# Cyclometallation Reactions of 6-Phenyl-2,2′-bipyridine; a Potential C,N,N-Donor Analogue of 2,2′:6′,2″-Terpyridine. Crystal and Molecular Structure of Dichlorobis(6-phenyl-2,2′-bipyridine)ruthenium(II)†

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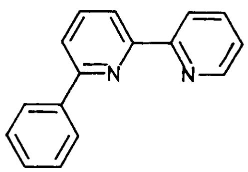
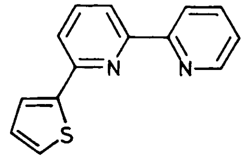
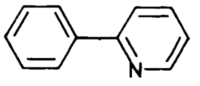
Metallated and non-metallated complexes of the ligand 6-phenyl-2,2′-bipyridine (HL) with ruthenium(II), rhodium(III), platinum(II), palladium(II), and gold(III) have been prepared. The crystal and molecular structure of the complex $[Ru(HL)_2Cl_2]$ [triclinic, $a$ = 8.671(1), $b$ = 10.360(2), $c$ = 16.139(3) Å, $\alpha$ = 89.18(2), $\beta$ = 81.26(1), $\gamma$ = 67.11(1)°, direct methods, least-squares refinement and Fourier difference synthesis, $R$ = 0.0310, $R'$ = 0.0359] indicates that it contains two *N*-bonded ligands and a *cis* arrangement of the chlorides.

Cyclometallated complexes containing polydentate ligands presenting *X,C*-donor atoms to a metal centre are well known.[1] Compounds containing *N,C*-donor ligands have proved to be of particular interest in terms of their photochemical and photophysical properties, and also as models for the development of synthetic methodology for the preparation of specific metallated complexes.[2] We have recently demonstrated the use of organomercury(II) compounds in the preparation of cyclometallated transition-metal complexes.[3] We have also demonstrated that a variety of cyclometallated and non-metallated complexes may be obtained from 2-phenyl- and 2-(2-thienyl)-pyridine derivatives.[4] In this paper we report the preparation of complexes of 6-phenyl-2,2′-bipyridine (HL), a ligand which may be regarded as a potential *C,N,N*-donor analogue of 2,2′:6′,2″-terpyridine,[5] and the structural characterisation of the *N,N*-bonded complex $[Ru(HL)_2Cl_2]$.


HL


HL$^1$


HL$^2$

## Experimental

Proton and $^{13}C$ n.m.r. spectra were recorded on Brüker WM250 or AM400 spectrometers in $CD_2Cl_2$, $CD_3CN$, or $CD_3SOCD_3$ solution, i.r. spectra on Perkin-Elmer 1710FT or 983 spectrophotometers as compressed KBr discs, and fast atom bombardment (f.a.b.) mass spectra using a Kratos MS-50 spectrometer, with acetonitrile as solvent and 3-nitrobenzyl alcohol as supporting matrix. 2-Acetylpyridine (Aldrich), acetophenone (Aldrich), gold, palladium, platinum, ruthenium, and rhodium salts (Johnson Matthey) were used as supplied; dimethyl(3-oxo-3-phenylpropyl)ammonium chloride and *N*-[2-(2-pyridyl)-2-oxoethyl]pyridinium iodide were prepared by the literature methods.[6]

*Preparations.*—*6-Phenyl-2,2′-bipyridine* (HL). Ammonium acetate (20.0 g) and *N*-[2-(2-pyridyl)-2-oxoethyl]pyridinium iodide (3.0 g, 9.2 mmol) were dissolved in acetic acid (19 cm$^3$) and heated to 115 °C for 10 min, after which dimethyl(3-oxo-3-phenylpropyl) ammonium chloride (2.0 g, 9.4 mmol) was added, and the mixture maintained at this temperature for 5 h. After this period the dark coloured solution was allowed to cool, treated with aqueous methanol, and the pale brown solid so precipitated collected by filtration. Recrystallisation from methanol yielded HL as pale brown needles (1.63 g, 76%) (m.p. 85—86 °C) (Found: C, 82.7; H, 5.2; N, 12.0. $C_{16}H_{12}N_2$ requires C, 82.8; H, 5.2; N, 12.1). I.r.: 1 561s, 1 424vs, 758vs, and 691s cm$^{-1}$. $m/z$ 232 ([HL]$^+$), and 204.

$[\{HgL(Cl)\}_n]$. Mercury(II) acetate (0.159 g, 0.5 mmol) was added to a solution of HL (0.116 g, 0.5 mmol) in EtOH (10 cm$^3$) and the mixture heated to reflux for 24 h, after which period LiCl (0.05 g) and MeOH (10 cm$^3$) were added, and the heating continued for 15 min. The hot solution was filtered through Celite, and allowed to cool, when an off-white solid was precipitated. Recrystallisation from MeOH yielded $[\{HgL(Cl)\}_n]$ (0.035 g, 15%) (Found: C, 39.9; H, 2.3; N, 5.8, $C_{16}H_{11}ClHgN_2 \cdot 0.5H_2O$ requires C, 40.25; H, 2.5; N, 5.9%). I.r.: 1 654m, 1 582m, 1 565m, 1 560m, 1 425vs, 782m, 752vs, 669m, 353m, and 329s cm$^{-1}$; $m/z$ 468 {$[HgL(Cl)]^+$}, 433 ($[HgL]^+$), and 232 ($[HL]^+$).

$[Au(HL)Cl_3]$. A solution of HL (0.024 g, 0.1 mmol) in MeCN (2.5 cm$^3$) was added to a solution of $Na[AuCl_4] \cdot 2H_2O$ (0.04 g, 0.1 mmol) in water (2.5 cm$^3$). The yellow solution was heated to reflux for 18 h, and then cooled. The yellow crystalline product was collected by filtration, washed with water (5 cm$^3$) and MeOH (5 cm$^3$), and dried to yield $[Au(HL)Cl_3]$ (0.025 g, 47%)

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

(Found: C, 36.3; H, 2.2; N, 5.4. $C_{16}H_{12}AuCl_3N_2$ requires C, 35.9; H, 2.3; N, 5.2%). I.r.: 1 588m, 1 569m, 1 447s, 819w, 760s, 698m, and 362s cm$^{-1}$.

