound to rhodium. The ^{13}C n.m.r. spectrum in CD_3CN revealed only one rhodium-coupled doublet signal for the bound carbonyl ($\delta_{\text{C}} 189$ p.p.m., $J_{\text{RhC}} 69$ Hz). The ^1H n.m.r. spectrum showed an AB quartet for the diastereotopic benzylic protons and a sharp doublet and triplet for the *meta* and *para* ring protons respectively, consistent with the symmetrical dinuclear complex $[\text{Rh}_2\text{L}^2(\text{CO})_2][\text{PF}_6]_2$ (9). In $[\text{H}_6]$ dimethyl sulphoxide successive formation of mono- and di-rhodium complexes may be monitored by ^1H n.m.r.; after addition of 0.5 equivalents of $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ to the ligand solution, a statistical mixture of resonances due to the free ligand and the mono- and di-cationic species were distinguished, suggesting the possibility of isolating a monomeric complex with one vacant co-ordination site.

Reaction of two equivalents of $[\text{PdCl}_2(\text{PhCN})_2]$ with L^2 in refluxing dichloromethane yielded the bright yellow compound $[\text{Pd}_2\text{L}^2\text{Cl}_2]\text{Cl}_2$ (10), soluble in water. The ^1H n.m.r. spectrum revealed a single AB quartet for the benzylic protons and the two pyridine rings are equivalent giving a simple doublet and triplet for the ring protons. The positive-ion fast-atom bombardment (f.a.b.) mass spectrum of complex (10), using a thioglycerol matrix, revealed a weak molecular ion at m/z (707 , 705) $^+$ together with fragments, with the expected palladium isotope patterns, due to successive loss of chlorine and palladium at (670 and 672) $^+$ $[\text{Pd}_2\text{L}^2\text{Cl}]^+$, (635 and 637) $^+$ $[\text{Pd}_2\text{L}^2]^+$, (563 and 561) $^+$ $[\text{PdL}^2\text{Cl}]^+$, and (531 and 529) $^+$ $[\text{PdL}^2]^+$. I.r. data and combustion analysis agree with the assignment of the structure of (10) in which both palladiums are co-ordinated to the macrocycle. Removal of both chloride ligands would make available two co-ordination sites in close proximity, to which other ligands may be bound.

In both (9) and (10) the metal ions are bound inside the macrocycle and the ligand species, X, which they bear are directed towards each other. Such an arrangement is favourable for inducing reactions between the two X groups. On the other hand, in a mononuclear complex like $[\text{RhL}^2(\text{CO})]^+$, occupation of the second site by another metal ion might allow activation of the bound CO to nucleophilic attack. Macrocyclic L^2 and analogues containing larger bridges between the two binding sub-units thus represent suitable ditopic ligands for investigating cation-cation interaction at short distances and reaction of bound substrates at further separation.³

Experimental

Reactions were carried out under an argon atmosphere, with argon purified by sequential passage through concentrated H_2SO_4 , KOH pellets, and glass wool. Commercial solvents were distilled prior to use from an appropriate drying agent according to standard procedures. Proton n.m.r. spectra were recorded using either a Bruker WP200 (200.13 MHz) or a Bruker WH360 (360.13 MHz); carbon-13 spectra were recorded on either a Bruker WP200 (50.33 MHz) or a Varian XL100 instrument (25.8 MHz). Chemical shifts are given in p.p.m. relative to SiMe_4 (0 p.p.m.). Infrared spectra were recorded as Nujol mulls or in the stated solvent using a Perkin-Elmer 297 spectrophotometer. Mass spectra were recorded on LKB9000S and Thomson THW208 spectrometers. Conductivities were measured on a Portland Electronics P335 conductivity meter.

