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Selective synthesis of U-shaped terpyridines. Versatile ligands for the preparation of platinum complexes

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The development of a simple and highly selective method for the preparation of substituted U-shaped terpyridines is described. The treatment of imine **5** with ternary iminium salts **2** leads to the terpyridines **4**. A possible mechanism is discussed. The terpyridine derivatives are used for the preparation of several platinum(II) complexes **14**. Complex **14e** is characterized by single-crystal X-ray analysis.

Introduction

The design of oligopyridines and related compounds has recently been the subject of intensive investigations. Ligands bearing 2,2′-bipyridine, 2,2′:6′,2″-terpyridine or 1,10-phenanthroline subunits are extremely versatile building blocks for the construction of metallo-supramolecular systems.[1–3] In recent years, interest has focused on polypyridine derivatives, which can be used for the synthesis of luminescent and redox-active polynuclear ruthenium complexes where energy- and/or electron-transfer processes can be induced by light.[4–7] A variety of potential applications such as artificial photosynthesis,[8] photocatalysis,[9] molecular photovoltaic cells,[10] molecular informatics[11] and opto-electronic devices[12,13] are beginning to emerge from this new field of research. Fused polypyridine compounds also constitute an effective route to preorganised clefts and cavities for the complexation of metals[14–16] and organic guests.[17,18] Previously, several toroidal macrocycles having potentially useful metal binding properties[15] have been synthesized.[19]

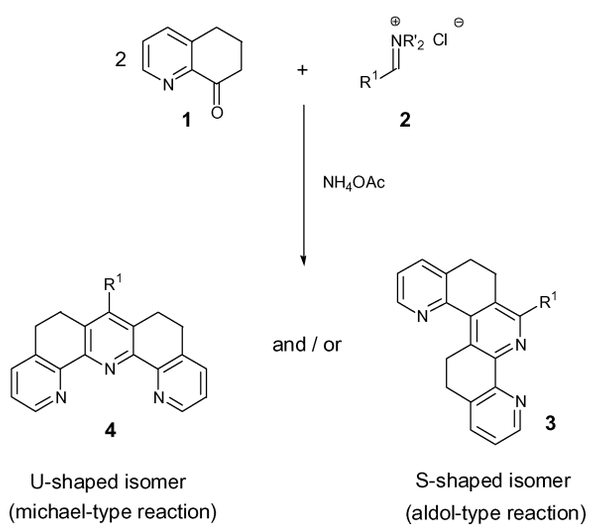
Lippard's findings that (2,2′:6′,2″-terpyridine)-platinum(II) complexes bind to double-stranded DNA by intercalation have led to new approaches in cancer therapy.[20] Recently, Lowe *et al*. have shown that terpyridine–platinum(II) complexes also exhibit cytotoxity against a number of ovarian tumour cell lines.[21–25] Several of these compounds showed even greater activities than carboplatin, a therapeutic agent widely used for the treatment of human ovarian cancers.

In view of these attractive applications, we were interested in simple synthetic methods for the preparation of oligopyridines bearing either 2,2′-bipyridine, 2,2′:6′,2″-terpyridine or 1,10-phenanthroline subunits.

Different methologies[26–30] have been developed for these heterocycles, but due to their great importance, the development of novel and more flexible synthetic methods still remains an active area of research. Our studies in the field of ternary iminium salts have led to the development of highly efficient one-pot domino-type reactions yielding a wide range of substituted pyridines, bipyridines or terpyridines.[31–36] Domino reactions offer many advantages compared to traditional syntheses, such as minimization of waste and the consumption of solvents, reagents, adsorbents and energy.

Results and discussion

As shown earlier, the reaction of one equivalent of an iminium salt and two equivalents of 5,6,7,8-tetrahydroquinolinone in the presence of ammonium acetate leads to the formation of a mixture of S- and U-shaped substituted terpyridines (Scheme 1).[31] The two isomers are formed *via* different reaction pathways. So far, we assumed them to be comparable with an aldol-type and a Michael-type reaction. Yet, it has not been possible to influence the ratio in which the two isomers are formed. Therefore, our efforts concentrated on mechanistic studies. Our main goal was to develop a new method, that allows us to synthesize the U-shaped terpyridines selectively in good yields.



Scheme 1 Synthesis of U- and S-shaped terpyridines **3** and **4** in a domino reaction.