[PdL(Cl)]. *Method (i).* A solution of HL (0.024 g, 0.1 mmol) in MeCN (2.5 cm$^3$) was added to a solution of $K_2[PdCl_4]$ (0.033 g, 0.1 mmol) in water (2.5 cm$^3$). The solution was heated to reflux for 18 h, and then cooled. The yellow crystalline product was collected by filtration, washed with water (5 cm$^3$) and hexane (5 cm$^3$), and dried to yield [PdL(Cl)] (0.032 g, 86%) (Found: C, 51.3; H, 2.9; N, 7.8. $C_{16}H_{11}ClN_2Pd$ requires C, 51.5; H, 3.0; N, 7.5%). I.r.: 1 578m, 1 569m, 1 491m, 1 464s, 757s, 469w, and 419w cm$^{-1}$. F.a.b.: *m/z* 373 {$[PdL(Cl)]^+$}, 337 ($[PdL]^+$), and 232 ($[HL]^+$).

*Method (ii).* A solution of [HgL(Cl)] (0.023 g, 0.0503 mmol) in MeCN (5 cm$^3$) was added to a hot solution of $[Pd(MeCN)_2Cl_2]$ (0.017 g, 0.0503 mmol) in MeCN (5 cm$^3$), and the mixture heated to reflux for 8 h, filtered hot, and the filtrate cooled to yield [PdL(Cl)] as a yellow microcrystalline solid (0.015 g, 81%).

$[PdL(MeCN)][PF_6]$. A solution of $[Pd(MeCN)_2Cl_2]$ (0.026 g, 0.1 mmol) in MeCN (5 cm$^3$) was heated to reflux for 2 h with HL (0.023 g, 0.1 mmol), water (3 cm$^3$) was added, and the mixture heated for a further 1 h, filtered hot, and the filtrate treated with $[NH_4][PF_6]$ to yield $[PdL(MeCN)][PF_6]$ as a yellow solid (0.044 g, 84%) (Found: C, 40.8; H, 2.9; N, 8.0. $C_{18}H_{14}F_6N_3PPd$ requires C, 41.3; H, 2.7; N, 8.0%). F.a.b.: *m/z* 337 ($[PdL]^+$).

[PtL(Cl)]. *Method (i).* A solution of $K_2[PtCl_4]$ (0.044 g, 0.106 mmol) in water (2.5 cm$^3$) was treated with a solution of HL (0.026 g, 0.112 mmol) in MeCN (2.5 cm$^3$) and the mixture heated to reflux for 14 h allowing the MeCN slowly to evaporate. The orange solid so obtained was collected by filtration, washed with water and water–EtOH (5:1), and dried *in vacuo* to yield [PtL(Cl)] (0.046 g, 94%) (Found: C, 41.6; H, 2.5; N, 6.0. $C_{16}H_{11}ClN_2Pt$ requires C, 41.6; H, 2.4; N, 6.1%). F.a.b.: *m/z* 548 ($[PtL + 122]^+$) and 426 ($[PtL]^+$).

*Method (ii).* A solution of [HgL(Cl)] (0.023 g, 0.0503 mmol) in MeCN (5 cm$^3$) was added to a hot solution of $[Pt(MeCN)_2Cl_2]$ (0.017 g, 0.0503 mmol) in MeCN (5 cm$^3$), and the mixture heated to reflux for 8 h, filtered hot, and the filtrate cooled to yield [PtL(Cl)] as an orange microcrystalline solid (0.014 g, 61%).

$[PtL(MeCN)][PF_6]$. *Method (i).* A solution of $K_2[PtCl_4]$ (0.084 g, 0.202 mmol) in water (3 cm$^3$) was treated with a solution of HL (0.050 g, 0.215 mmol) in MeCN (5.5 cm$^3$) and the mixture heated to reflux for 2 d, after which the orange precipitate was collected by filtration to yield [PtL(Cl)] (0.041 g, 44%). The filtrate was treated with an excess of $[NH_4][PF_6]$; the purple solid so obtained was collected by filtration and washed with water and water–EtOH (1:1) to yield $[PtL(MeCN)][PF_6]$ (0.04 g, 32%). Recrystallisation from MeCN by vapour diffusion of diethyl ether into the solution yielded orange needles of the complex (Found: C, 35.2; H, 2.2; N, 6.9. $C_{18}H_{14}F_6N_3PPt$ requires C, 35.3; H, 2.3; N, 6.9%). F.a.b.: *m/z* 548 ($[PtL + 122]^+$), 467 {$[PtL(MeCN)]^+$}, and 426 ($[PtL]^+$).

*Method (ii).* A solution of [PtL(Cl)] (0.023 g, 0.05 mmol) in water (3 cm$^3$) and MeCN (3 cm$^3$) was heated to reflux for 10 min, and then reduced to 4 cm$^3$ volume *in vacuo*. The orange solution was then treated with $[NH_4][PF_6]$ to yield $[PtL(MeCN)][PF_6]$ as a purple-red solid (0.027 g, 89%).

$[PtL(PhCN)][PF_6]$. The complex [PtL(Cl)] (0.019 g, 0.041 mmol) was dissolved in the minimum volume of PhCN; water (3 cm$^3$) and sufficient $Me_2CO$ were added to yield a single-phase system. An excess of $[NH_4][PF_6]$ was added and the mixture heated to reflux for 30 min, allowing the $Me_2CO$ to evaporate. The two-phase system so obtained was maintained at 0 °C for 3 d, after which the orange-red crystals formed at the interface of the aqueous and organic phases were collected by filtration to yield $[PtL(PhCN)][PF_6]$ (0.008 g, 65%) (Found: C, 41.1; H, 2.4; N, 6.0. $C_{23}H_{16}F_6N_3PPt$ requires C, 41.0; H, 2.4; N, 6.2%).