Synthesis of Ligands L^1 – L^4 .—13-Aza-3,7-dithiabicyclo[7.3.1]trideca-1(13),9,11-triene (L^1) and 25,26-diaza-3,7,15,19-tetrathiatricyclo[19.3.1.1^{9,13}]hexacos-1(25),9(26),10,12,21,23-hexaene (L^2).—A solution of propane-1,3-dithiol (2.0 g, 18.5 mmol) in butan-1-ol (150 cm^3) was heated to reflux with potassium hydroxide (2.2 g, 39 mmol) for 0.5 h. A solution of 2,6-di(bromomethyl)pyridine (4.88 g, 18.4 mmol) in butan-1-ol (50 cm^3) was added slowly (4 h) and after filtration through Celite and removal of solvent *in vacuo*, the residue was extracted with dichloromethane ($4 \times 25\text{ cm}^3$) and the solution reduced to a small volume under reduced pressure. Chromatography on alumina [dichloromethane–toluene (1:1)] enabled L^1 and L^2 to be separated. Yields: L^1 , 1.26 g (30%); L^2 , 430 mg (11%).

L^1 : m.p. 79 – 80°C (lit.⁵ 78 – 79°C); R_f 0.73 (Al_2O_3 , CH_2Cl_2); δ_{H} (200 MHz, CD_2Cl_2), 7.57 (1 H, t, J 7.9 Hz), 7.09 (2 H, d), 3.89 [4 H, s, CH_2 -py (py = pyridine)], 2.84 (4 H, t, CH_2S), and 1.09 (2 H, quin); δ_{C} (50.3 MHz, CDCl_3), 31.7 (CH_2S), 34.1 ($\text{CH}_2\text{CH}_2\text{S}$), 39.8 (CH -py), 120.2, 138.3, and 158.2 p.p.m. (py).

L^2 : m.p. 144 – 145°C (Found: C, 57.1; H, 6.20; N, 6.85. $\text{C}_{20}\text{H}_{26}\text{N}_2\text{S}_4$ requires C, 56.9; H, 6.15; N, 6.65%); R_f 0.06 (Al_2O_3 , CH_2Cl_2); δ_{H} (200 MHz, CDCl_3), 7.50 (2 H, t, J 7.7), 7.12 (4 H, d), 3.62 (8 H, s, CH_2 -py), 2.37 (8 H, t, J 7.1 Hz), and 1.61 (4 H, quin); δ_{C} (25.8 MHz, CDCl_3), 28.7, 30.3, 37.9, 121.3, 137.6, and 158.8 p.p.m.; m/e 422 [M] $^+$, 389, 347, 316, 282, and 242.

15-Aza-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene (L^3). A solution of pentane-1,5-dithiol (2.0 g, 14.7 mmol) in butan-1-ol (20 cm^3) was heated with potassium hydroxide (1.8 g, 32.1 mmol) at reflux (0.3 h). A solution of 2,6-di(bromomethyl)pyridine (3.90 g, 14.7 mmol) in butan-1-ol (40 cm^3) was added slowly (2 h); after further reflux (2 h) the mixture was filtered, solvent removed under reduced pressure, and the residue chromatographed on alumina [toluene–dichloromethane (1:1)] to give a crystalline solid, 500 mg (14%), m.p. 82 – 83°C (Found: C, 60.2; H, 7.30; N, 5.95. $\text{C}_{12}\text{H}_{17}\text{NS}_2$ requires C, 60.4; H, 7.10; N, 5.85%); m/e 239 [M] $^+$, 206, 196, 184, 171, and 139; δ_{H} (200 MHz, CDCl_3), 7.51 (1 H, t, J 7.7 Hz), 7.18 (2 H, d), 3.72 (4 H, s, CH_2 -py), 2.32 (4 H, m, CH_2S), and 1.20 (6 H, m); δ_{C} (25.8 MHz, CDCl_3) 26.2, 27.0, 28.4, 37.1, 121.7, 138.1, and 158.2 p.p.m.

2,6-Bis(p-tolylthiomethyl)pyridine (L^4). To a solution of potassium hydroxide (2.4 g, 43 mmol) in butan-1-ol (40 cm³) was added *p*-thiocresol (4.97 g, 40 mmol) as a solid and the mixture refluxed (0.3 h). After cooling to room temperature 2,6-di(bromomethyl)pyridine (5.30 g, 20 mmol) was added in small portions and the mixture refluxed (2 h). After filtration and evaporation under reduced pressure, the residue was recrystallised from hot ethanol to give a colourless, crystalline solid, 6.93 g (95%), m.p. 69–70 °C (Found: C, 71.7; H, 6.10; N, 4.00. $C_{21}H_{21}NS_2$ requires C, 71.7; H, 6.00; N, 4.00%); m/e 351 [M]⁺, 352 [$M + 1$]⁺ 336, 229, 228, and 195; δ_H (200 MHz, $CDCl_3$), 7.37 (1 H, t, J 7.7), 7.10 (4 H, d, J 8.1 Hz), 7.01 (2 H, d), 6.93 (4 H, d), 4.08 (4 H, s, CH_2 -py), and 2.18 (6 H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$), 21.1 (CH_3), 40.9, 121.3 (*meta* py), 129.7, 130.3 (aryl), 132.2, 136.3 (*para* py) 137.1, and 157.5 p.p.m.