The method we used in the past was a one-pot reaction in which ketone **1** and iminium salt **2** are reacted in the presence of a large excess of ammonium acetate (3 eq.). These conditions result in the formation of rather large quantities of the S-shaped isomer **3** whereas the U-isomers **4** often can only be isolated in low yields (Table 1, Method A). We presume, that imine **5** is initially formed by the reaction of ammonium acetate with ketone **1** as similar conditions are often used in the literature for the preparation of imines.[37] The nucleophilic addition of **5** to the iminium salt **2** affords **6**. Previously, intermediates such as **6** have been isolated in our research group.[38] The reaction sequence is expected to be initiated by the formation of imine **5**, as NMR experiments showed that ternary iminium salts do not react with ketone **1**. Consecutive deprotonation of the iminium salt and reprotonation at the secondary amino group affords hydrochlorides **7**. It is well

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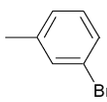
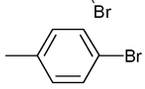
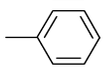
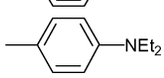
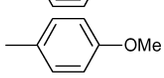
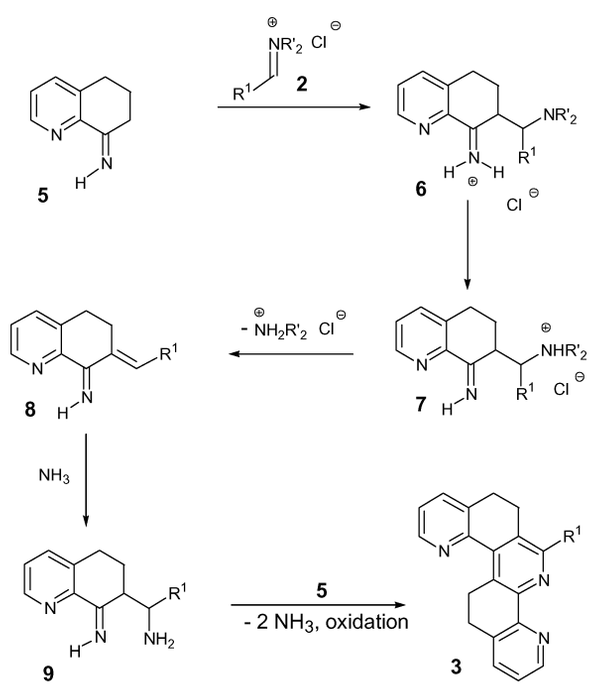
Table 1 Product distribution using the one-pot method (method A) and the sequential method (method B)

Iminium salt **2**	R^1	Method	Solvent	Product	Ratio S : U isomer	Yield (%)[b]
2a		A	$CHCl_3$	**3a**	72 : 0	72
		B	DMSO	**4a**	5 : 65	70
2b		A	$CHCl_3$	**3b**	52 : 8	71
		B	DMSO	**4b**	7 : 66	73
2c		A	CH_3CN	**3c**	45 : 39	84
		B	DMSO	**4c**	0 : 64	64
2d[a]		A	$CHCl_3$	**3d**	46 : 49	95
		B	DMSO	**4d**	0 : 44	44
2e		A	DMF	**3e**	31 : 29	60
		B	DMSO	**4e**	0 : 61	61
2f		A	CH_3CN	**3f**	5 : 19	24
		B	DMSO	**4f**	0 : 73	73

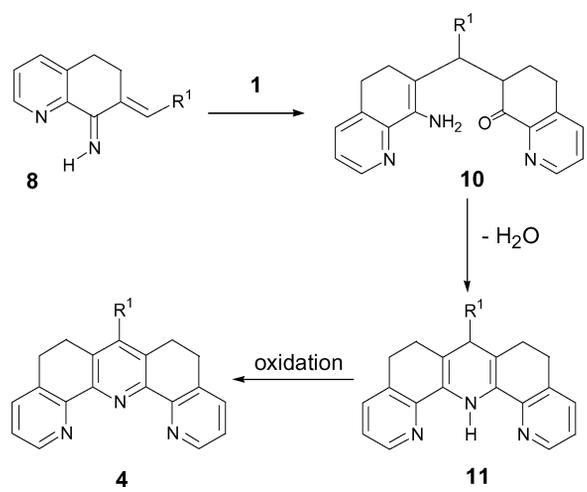
[a] Perchlorate. [b] Isolated yield after column chromatography on neutral Al_2O_3.

known, that Mannich bases easily undergo thermal elimination of amine yielding α,β-unsaturated ketones.[32,39] Here, the reaction leads to the Michael acceptor **8**. The S-shaped terpyridines **3** result from a condensation of **5** with β-amino imine **9**, which is formed by Michael-addition of ammonia to **8** (Scheme 2). A very similar mechanism has been discussed by Bell *et al.*, who have applied this method successfully to the synthesis of heptacyclic terpyridyl clefts.[15] Both studies let us conclude, that the large excess of ammonia present in the reaction mixture strongly favours the formation of **9** which in consequence leads to the S-shaped terpyridine **3**.



Scheme 2 Postulated mechanism for the formation of the S-shaped isomer **3**.

As a result of these considerations, a new method (Table 1, method B) was evolved in which imine **5** is synthesized separately by preheating ketone **1** with one equivalent of ammonium acetate in DMSO. Thereafter, the iminium salt **2** (1 eq.) and further ketone **1** (1 eq.) are added to the solution of **5**. Actually, the formation of the S-isomer is suppressed while the yield of the U-isomer is strongly increased. The postulated mechanism is shown in Scheme 3. Just like in case of the S-shaped isomer **3** the reaction sequence proceeds via intermediate **8**. The Michael acceptor **8** is efficiently trapped by the ketone **1** (and not by ammonia) to afford the Michael-addition product **10**. Subsequent cyclization to **11** and oxidation of this dihydropyridine then leads to the U-shaped terpyridines **4**.