$[AuL(Cl)][AuCl_4]$. A solution of $Na[AuCl_4]$ (0.017 g, 0.043 mmol) in water (2 cm$^3$) was added to a solution of [HgL(Cl)] (0.020 g, 0.043 mmol) in MeCN (5 cm$^3$), and the solution maintained at 50 °C for 5 min, after which a yellow solid had separated. This was collected by filtration, washed with water (5 cm$^3$), MeCN (5 cm$^3$) and ether (10 cm$^3$), and dried to yield $[AuL(Cl)][AuCl_4]$ (0.008 g, 38%) (Found: C, 24.8; H, 1.35; N, 3.6. $C_{16}H_{11}Au_2Cl_5N_2$ requires: C, 23.9; H, 1.4; N, 3.5%). I.r.: 1 597vs, 1 431s, 1 311s, 783s, 772vs, 727m, 651m, 466m, 377m, and 343w cm$^{-1}$.

$[Ru(HL)_2Cl_2]$. *Method (i).* The compound $RuCl_3{\cdot}3H_2O$ (0.3 g, 0.115 mmol) and HL (0.056 g, 0.241 mmol) were heated to reflux in EtOH (7 cm$^3$) for 3 d, after which the solution was cooled and the black precipitate was collected by filtration. The solid was washed with EtOH and EtOH–$Et_2O$ (1:1) and dried *in vacuo* to yield $[Ru(HL)_2Cl_2]$ (0.038 g, 52%) (Found: C, 59.6; H, 3.6; N, 8.6. $C_{32}H_{24}Cl_2N_4Ru$ requires C, 60.4; H, 3.8; N, 8.8%). F.a.b.: *m/z* 723 {$[Ru(HL)_2Cl + 122]^+$}, 636 {$[Ru(HL)_2Cl_2]^+$}, 601 {$[Ru(HL)_2Cl]^+$}, and 565 {$[Ru(HL)_2]^+$}.

*Method (ii).* The complex $[Ru(dmso)_4Cl_2$ (dmso = dimethyl sulphoxide) (0.036 g, 0.074 mmol) and HL (0.043 g, 0.185 mmol) were heated to reflux in EtOH (4 cm$^3$) for 3 h. Work-up as above yielded $[Ru(HL)_2Cl_2]$ (0.028 g, 59%).

$[Rh(HL)_2Cl_2]Cl$. A solution of $RhCl_3{\cdot}3H_2O$ (0.027 g, 0.1 mmol) in water (2 cm$^3$) was added to a solution of HL (0.05 g, 0.217 mmol) in MeCN (3 cm$^3$) and the mixture heated to reflux for 18 h, after which the solution was filtered through Celite and the filtrate cooled to give a yellow precipitate. This was collected by filtration, washed with water and water–EtOH (5:1), and dried *in vacuo* to yield $[Rh(HL)_2Cl_2]Cl$ (0.027 g, 40%). Treatment of a solution of this complex in aqueous MeCN with $[NH_4][PF_6]$ resulted in the precipitation of $[Rh(HL)_2Cl_2][PF_6]$ as a yellow microcrystalline solid (Found: C, 48.8; H, 3.10; N, 7.45. $C_{16}H_{11}Cl_2F_6N_2PPh$ requires C, 49.1; H, 3.1; N, 7.15%). F.a.b.: *m/z* 637 {$[Rh(HL)_2Cl_2]^+$}, 566 {$[Rh(HL)_2]^+$}, 404 ($[RhLCl_2]^+$), and 334 ($[RhL]^+$).

$[RhL(MeCN)Cl_2]$. A solution of $RhCl_3{\cdot}3H_2O$ (0.10 g, 0.38 mmol) in water (4 cm$^3$) was added to a solution of HL (0.088 g, 0.38 mmol) in MeCN (4 cm$^3$) and the mixture heated to reflux for 14 h, after which period a yellow precipitate had formed. This was collected by filtration, washed with water and EtOH, and dried *in vacuo* to yield $[RhL(MeCN)Cl_2]$ (0.11 g, 65%) (Found: C, 48.3; H, 3.1; N, 9.3. $C_{18}H_{14}Cl_2N_3Rh$ requires C, 48.4; H, 3.2; N, 9.4%). F.a.b.: *m/z* 447 {$[RhL(MeCN)Cl_2]^+$}, 410 {$[RhL(MeCN)Cl]^+$}, 404 ($[RhLCl_2]^+$), 369 {$[RhL(Cl)]^+$}, and 334 ($[RhL]^+$).

*Crystal Structure Determination of* $[Ru(HL)_2Cl_2]$.—Suitable single crystals of $[Ru(HL)_2Cl_2]$ were obtained as dark red blocks by the slow diffusion of diethyl ether vapour into a $CH_2Cl_2$ solution of the complex.

*Crystal data.* $C_{32}H_{24}Cl_2N_4Ru$, dark red crystals, $M$ = 636.57, triclinic, $a$ = 8.671(1), $b$ = 10.360(2), $c$ = 16.139(3) Å, $\alpha$ = 89.18(2), $\beta$ = 81.26(1), $\gamma$ = 67.11(1)°, $U$ = 1 318.6(4) Å$^3$, $F(000)$ = 644, space group $P\bar{1}$, $Z$ = 2, $D_m$ not measured, $D_c$ = 1.60 g cm$^{-3}$, Mo-$K_\alpha$ radiation ($\lambda$ = 0.710 73 Å), $\mu$(Mo-$K_\alpha$) = 8.16 cm$^{-1}$.