Synthesis of Complexes.—[$\{RhL^1(CO)_2\}_2\}[PF_6]_2$ (3). To freshly sublimed [$Rh_2Cl_2(CO)_4$] (19.5 mg, 0.05 mmol) was added a solution of L^1 (22 mg, 0.1 mmol) in methanol (2 cm³) and the mixture was stirred at room temperature (0.1 h). After filtration, excess ammonium hexafluorophosphate (0.1 g) was added as a solution in methanol (2 cm³) and the resultant bright orange-red precipitate was filtered off, washed with methanol (2 × 2 cm³), diethyl ether (2 × 1 cm³), and dried *in vacuo* (0.1 mmHg), 41 mg (85%) (Found: C, 27.8; H, 2.80; N, 2.95. $C_{24}H_{26}F_{12}N_2O_4P_2Rh_2S_4$ requires C, 27.9; H, 2.55; N, 2.70%; δ_C (90.6 MHz, 198 K), 185.8 (d, J_{RhC} 61, terminal CO), 186.0 (d, J_{RhC} 61, terminal CO); 230.0 (t, J_{RhC} 43 Hz, bridging CO, *E* isomer); 229.1, 230.5 (t + t, bridging CO, *Z* isomer).

The following organorhodium complexes were prepared analogously. [$Rh_2L^2(CO)_2\}[PF_6]_2$ (9) (Found: C, 27.3; H, 2.75; N, 2.85. $C_{22}H_{26}F_{12}N_2O_2P_2Rh_2S_4$ requires C, 27.2; H, 2.70; N, 3.00%; δ_H (200 MHz, CD_3CN), 7.95 (2 H, t, J 7.5), 7.58 (4 H, d), 4.77 (8 H, q, J 16 Hz), and 3.4–2.9 (12 H, br m); δ_C (50.3 MHz, CD_3CN), 188.5 p.p.m. (d, Rh–CO, J_{RhC} 69.1 Hz). [RhL^3 -(CO)] PF_6 (1) (Found: C, 30.0; H, 3.50; N, 2.95. $C_{13}H_{17}F_6$ -NOPRhS₂ requires C, 30.2; H, 3.30; N, 2.70%; δ_H [200 MHz, (CD_3)₂CO], 8.18 (1 H, t, J 7.4), 7.90 (2 H, d), 5.10 (4 H, q, J 18), 4.33 (1 H, m, $CHCH_2CH_2S$), 3.74 (2 H, m, CHS), 3.40 (2 H, dt, J 13.7, J 1.2 Hz, CHS), 2.3–1.95 (3 H, m), and 0.68 p.p.m. (2 H, m, SCH_2CH). [$RhL^4(CO)]PF_6$ (2). M.p. 159–160 °C (Found: C, 42.2; H, 3.20; N, 2.25. $C_{22}H_{21}F_6$ -NOPRhS₂ requires C, 42.1; H, 3.55; N, 2.25%; δ_H (200 MHz, CD_2Cl_2), 8.18 (1 H, t, J 7.5), 7.92 (4 H, t, J 7.7 Hz), 7.85 (2 H, d), 7.35 (4 H, d), 5.40 (4 H, m), and 2.38 (6 H, s, CH_3); δ_C [50.3 MHz, (CD_3)₂CO], 19.4, 51.2, 121.4 (*meta* py), 129.8, 131.6, 131.8 (aryl), 139.8 (*para* py), 140.7, 159.5 (*ortho* py), and 182.9 p.p.m. (d, J_{RhC} 64 Hz).