Scheme 3 Synthesis of U-shaped terpyridines **4**.

Since the iminium salts **2d–f** are hydrolyzed very easily, the imine **5** should be prepared in the presence of molecular sieves, trapping the water formed during the condensation reaction. The hydrolysis of the iminium salts can be prevented increasing the yield of the U-shaped terpyridine. In conclusion, this new method allows synthesizing U-shaped terpyridines in very good yields, selectively.

Another of our interests was to investigate, if these terpyridine derivatives **4** could be used for the preparation of platinum(II) complexes. On the preparative basis of the reaction described above, we employed a procedure developed by Lowe and Vilaivan.[25] $Pt(COD)I_2$ (**12**) is treated with silver tetrafluoroborate in acetone followed by the addition of the U-shaped terpyridine **4** in acetonitrile to give an acetonitrile terpyridine–platinum(II) bis(tetrafluoroborate) complex **13**. The acetonitrile ligand can be displaced easily by donor-ligands, such as 4-picoline, to yield the platinum complexes **14** (Scheme 4). This protocol was applied to several differently substituted terpyridines to give the products in very good yields (Table 2).

The crystal structure of **14e** shows distorted square planar coordination geometry of the Pt atom (Fig. 1).

Since the terpyridine ligand does not have an ideal tridentate bite, the bond length Pt–N(2) (1.926(7) Å) is significantly shorter than the Pt–N(1) and Pt–N(3) bonds (2.043(8) Å,

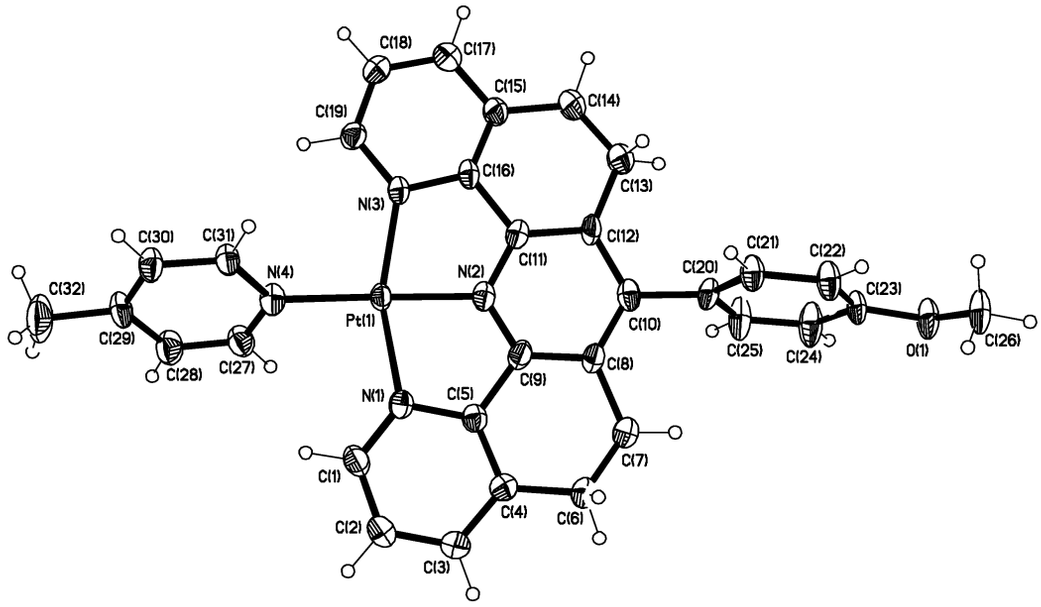
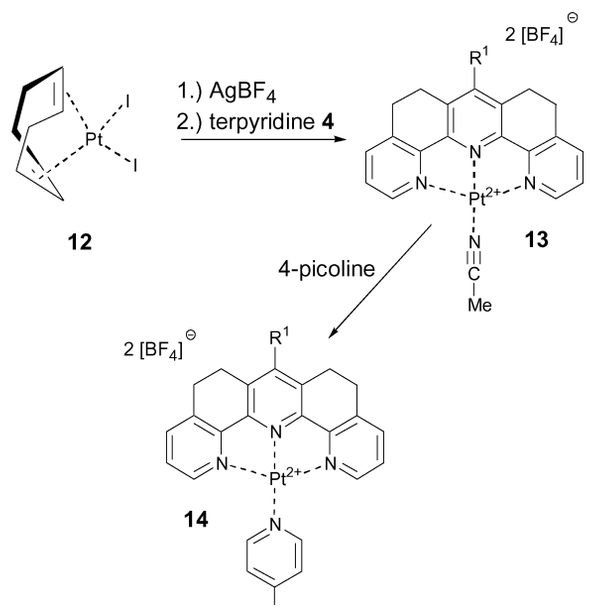


Fig. 1 Molecular structure of the cation of **14e**. Selected bond lengths (Å) and angles (°): Pt–N1 2.043(8), Pt–N2 1.926(7), Pt–N3 2.048(8), Pt–N4 2.021(7), N2–Pt–N4 178.6(3), N2–Pt–N1 79.6(3), N4–Pt–N1 99.6(3), N2–Pt–N3 80.4(3), N4–Pt–N3 100.4(3), N1–Pt–N3 160.0(3). The Pt atom lies 0.016 Å above the N_4-plane.