*Data collection and processing.* A dark red crystal of approximate size 0.20 × 0.20 × 0.35 mm was mounted on a glass fibre. All geometric and intensity data were taken from this crystal using an automated four-circle Nicolet R3mV diffractometer equipped with graphite-monochromated Mo-$K_\alpha$ radiation. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 30 reflections taken from a rotation photograph and centred by the diffractometer. Axial photography was

**Table 1.** Atomic co-ordinates ( × $10^4$) for $[Ru(HL)_2Cl_2]$

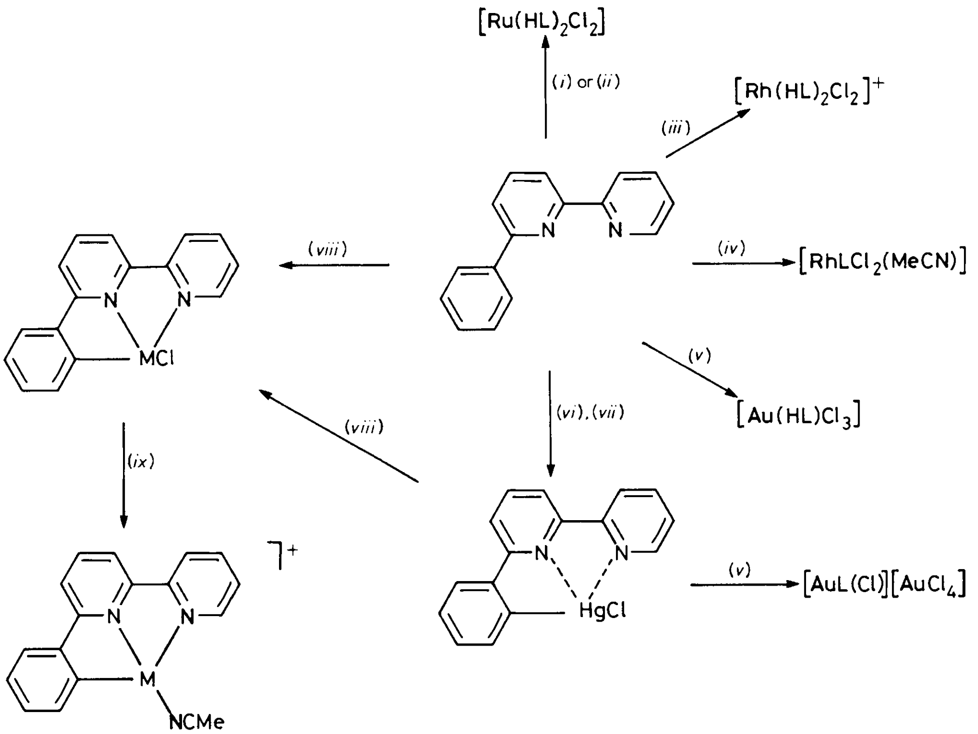
| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ru | 670(1) | −1(1) | 7 442(1) |
| Cl(1) | 1 623(1) | 1 389(1) | 6 443(1) |
| Cl(2) | 3 211(1) | −831(1) | 8 103(1) |
| N(1) | 1 796(3) | −1 491(3) | 6 466(2) |
| N(2) | −1 378(3) | 317(2) | 6 802(2) |
| N(3) | −138(3) | 1 548(3) | 8 374(2) |
| N(4) | −618(3) | −800(3) | 8 372(2) |
| C(1) | 3 485(4) | −2 248(4) | 6 278(2) |
| C(2) | 4 223(5) | −3 006(4) | 5 527(3) |
| C(3) | 3 222(5) | −2 997(4) | 4 942(2) |
| C(4) | 1 503(5) | −2 234(3) | 5 116(2) |
| C(5) | 829(4) | −1 480(3) | 5 888(2) |
| C(6) | −983(4) | −601(3) | 6 133(2) |
| C(7) | −2 201(4) | −759(4) | 5 734(2) |
| C(8) | −3 893(5) | −15(4) | 6 025(2) |
| C(9) | −4 314(4) | 937(4) | 6 693(2) |
| C(10) | −3 042(4) | 1 121(3) | 7 046(2) |
| C(11) | −3 594(4) | 2 310(3) | 7 678(2) |
| C(12) | −3 006(4) | 3 375(3) | 7 543(2) |
| C(13) | −3 668(5) | 4 566(4) | 8 076(3) |
| C(14) | −4 910(5) | 4 681(4) | 8 764(3) |
| C(15) | −5 487(5) | 3 623(4) | 8 907(2) |
| C(16) | −4 851(4) | 2 443(4) | 8 362(2) |
| C(17) | 336(5) | 2 649(4) | 8 358(2) |
| C(18) | −24(5) | 3 538(4) | 9 046(3) |
| C(19) | −901(5) | 3 319(4) | 9 784(2) |
| C(20) | −1 377(4) | 2 191(4) | 9 818(2) |
| C(21) | −961(4) | 1 318(3) | 9 105(2) |
| C(22) | −1 372(4) | 78(3) | 9 074(2) |
| C(23) | −2 531(4) | −142(4) | 9 698(2) |
| C(24) | −2 978(5) | −1 250(4) | 9 614(3) |
| C(25) | −2 257(5) | −2 139(4) | 8 911(2) |
| C(26) | −1 043(4) | −1 935(3) | 8 315(2) |
| C(27) | −169(5) | −3 014(4) | 7 629(2) |
| C(28) | 1 565(6) | −3 775(4) | 7 544(3) |
| C(29) | 2 353(8) | −4 878(4) | 6 946(3) |
| C(30) | 1 458(11) | −5 216(5) | 6 443(4) |
| C(31) | −271(11) | −4 482(7) | 6 510(3) |
| C(32) | −1 120(7) | −3 365(5) | 7 115(3) |