[$Pd_2L^2Cl_2$] Cl_2 (10). To a solution of L^2 (42.2 mg, 0.1 mmol) in dichloromethane (10 cm³) was added a solution of [$PdCl_2$ -(PhCN)₂] (76.6 mg, 0.2 mmol) in dichloromethane (5 cm³) and the mixture refluxed (15 h). The bright yellow precipitate was filtered off, washed with dichloromethane (2 × 2 cm³), dried *in vacuo* (0.06 mmHg), and recrystallised by vapour diffusion of ether into a wet methanol solution of the complex, 72 mg (88%) (Found: C, 29.6; H, 3.75; N, 3.25. $C_{20}H_{26}Cl_4N_2Pd_2S_4 \cdot 2H_2O$ requires C, 29.6; H, 3.70; N, 3.45%; δ_H (200 MHz, D_2O), 8.15 (2 H, t, J 8.1), 7.74 (4 H, d), 5.14, 4.92 (4 H + 4 H, quartet J 16 Hz), and 3.5–3.2 (12 H, m); m/e (f.a.b., thioglycerol matrix) 707, 705 [$Pd_2L^2Cl_2$]⁺; 672, 670 [Pd_2L^2Cl]⁺; 637, 635 [Pd_2L^2]⁺; 563, 561 [PdL^2Cl]⁺.

The following organopalladium complexes were prepared analogously. [PdL^1Cl_2] (6). M.p. > 250 °C (Found: C, 31.1; H, 3.60; N, 3.55; Pd, 26.9. $C_{20}H_{26}Cl_4N_2Pd_2S_4$ requires C, 31.0; H, 3.35; N, 3.60; Pd, 27.3%). [PdL^3Cl] Cl (4). M.p. 164–166 °C (Found: C, 34.4; H, 4.00; N, 3.45; Pd, 25.3. $C_{12}H_{17}Cl_2NPdS_2$

requires C, 34.6; H, 4.10; N, 3.35; Pd, 25.6%). Molar conductivity 132 S cm² mol⁻¹ (H_2O , 10⁻⁴ mol dm⁻³). I.r.: 1 602, 1 565 cm⁻¹ (pyridine ring). [PdL^4Cl] Cl (5). M.p. 157–158 °C (Found: C, 46.1; H, 4.30; N, 2.45; Pd, 18.9. $C_{21}H_{21}Cl_2NPdS_2$ requires C, 46.1; H, 4.20; N, 2.55; Pd, 19.2%). Molar conductivity 136 S cm² mol⁻¹ (H_2O , 10⁻⁴ mol dm⁻³).

[CuL^2] $[ClO_4]_2 \cdot H_2O$ (7). To a solution of copper(II) perchlorate (37 mg, 0.1 mmol) in dry acetone (2 cm³) was added a solution of L^2 (21.1 mg, 0.05 mmol) in dichloromethane (2 cm³). On standing, green needles formed which were filtered off, washed with acetone, and dried *in vacuo* (0–1 mmHg), 30 mg (86%) (Found: C, 34.2; H, 4.10; Cu, 8.85; N, 4.20. $C_{20}H_{26}Cl_2CuN_2O_8S_4 \cdot H_2O$ requires C, 34.2; H, 4.00; Cu, 9.05; N, 4.00%).

[CuL^2] $BF_4 \cdot CH_3CN$ (8). To a solution of [$Cu(MeCN)_4$] BF_4 (31.4 mg, 0.1 mmol) in dry acetonitrile (1 cm³) was added a solution of L^2 (21.1 mg, 0.05 mmol) in dichloromethane (1 cm³). After stirring (0.3 h), the mixture was filtered and the solution reduced to a small volume under an argon stream. A yellow microcrystalline solid separated which was filtered off, washed with ether (2 × 2 cm³), and dried *in vacuo* (0.1 mmHg), 55 mg (89%) (Found: C, 42.8; H, 4.75; N, 6.95. $C_{20}H_{26}BCuF_4N_2S_4 \cdot CH_3CN$ requires C, 42.9; H, 4.70; N, 6.80%; δ_H (200 MHz, CD_2Cl_2 – CD_3CN), 7.91 (2 H, t, J 7.0), 7.50 (4 H, d), 4.00 (8 H, s, CH_2 -py), 2.44 (8 H, t, J 6.3 Hz, CH_2S), and 1.79 p.p.m. (4 H, quintet).

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