Scheme 4 Preparation of terpyridine platinum(II) complexes **14**.

Table 2 Synthesis of terpyridine platinum(II) complexes **14**

P(II)-complex **14**	U-terpyridine **4**	Yield (%)[a]
14a	**4a**	66
14b	**4b**	63
14c	**4c**	72
14d	**4d**	50
14e	**4e**	60
14f	**4f**	51

[a] Isolated yield after crystallization from CH_3CN–E_2O.

2.048(8) Å respectively). Observations for similar complexes made by Lowe *et al*. suggest that this distortion results in a *trans*-effect which in consequence should weaken the Pt–N(4) (2.021(7) Å) bond.[24] Therefore, the substitution of the 4-picoline ligand by an associative mechanism is strongly favoured. Obviously, the *trans*-effect is responsible for the unusual ease of substitution of the 4-picoline ligand by a nucleobase. The high activity of terpyridine–platinum(II) complexes against ovarian tumour cell lines is likely to be a result of this property.[21,40]

So far, only derivatives with ethylene bridges have been synthesized. Since this new method should allow the preparation of terpyridines with varying tridentate bite angles, a large number of complexes with high chemical diversity can be envisioned. The direct modulation of the Pt–N(2) bond length should be possible thereby determining the activity of platinum complexes.

Experimental

General

All reagents were purchased from commercial sources and used without further purification unless specified. All solvents were dried and distilled according to standard procedures and stored under argon. Chromatographic separation was performed on aluminum oxide (neutral, Akt. III, Fa. Macherey & Nagel, 0.063–0.200 mm). Melting points were obtained on a Büchi SMP-20 mp apparatus and are uncorrected. IR spectra were measured on a Nicolet 510 P FT-IR spectrometer. All NMR spectra were recorded on a Bruker ARX 200 instrument (200 bzw, 50 MHz). Mass spectrometry was carried out using a Finigan MAT 8200 (EI MS, 70 eV) or a Finnigan MAT 8230 apparatus (FAB MS, *m*-nitrobenzyl alcohol matrix). Elemental analyses were obtained on a Perkin-Elmer M240 analyzer. UV spectra were measured on a Shimadzu UV-2101 PC spectrometer. Ketone **1** and iminium chlorides **2** were prepared by procedures described in the literature.[41–45]

General procedure for the synthesis of substituted U-shaped terpyridines 4a–c

A solution of 5,6,7,8-tetrahydroquinolinone **1** (150 mg, 1.01 mmol) and ammonium acetate (85 mg, 1.1 mmol) in dry DMSO (10 ml) was heated at 85 °C for 5 min. In a second flask 5,6,7,8-tetrahydroquinolinone **1** (150 mg, 1.01 mmol) and iminium salt **2** (291 mg, 1.01 mmol) were dissolved in dry DMSO (10 ml). The solution of the iminium salt and the ketone was then added to the solution of the freshly prepared imine **5** and heated for 16 h at 120 °C. The reaction mixture was cooled to room temperature and water (40 ml) was added. The solution was then extracted with CH_2Cl_2 (3 × 30 ml). The combined organic layers were washed with water (3 × 20 ml)

and dried over $MgSO_4$. After removal of the solvent, the residue was purified by chromatography on Al_2O_3.[46]

5,6,8,9-Tetrahydro-7-(3′-bromophenyl)quino[8,7-*b*][1,10]-phenanthroline (4a). Prepared from **1** (600 mg, 4.02 mmol), 3-brombenzylidenemorpholinium chloride **2a** (580 mg, 2.01 mmol) and ammonium acetate (170 mg, 2.20 mmol). Yield: 573 mg (65%), yellow powder, after chromatography on Al_2O_3, CH_2Cl_2; CH_2Cl_2–MeOH, 25 : 1, mp >270 °C[46] (Found: C, 68.23; H, 4.05; N 9.41. $C_{25}H_{18}BrN_3$ requires C, 68.19; H, 4.12; N, 9.54%); ν_{max}(KBr)/cm^{-1} 3934, 2945, 2836, 1553, 1440, 1393, 1222, 1114, 928, 906, 793, 726; δ_H(200 MHz; $CDCl_3$; $SiMe_4$) 2.72 (m_c, 4 H, CH_2), 2.89 (m_c, 4 H, CH_2), 7.24 (m_c, 3 H), 7.41 (m_c, 2 H), 7.58 (m_c, 3 H), 8.71 (d, ^3J = 4.7 Hz, 2 H); δ_C(50 MHz, $CDCl_3$, $SiMe_4$) 25.9 (t), 27.8 (t), 123.3 (s), 123.7 (d), 127.8 (d), 130.8 (d), 131.9 (d), 132.3 (s), 133.4 (s), 135.5 (d), 139.8 (s), 146.4 (s), 149.6 (d), 151.4 (s), 152.6 (s); *m*/*z* (EI MS): 441 ([M(^{81}Br)$^+$], 77), 440 ([M(^{81}Br)$^+$] − H, 91), 439 ([M(^{79}Br)$^+$], 100), 438 ([M(^{79}Br)$^+$] − H, 85), 360 (17), 358 (21), 284 (10), 282 (15), 220 (6), 180 (39), 178 (41).