**Table 2.** Selected bond lengths (Å) and angles (°) for $[Ru(HL)_2Cl_2]$

| | | | |
|---|---|---|---|
| Ru–Cl(1) | 2.410(1) | Ru–N(2) | 2.103(3) |
| Ru–Cl(2) | 2.439(1) | Ru–N(3) | 2.050(3) |
| Ru–N(1) | 2.061(2) | Ru–N(4) | 2.089(3) |
| Cl(1)–Ru–Cl(2) | 95.3(1) | N(1)–Ru–N(3) | 171.5(1) |
| Cl(1)–Ru–N(1) | 81.4(1) | N(2)–Ru–N(3) | 107.4(1) |
| Cl(2)–Ru–N(1) | 92.5(1) | Cl(1)–Ru–N(4) | 167.6(1) |
| Cl(1)–Ru–N(2) | 89.3(1) | Cl(2)–Ru–N(4) | 92.2(1) |

## Results and Discussion

The ligand 6-phenyl-2,2′-bipyridine (HL) is readily prepared in 76% yield by a Kröhnke synthesis of an enone equivalent with an enolate equivalent in the presence of a large excess of ammonium acetate.[6] The electron-impact mass spectrum of HL exhibits a highest mass peak at *m*/*z* 232, which corresponds to the parent ion. The $^1H$ and $^{13}C$ n.m.r. spectra of the free ligand were analysed in some detail, as chemical shift differences provide a sensitive means of determining the site of metallation



**Scheme.** (*i*) $RuCl_3$; (*ii*) $[Ru(dmso)_4Cl_2]$; (*iii*) $RhCl_3$, 2 equiv. HL; (*iv*) $RhCl_3$, 1 equiv. HL; (*v*) $[AuCl_4]^-$; (*vi*) $Hg(O_2CMe)_2$; (*vii*) LiCl; (*viii*) $[MCl_4]^{2-}$ (M = Pd or Pt); (*ix*) MeCN

to be a mononuclear species, in which the cyclometallated ligand acts as a terdentate *C,N,N*-donor.

The interaction of HL with gold(III) compounds was investigated under a number of conditions. In aqueous acetonitrile solution, at 100 or 30 °C, the only product obtained from the reaction of HL with $M[AuCl_4]$ (M = H or Na) was the complex $[Au(HL)Cl_3]$. The same product was obtained after prolonged reaction times, or upon performing the reaction in 2-methoxyethanol. The complex is insoluble in water but is readily soluble in chlorinated solvents or $CD_3SOCD_3$. The $^1H$ n.m.r. spectra in $CD_2Cl_2$ and $CD_3SOCD_3$ differ considerably (Table 3), but COSY spectra reveal a total of 12 aromatic protons in each case. The phenyl ring is rotating freely and gives rise to only three resonances, of intensity 2:2:1. The differences are probably due to the displacement of a co-ordinated chloride by dmso in the latter solvent. The i.r. spectrum exhibits an Au–Cl stretching mode at 362 $cm^{-1}$ similar to that observed at 363—366 $cm^{-1}$ for $[Au(py)Cl_3]$ (py = pyridine)[9] Accordingly, we consider that this complex contains a monodentate *N*-donor HL ligand, and an analysis of the chemical shift data suggests that it is the terminal pyridine ring that is co-ordinated. This is similar to the bonding mode observed in the complex $[Au(HL^1)Cl_3]$ [$HL^1$ = 6-(2-thienyl)-2,2′-bipyridine] which we have previously described.[4] However, the complex with HL differs from $[Au(HL^1)Cl_3]$ in its chemical behaviour. The latter compound is readily converted into the cyclometallated species $[AuL^1Cl_2]$ upon warming to 60 °C in MeCN; in contrast, $[Au(HL)Cl_3]$ is recovered unchanged after prolonged heating in a range of solvents. We have been unable to convert $[Au(HL)Cl_3]$ into a cyclometallated compound under any conditions.

However, the reaction of $[HgL(Cl)]$ with $[AuCl_4]^-$ in aqueous acetonitrile results in a transmetallation reaction and the precipitation of the yellow cyclometallated salt $[AuL(Cl)][AuCl_4]$. The $^1H$ n.m.r. spectrum of the complex clearly shows only 11 resonances, and a COSY spectrum allows an unambiguous assignment. The significant feature is the loss of one of the aromatic resonances assigned to the phenyl ring, and a change in symmetry such that the four remaining phenyl protons are all non-equivalent. The chemical shifts of the phenyl protons are remarkably similar to those observed for $[AuL^2Cl_2]$, ($HL^2$ = 2-phenylpyridine) lending further support to the metallated formulation.

The reaction of HL with $[MCl_4]^{2-}$ (M = Pd or Pt) in aqueous MeCN results in the formation of the complexes $[ML(Cl)]$, with no evidence for the intermediate formation of non-metallated compounds. The f.a.b. mass spectra of the complexes exhibit peaks due to $[ML]^+$, and in the case of the palladium compound $[PdL(Cl)]^+$ also. The complexes frequently exhibit echo peaks at 122 mass units higher than the expected ions; we have observed this feature in other f.a.b. mass spectra using 3-nitrobenzyl alcohol as a matrix. Solutions of the complexes give the expected $^1H$ n.m.r. spectra containing 11 aromatic resonances (Table 3), and COSY spectra allow unambiguous assignment of these. The combination of the available spectroscopic data suggests a distorted square-planar C,N,N,Cl environment about the metal ions, in which the ligand is cyclometallated and terdentate. The same metallated complexes were obtained from the transmetallation reactions of $[HgL(Cl)]$ with $[MCl_4]^{2-}$.