5,6,8,9-Tetrahydro-7-(4′-bromophenyl)quino[8,7-*b*][1,10]-phenanthroline (4b). Prepared from **1** (600 mg, 4.02 mmol), 4-brombenzylidenemorpholinium chloride **2b** (580 mg, 2.01 mmol) and ammonium acetate (180 mg, 2.20 mmol). Yield: 582 mg (66%), yellow powder, after chromatography on Al_2O_3, CH_2Cl_2; CH_2Cl_2–MeOH, 25 : 1, mp 290 °C (dec.) (lit.,[47] yield: 8%, mp 291 °C) (Found: C, 68.06; H, 4.13; N 9.33. $C_{25}H_{18}BrN_3$ requires C, 68.19; H, 4.12; N, 9.54%); ν_{max}(KBr)/cm^{-1} 3062, 3003, 2942, 2885, 2844, 1678, 1579, 1540, 1490, 1457, 1452, 1401, 1222, 1201, 1113, 1067, 1011, 847; δ_H(200 MHz, $CDCl_3$, $SiMe_4$) 2.75 (m_c, 4 H, CH_2), 2.94 (m_c, 4 H CH_2), 7.34 (m_c, 4 H), 7.75 (m_c, 4 H), 8.66 (m_c, 2 H); δ_C(50 MHz, $CDCl_3$, $SiMe_4$) 25.6 (t), 27.6 (t), 122.7 (s), 124.1 (d), 130.7 (d), 132.6 (d), 132.6 (s), 133.8 (s), 136.3 (d), 147.2 (s), 148.9 (d), 150.6 (s), 152.2 (s); *m*/*z* (EI MS): 441 ([M(^{81}Br)$^+$], 81), 440 ([M(^{81}Br)$^+$] − H, 97), 439 ([M(^{79}Br)$^+$], 100), 438 ([M(^{79}Br)$^+$] − H, 89), 360 (28), 358 (33), 284 (12), 282 (18), 220 (6), 180 (37), 178 (36).

5,6,8,9-Tetrahydro-7-phenylquino[8,7-*b*][1,10]phenanthroline (4c). Prepared from **1** (600 mg, 4.02 mmol), benzylidenemorpholinium chloride **2c** (422 mg, 2.01 mmol) and ammonium acetate (180 mg, 2.20 mmol). Yield: 467 mg (65%), yellow crystals, after chromatography on Al_2O_3, CH_2Cl_2–MeOH, 25 : 1, mp 254 °C (dec.) (lit.,[31] yield: 45%, mp 254 °C). The compound is isolated as the mono hydrate (Found C, 77.75; H, 5.53; N, 11.17. $C_{25}H_{21}N_3O$ requires C, 79.13; H, 5.58; N, 11.07%); ν_{max}(KBr)/cm^{-1} 3650, 3040, 2972, 2828, 1564, 1540, 1433, 1382, 1217, 1110, 810; δ_H(200 MHz, $CDCl_3$, $SiMe_4$) 2.70 (m_c, 4 H, CH_2), 2.88 (m_c, 4 H, CH_2), 7.19 − 7.24 (m, 4 H), 7.45 − 7.56 (m, 5 H), 8.75 (dd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, 2 H); δ_C(50 MHz, $CDCl_3$, $SiMe_4$) 25.4 (t), 27.4 (t), 123.5 (d), 128.0 (d), 128.6 (d), 128.9 (d), 132.4 (s), 133.4 (s), 135.6 (d), 137.3 (s), 147.9 (s), 148.7 (d), 150.4 (s), 152.2 (s); *m*/*z* (EI MS): 361 ([M$^+$], 100), 360 (66), 359 (16), 358 (21), 356 (10), 180 (11), 179 (11), 178 (15).

General procedure for the synthesis of substituted terpyridines 4d–f

A suspension of **1** (150 mg, 1.01 mmol), ammonium acetate (85 mg, 1.1 mmol) and ground molecular sieves (4 Å, 200 mg) in dry DMSO (10 ml) was heated at 85 °C for 5 min. Iminium salt **2** (291 mg, 1.01 mmol) dissolved in dry DMSO (5 ml) was then added; finally, after another 5 min at 85 °C, **1** (150 mg, 1.01 mmol) was added. The resulting mixture was heated for 16 h at 120 °C and then cooled to room temperature. Water (40 ml) was added and the resulting mixture was extracted with CH_2Cl_2 (3 × 30 ml). The combined organic layers were washed with water (3 × 20 ml) and dried over $MgSO_4$. After removal of the solvent, the residue was purified by chromatography on Al_2O_3.[46]

5,6,8,9-Tetrahydro-7-(4′-*N*,*N*-diethylaminophenyl)quino-[8,7-*b*][1,10]phenanthroline (4d). Prepared from **1** (294 mg, 2.0 mmol), *N*,*N*-dimethyl-4′-(diethylamino)benzylidene ammonium chloride **2d** (205 mg, 1.0 mmol) and ammonium acetate (80 mg, 1.0 mmol). Yield: 190 mg (44%), brown powder, after chromatography on Al_2O_3, CH_2Cl_2–MeOH, 50 : 1, mp >300 °C (lit.,[31] yield: 37%, mp >300 °C) (Found C, 80.62; H, 6.52; N, 12.95. $C_{29}H_{28}N_4$ requires C, 80.52; H, 6.52; N, 12.95%); ν_{max}(KBr)/cm^{-1} 2100, 2009, 1981, 1945, 1923, 1894, 1462, 1365, 1190; δ_H(200 MHz, $CDCl_3$, $SiMe_4$) 1.19 (t, ^3J = 6.50 Hz, 6 H), 2.68–2.98 (m, 8 H), 3.40 (m_c, 4 H), 6.75 (m_c, 2 H), 7.00 (m_c, 2 H), 7.19 (m_c, 2 H), 7.52 (m_c, 2 H), 8.67 (m_c, 2 H); δ_C(50 MHz, $CDCl_3$, $SiMe_4$) 11.9 (q), 24.8 (t), 26.7 (t), 43.5 (t), 110.5 (t), 11.4 (d), 122.1 (s), 122.7 (d), 129.1 (d), 129.3 (d), 132.5 (s), 132.9 (s), 134.9 (d), 146.6 (s), 147.4 (d), 147.7 (s), 149.3 (s), 151.6 (s).

5,6,8,9-Tetrahydro-7-(4′-methoxyphenyl)chino[8,7-*b*][1,10]-phenanthroline (4e). Prepared from **1** (294 mg, 2.0 mmol), *N*,*N*-dimethyl-4′-(methoxy)benzylidene ammonium chloride **2e** (199 mg, 1.0 mmol) and ammonium acetate (80 mg, 1.0 mmol). Yield: 241 mg (61%), brown powder, after chromatography on Al_2O_3, CH_2Cl_2–MeOH, 50 : 1, mp >300 °C (lit.,[31] yield: 28%, mp >300 °C) (Found C, 80.02; H, 5.51; N, 10.56. $C_{26}H_{21}N_3O$ requires C, 79.77; H, 5.41; N, 10.73%); ν_{max}(KBr)/cm^{-1} 3050, 2930, 2835, 1605, 1570, 1505, 1450, 1430, 1400, 1385, 1285, 1240, 1170, 1110, 1025, 845; δ_H(200 MHz, $CDCl_3$, $SiMe_4$) 2.70–2.75 (m, 4 H, CH_2), 2.83–2.89 (m, 4 H, CH_2), 3.89 (s, 3 H, OCH_3), 7.04 (m_c, 2 H), 7.14 (m_c, 2 H), 7.21 (dd, ^3J = 7.6, 4.8 Hz, 2 H), 7.52 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 2 H), 8.75 (dd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, 2 H); δ_C(50 MHz, $CDCl_3$, $SiMe_4$) 25.5 (t), 27.5 (t), 55.4 (q), 114.2 (d), 123.2 (d), 129.3 (s), 129.9 (d), 132.7 (s), 132.2 (s9, 135.2 (d), 147.5 (s), 148.9 (d), 150.5 (s), 152.4 (s), 159.3 (s).

5,6,8,9-Tetrahydro-7-(1-furfuryl)quino[8,7-*b*][1,10]phenanthroline (4f). Prepared from **1** (294 mg, 2.0 mmol), 2-furfurylpiperidinium chloride **2f** (199 mg, 1.00 mmol) and ammonium acetate (80 mg, 1.0 mmol). Yield: 255 mg (73%), brown powder, after chromatography on Al_2O_3, CH_2Cl_2–MeOH, 50 : 1, mp >300 °C (lit.,[31] yield: 75%, mp >300 °C) (Found C, 78.44; H, 5.02; N, 12.05. $C_{23}H_{17}N_3O$ requires C, 78.61; H, 4.88; N, 11.96%); ν_{max}(KBr)/cm^{-1} 3292, 3051, 2934, 2838, 1698, 1576, 1547, 1456, 1370, 1208, 1113, 1013, 884, 818; δ_H(200 MHz, $CDCl_3$, $SiMe_4$) 2.89 (m_c, 8 H, CH_2), 6.48 (m_c, 1 H), 6.56 (m_c, 1 H), 7.19 (m_c, 2 H), 7.51 (m_c, 2 H), 7.59 (s, 1 H), 8.72 (m_c, 2 H); δ_C(50 MHz, $CDCl_3$, $SiMe_4$) 25.8 (t), 27.6 (t), 11.3 (d), 112.5 (d), 123.6 (d), 133.6 (s), 135.6 (s), 135.5 (d), 137.1 (s), 143.3 (d), 148.4 (s), 149.3 (d), 151.3 (s), 152.5 (s), 197.1 (s); *m*/*z* (EI MS): 351 ([M$^+$], 97), 350 (100), 349 (88), 320 (57), 282 (85), 255 (10), 175 (7), 160 (22).