The solution chemistry of $[PtL(Cl)]$ in MeCN {but *not* $[PdL(Cl)]$} exhibits a variety of confusing but repeatable colour changes. The reactiom of $[PtL(Cl)]$ with nitriles leads to the formation of *orange* solutions containing the cations $[PtL(RCN)]^+$, from which the salts $[PtL(RCN)][PF_6]$ may be obtained by the addition of $[NH_4][PF_6]$. The addition of $[NH_4][PF_6]$ to *orange* solutions containing $[PtL(MeCN)]^+$ results in the precipitation of ***purple-red*** solids for which microanalysis confirms the stoicheiometry $[PtL(MeCN)][PF_6]$. The salt $[PtL(MeCN)][PF_6]$ dissolves in $CD_3CN$ to give an *orange* solution in which the aromatic region of the $^1H$ n.m.r. spectrum is identical to that of a solution of $[PtL(CD_3CN)]^+$ prepared *in situ*. The $^1H$ n.m.r. spectrum of $[PtL(MeCN)][PF_6]$ in $CD_3CN$ exhibits a resonance at δ 2.65 showing satellites due to $^1H$–$^{195}Pt$

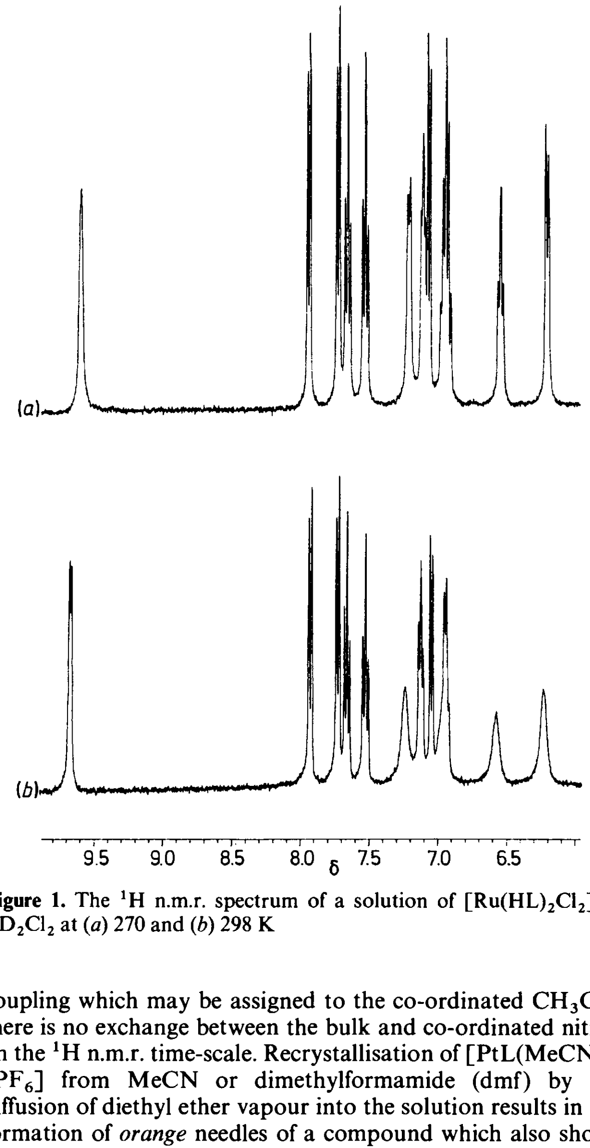


**Figure 1.** The $^1H$ n.m.r. spectrum of a solution of $[Ru(HL)_2Cl_2]$ in $CD_2Cl_2$ at (*a*) 270 and (*b*) 298 K

coupling which may be assigned to the co-ordinated $CH_3CN$; there is no exchange between the bulk and co-ordinated nitrile on the $^1H$ n.m.r. time-scale. Recrystallisation of $[PtL(MeCN)][PF_6]$ from MeCN or dimethylformamide (dmf) by the diffusion of diethyl ether vapour into the solution results in the formation of *orange* needles of a compound which also shows the stoicheiometry $[PtL(MeCN)][PF_6]$. The $^1H$ n.m.r. spectrum of the *orange* solution of this salt is identical to that of the red-purple compound and the salt prepared *in situ*. We believe that these colour changes are indicative of linear metal–metal stacking interactions in the freshly precipitated (red-purple) form of the complex. Support for this comes from the observation that the addition of $[PtCl_4]^{2-}$ to solutions containing $[PtL(MeCN)]^+$ results in the formation of dark blue solids. We have been unable to obtain the red-purple form of the complex in crystalline form. The phenomenon is not simply due to microcrystallite size; streaking the two complexes on a porous plate results in the formation of red and orange streaks respectively. In contrast to this behaviour, salts of $[PtL(PhCN)]^+$ or $[PdL(MeCN)]^+$ {prepared from the reaction of $[Pd(MeCN)_2Cl_2]$ with HL} can only be obtained in the orange form. This latter observation is consistent with metal–metal interactions involving *d*-orbital overlap in the case of the red-purple form of $[PtL(MeCN)][PF_6]$. The orange form of $[PtL(MeCN)][PF_6]$ forms long, thin needle-like crystals, and a preliminary structural investigation confirms the presence of the expected *C,N,N*-bonded ligand and *N*-bonded nitrile. The cations form discrete dimeric units with short Pt $\cdots$ Pt contacts of approximately 3.3 Å.[10]

In view of the facile formation of cyclometallated complexes with HL we have attempted to form octahedral complexes of $d^6$ metal ions containing this form of the ligand. Related complexes of *N,C*-donor ligands have been shown to possess useful photochemical and photophysical properties,[2] and we considered that terdentate analogues might prove to be of interest. The reaction of HL with $RuCl_3{\cdot}3H_2O$ in ethanol yields the complex $[Ru(HL)_2Cl_2]$ as a very dark red crystalline solid. The same complex was also obtained from the reaction of $[Ru(dmso)_4Cl_2]$ with HL in EtOH. A complex of this stoicheiometry may form two *trans* and three *cis* isomers, which differ in the relative orientation of the phenyl groups. The $^1H$ n.m.r. spectrum of either crude or recrystallised samples of the complex exhibited aromatic resonances due to a single environment for the HL ligand, and also confirmed the non-metallated nature of the ligand. The $^1H$ n.m.r spectra of samples prepared from the ruthenium(III) starting material were often broadened and shifted, and considerable care was required to remove traces of paramagnetic impurities. The $^1H$ n.m.r. spectra of highly purified samples reveal sharp resonances for the pyridine protons, but at room temperature the resonances assigned to the phenyl ring are considerably broadened; upon cooling these resonances become well resolved (Figure 1). We have observed a similar phenomenon in ruthenium(II) and rhodium(III) complexes of 6-(2-thienyl)-2,2′-bipyridine ($HL^1$) in which the ligand acts as an *N,N*-donor.[4] We believe that this broadening is associated with restricted rotation of the non-co-ordinated aryl groups about the interannular C–C bonds. Specifically, we have shown that the non-co-ordinated aryl rings in complexes of HL and $HL^1$ are involved in stacking interactions with adjacent pyridine rings; the stacking interaction essentially 'locks' the aryl ring. At low temperatures the free aryl ring is static, but at higher temperatures a rocking motion about the interannular bond becomes accessible. We have not observed a coalescence of the signals, and at room temperature the complexes are close to a frozen limit. In no case have we observed free rotation of non-co-ordinated aryl groups in octahedral complexes. Of the five possible isomers, all but one of the *cis* forms possess only one ligand environment, and to clarify which single isomer is formed the crystal structure of the complex was determined.