Preparation of terpyridine-platinum complexes 14a–f

To a suspension of diiodo(cycloocta-1,5-diene)platinum **12** (55 mg, 0.10 mmol) in acetone (1 ml) was added silver tetrafluoroborate (40 mg, 0.21 mmol). The resulting mixture was stirred at room temperature until a colorless solution was obtained (20–30 min). The AgI precipitate was then removed by filtration. The solution was added to a suspension of terpyridine **4** (0.08 mmol) in acetonitrile (0.5 ml) and the reaction mixture was stirred at room temperature for another 30 min. The acetonitrile complex precipitating was collected by centrifugation, suspended in acetonitrile (1 ml) and treated with 4-picoline (20 µl) for 30 min to give a clear solution. The picoline complex was precipitated by addition of diethyl ether to give the crude complex, which was recrystallized from acetonitrile by slow diffusion of diethyl ether vapour.[46]

Complex 14a: [Pt(L)4-picoline][BF_4]$_2$ (L = 4a). Prepared from $PtCODI_2$ (55 mg, 0.10 mmol), $AgBF_4$ (40 mg, 0.20 mmol), **4a** (35 mg, 0.04 mmol) and 4-picoline (25 μl). Yield 47 mg (66%), yellow crystals, after crystallization from CH_3CN–Et_2O, mp >250 °C;[46] ν_{max}(KBr)/cm^{-1} 3048, 1631, 1610, 1439, 1418, 1067; δ_H(200 MHz, CD_3CN, $SiMe_4$) 2.68 (s, 3 H, CH_3), 2.99 (m_c, 4 H, CH_2), 3.31 (m_c, 4 H, CH_2), 7.41 (m_c, 1 H), 7.54–7.87 (m, 19 H), 8.16 (m_c, 2 H), 8.87 (m_c, 1 H); δ_C(50 MHz, CD_3CN, $SiMe_4$) 21.0 (q), 24.0 (t), 26.0 (t), 123.0 (s), 127.5 (d), 129.2 (d), 129.3 (d), 131.0 (d), 131.6 (d), 132.9 (d), 135.6 (s), 137.1 (s), 137.4 (s), 138.9 (s), 139.3 (s), 142.9 (d), 149.5 (s), 150.3 (d), 152.1 (d), 155.3 (s), 155.5 (s); *m*/*z* (FAB$^+$): 815 ([M − BF_4]$^+$, 20), 728 ([M − 2 BF_4]$^+$, 19), 635 ([M − 2 BF_4 − picoline]$^+$, 41).

Complex 14b: [Pt(L)4-picoline][BF_4]$_2$ (L = 4b). Prepared from $PtCODI_2$ (55 mg, 0.10 mmol), $AgBF_4$ (40 mg, 0.20 mmol), **4b** (35 mg, 0.04 mmol) and 4-picoline (25 μl). Yield: 45 mg (63%), yellow crystals, after crystallization from CH_3CN–Et_2O, mp >250 °C;[46] ν_{max}(KBr)/cm^{-1} 2913, 2365, 1610, 1403, 1051; δ_H (200 MHz, CD_3CN, $SiMe_4$) 2.68 (s, 3 H, CH_3), 2.99 (m_c, 4 H, CH_2), 3.30 (m_c, 4 H, CH_2), 7.32 (m_c, 2 H), 7.60–7.87 (m, 8 H), 8.14 (d, ^3J = 7.8 Hz, 2 H), 8.84 (m_c, 2 H); δ_C(50 MHz, CD_3CN, $SiMe_4$) 21.0 (q), 24.0 (t), 26.0 (t), 123.8 (s), 129.1 (d), 129.3 (d), 130.5 (d), 132.5 (d), 132.8 (d), 137.0 (s), 138.9 (s), 142.9 (d), 149.5 (s), 150.3 (d), 152.1 (d), 152.7 (s), 155.3 (s), 155.5 (s); *m*/*z*(FAB$^+$): 815 ([M−BF_4]$^+$, 23), 728 ([M − 2 BF_4]$^+$, 22), 635 ([M − 2 BF_4 − picoline]$^+$, 31).