The crystal and molecular structure of one of the two enantiomers of the complex $[Ru(HL)_2Cl_2]$ is shown in Figure 2, and relevant structural parameters are reported in Table 2. The structural determination confirms the *cis* configuration of the chloride ligands and the overall approximate octahedral $N_4Cl_2$ donor set in the complex. The Ru–Cl distances of 2.410(1) and 2.439(1) Å differ slightly from those observed in $[Ru(bipy)_2Cl_2]{\cdot}H_2O$,[11] whilst the two *trans* Ru–N distances [Ru(1)–N(1) 2.061(2); Ru–N(3) 2.050(3) Å] and the two *cis* Ru–N distances [Ru–N(2) 2.103(3); Ru–N(4) 2.089(3) Å] closely resemble those in $[Ru(bipy)_2Cl_2]{\cdot}H_2O$ (2.053 and 2.013 Å respectively).[11] The co-ordination geometry is distorted from octahedral by the constraints of the chelating ligand and the N–Ru–N angles within the same ligand [N(3)–Ru–N(4) 78.7(1); N(1)–Ru–N(2) 78.5(1)°] are typical of a co-ordinated 2,2′-bipyridine and closely resemble the N–Ru–N angle of 79.1° observed in $[Ru(bipy)_2Cl_2]{\cdot}H_2O$.[11] The structural analysis confirms the highly symmetric arrangement which renders the two ligands chemically and magnetically equivalent on the n.m.r. time-scale in solution. The configuration of the ligands is dictated by a stacking arrangement of the phenyl rings with the terminal pyridine ring of the other ligand in the molecule, and this results in a considerable distortion of the HL molecule from planarity. The torsion angles between the two pyridyl rings in the two crystallographically independent 2,2′-bipyridyl fragments are 17.5 and 13.0°; these angles are significantly larger than those observed in $[Ru(bipy)_2Cl_2]{\cdot}H_2O$[11] and represent a distortion of the 2,2′-bipyridyl fragment to allow the phenyl ring to move into an optimal position for stacking. It is

**Table 3.** Proton n.m.r. spectroscopic data for complexes of HL[a]

| | $H^{6'}$ | $H^{5'}$ | $H^{4'}$ | $H^{3'}$ | $H^{3}$ | $H^{4}$ | $H^{5}$ | $H^{2''}$ | $H^{3''}$ | $H^{4''}$ | $H^{5''}$ | $H^{6''}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HL[b] | 8.68 | 7.34 | 7.88 | 8.64 | 8.39 | 7.91 | 7.83 | 8.18 | 7.53 | 7.48 | 7.53 | 8.18 |
| [HgL(Cl)][b] | 8.72 | 7.39 | 7.89 | 8.36 | 8.43 | 7.99 | 7.86 | | | (7.58, 7.47, 7.50, 7.58) | | |
| $[Au(HL)Cl_3]$[b] | 9.07 | 7.78 | 8.27 | 8.21 | 8.10 | 7.88 | 8.10 | 8.35 | 7.56 | 7.53 | 7.56 | 8.35 |
| $[Au(HL)Cl_3]$[c] | 8.72 | 7.55 | 8.25 | 8.59 | 8.35 | 8.01 | 8.05 | 8.25 | 7.51 | 7.48 | 7.51 | 8.25 |
| [PdL(Cl)][b] | 8.73 | 7.54 | 8.00 | 8.00 | 7.67 | 7.90 | 7.56 | | | (7.37, 7.09, 7.09, 7.62) | | |
| [PdL(Cl)][c] | 8.66 | 7.80 | 8.24 | 8.24 | 8.53 | 8.19 | 8.04 | | | (7.66, 7.09, 7.09, 7.54) | | |
| [PtL(Cl)][b] | 8.96 | 7.56 | 8.05 | 7.90 | 7.60 | 7.82 | 7.56 | | | (7.32, 7.08, 7.18, 7.45) | | |
| [PdL(MeCN)]Cl[d] | 8.20 | 7.55 | 8.08 | 7.91 | 7.55 | 7.80 | 7.40 | | | (7.20, 6.95, 7.08, 6.85) | | |
| [PtL(MeCN)]Cl[d] | 8.47 | 7.68 | 8.18 | 7.99 | 7.60 | 7.85 | 7.50 | | | (7.29, 7.08, 7.08, 6.99) | | |
| $[AuL(Cl)][AuCl_4]$ | 8.95 | 8.11 | 8.59 | 8.86 | 8.65 | 8.48 | 8.65 | | | (8.05, 7.53, 7.42, 7.60) | | |
| $[Rh(HL)_2Cl_2]Cl$[b] | 9.38 | 7.42 | 7.97 | 8.24 | 8.60 | 8.29 | 7.39 | | (6.68, 6.97, 7.17, 7.08, 7.40) | | | |
| $[RhL(MeCN)Cl_2]$[b] | 9.25 | 7.82 | 8.11 | 8.21 | 7.83 | 7.92 | 7.83 | | | (7.72, 7.18, 7.36, 7.72) | | |
| $[Ru(HL)_2Cl_2]$[b] | 9.66 | 7.12 | 7.55 | 7.72 | 7.92 | 7.65 | 7.08 | | (6.21, 6.57, 6.95, 6.95, 7.23) | | | |

[a] Proton assignments as shown in Figure 3. [b] In $CD_2Cl_2$. [c] In $CD_3SOCD_3$. [d] In $CD_3CN$.

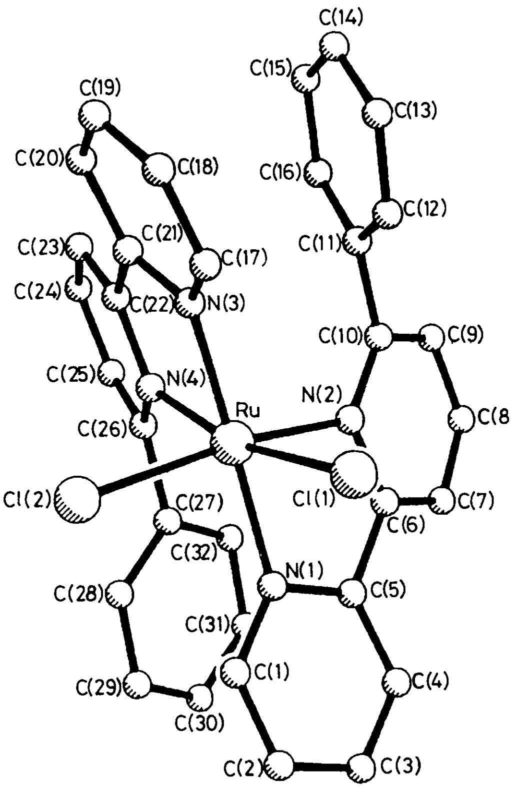


**Figure 2.** The crystal and molecular structure of one of the two enantiomers of $[Ru(HL)_2Cl_2]$ showing the numbering scheme adopted. Hydrogen atoms have been omitted for clarity

this twisting about the interannular bonds which results in the considerable differences between the n.m.r. spectra of $[Ru(bipy)_2Cl_2]$ and $[Ru(HL)_2Cl_2]$. We have observed very similar stacking phenomena in double helical binuclear complexes of 2,2′:6′,2″:6″,2‴,:6‴,2⁗-quinquepyridine, in which stacking interactions play a vital role in the self-assembly of the helix.[12] In order to achieve near-coplanarity and stack with the other ligand, it is necessary for a major twist about the C–C bond connecting the phenyl and pyridyl rings. The torsion angles in the two ligand molecules are 123.2 and 119.9° (yielding torsion angles between the phenyl rings and the terminal pyridine rings of the same ligand of 109.3 and 109.6° respectively). The outcome of these distortions is a stacking interaction between the phenyl group of one ligand and the terminal pyridine ring of the other; the two rings are not coplanar, but at 18.3 and 18.0° for the two independent interactions. The interplanar distances are 3.508 and 3.493 Å for the two interactions, which are extremely similar to the interplanar distances we have observed in pyridine–pyridine stacking interactions in double helical binuclear complexes.

The reaction of $RhCl_3 \cdot 3H_2O$ with 2 equivalents of HL in aqueous MeCN yields a yellow solid shown to be $[Rh(HL)_2Cl_2]Cl$. This compound could have a total of five isomers (excluding enantiomers) in the same way as $[Ru(HL)_2Cl_2]$; once again it is significant that the $^1H$ n.m.r. spectra of crude and recrystallised samples indicate the formation of a single isomer. The chemical shifts are consistent with the formation of the same isomer as has been structurally characterised for the ruthenium complex, indicating the importance of the π-stacking interactions in dictating the configuration of complexes of this type. In contrast to the ruthenium complex, the $^1H$ n.m.r. spectrum of this complex is sharp and well resolved at room temperature, with no evidence for any mobility of the phenyl groups. It is clear that in the rhodium complex the room-temperature spectrum represents a 'frozen' species rather than one with free rotation of the phenyl rings, as all five phenyl protons are chemically and magnetically inequivalent, as in the ruthenium(II) complex. The differences arise in the degree of motion which is permitted; in the case of the ruthenium(II) complex there is sufficient motion to broaden the signals due to the phenyl protons, although they still remain magnetically non-equivalent, indicating a 'rocking' rather than a rotation.

In contrast to the reaction with 2 equivalents of HL, treatment of $RhCl_3 \cdot 3H_2O$ with 1 equivalent of HL results in the formation of the cyclometallated complex $[RhL(MeCN)Cl_2]$. The $^1H$ n.m.r. spectrum of this complex clearly exhibits only 11 aromatic resonances in accord with the cyclometallated structure (Figure 3). We propose a cyclometallated *C,N,N*-terdentate bonding mode for the ligand in this complex, with one co-ordinated nitrile ligand. The co-ordinated nitrile is

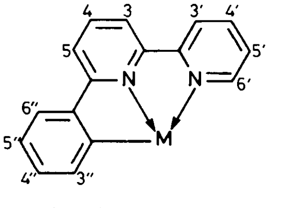


**Figure 3.** Cyclometallated bonding mode showing numbering scheme for protons

observed as a singlet at $\delta$ 2.65 in the $^{1}$H n.m.r. spectrum of the complex.

In conclusion, we have shown that the ligand 6-phenyl-2,2′-bipyridine may bond to transition metals in a variety of manners. In particular, the terdentate cyclometallated bonding mode is of interest as an analogue of the *N,N,N*-donor ligand 2,2′:6′,2″-terpyridine. The presence of a non-co-ordinated phenyl ring in complexes of HL may lead to intra- or inter-molecular stacking interactions which may distort the ligand and result in the formation of particularly stable complexes. We are currently investigating the photochemical properties of these complexes.

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