Complex 14c: [Pt(L)4-picoline][BF_4]$_2$ (L = 4c). Prepared from $PtCODI_2$ (55 mg, 0.10 mmol), $AgBF_4$ (40 mg, 0.20 mmol), **4c** (29 mg, 0.08 mmol) and 4-picoline (25 μl). Yield: 47 mg (72%), yellow crystals, after crystallization from CH_3CN–Et_2O, mp >250 °C;[46] ν_{max}(KBr)/cm^{-1} 3058, 1624, 1608, 1411, 1429, 1035, 803; δ_H(200 MHz, CD_3CN, $SiMe_4$) 2.68 (s, 3 H, CH_3), 2.99 (m, 4 H, CH_2), 3.30 (m, 4 H, CH_2), 7.41 (m_c, 2 H), 7.52–7.87 (m, 9 H), 8.15 (d, ^3J = 7.7 Hz, 2 H), 8.86 (d, ^3J = 5.4 Hz, 2 H); δ_C(50 MHz, CD_3CN, $SiMe_4$) 21.0 (q), 24.0 (t), 26.1 (t), 128.3 (d), 129.1 (d), 129.3 (d), 129.3 (d), 130.0 (d), 133.4 (s), 137.0 (s), 138.9 (s), 142.9 (d), 149.5 (s), 150.3 (d), 152.1 (d), 154.0 (s), 155.3 (s), 155.7 (s); *m*/*z* (FAB$^+$): 734 ([M − BF_4]$^+$, 8), 648 ([M − 2 BF_4]$^+$, 10), 576 ([M − 2 BF_4 − picoline + F]$^+$, 29), 555 ([M − 2 BF_4]$^+$, 30); λ_{max}(CH_3CN): 419 (ε/dm^3 mol^{-1} cm^{-1} 6000), 398 (4100), 317 (17700), 2667 (5900), 239 (4900).

Complex 14d: [Pt(L)4-picoline][BF_4]$_2$ (L = 4d). Prepared from $PtCODI_2$ (55 mg, 0.10 mmol), $AgBF_4$ (40 mg, 0.20 mmol), **4d** (35 mg, 0.08 mmol) and 4-picoline (25 μl). The solvent was removed *in vacuo* as the acetonitrile complex did not precipitate. The desired complex can be prepared following the procedure described for the other complexes. Yield: 32 mg (50%), violet crystals, after crystallization from CH_3CN–Et_2O, mp >250 °C;[46] ν_{max}(KBr)/cm^{-1} 2919, 1610, 1408, 1057; δ_H(200 MHz, CD_3CN, $SiMe_4$) 1.24 (t, ^3J = 6.9 Hz, –CH_2CH_3), 2.57 (s, 3 H, CH_3), 3.07 (m_c, 4 H, CH_2), 3.30 (m_c, 4 H, CH_2), 3.51 (q, ^3J = 6.9 Hz, 4 H, –CH_2CH_3), 6.91 (d, ^3J = 8.8 Hz, 2 H), 7.23 (d, ^3J = 8.8 Hz, 2 H), 7.58–7.77 (m, 6 H), 8.14 (d, ^3J = 7.7 Hz, 2 H), 8.86 (d, ^3J = 6.4 Hz, 2 H); δ_C(50 MHz, CD_3CN, $SiMe_4$) 12.2 (q), 21.0 (q), 24.4 (t), 26.3 (t), 44.5 (t), 111.5 (d), 118.6 (s), 128.9 (d), 129.3 (d), 130.2 (d), 136.9 (s), 138.8 (s), 142.7 (d), 149.0 (s), 149.2 (s), 150.1 (d), 152.1 (d), 154.8 (s), 155.2 (s), 156.0 (s); λ_{max}(CH_3CN): 496 (ε/dm^3 mol^{-1} cm^{-1} 4500), 419 (4000), 349 (3300), 316 (14100), 300 (13700), 282 (13600), 244 (800).

Complex 14e: [Pt(L)4-picoline][BF_4]$_2$ (L = 4e). Prepared from $PtCODI_2$ (55 mg, 0.10 mmol), $AgBF_4$ (40 mg, 0.20 mmol), **4e** (31 mg, 0.08 mmol) and 4-picoline (25 μl). Yield: 41 mg (60%), yellow crystals, after crystallization from CH_3CN–Et_2O, mp >250 °C;[46] ν_{max}(KBr)/cm^{-1} 3120, 2923, 1606, 1523, 1444, 1249, 1063, 812; δ_H(200 MHz, CD_3CN, $SiMe_4$) 2.70 (m_c, 3 H, CH_3), 3.03 (m_c, 8 H, CH_2), 3.34 (m_c, 8 H, CH_2), 3.93 (m_c, 3 *H*, CH_3), 7.18–7.38 (m, 4 H), 7.52–7.88 (m, 6 H), 8.13–8.27 (m, 2 H), 8.55–8.97 (m, 2 H); δ_C(50 MHz, CD_3CN, $SiMe_4$) 21.0 (q), 24.1 (t), 24.32 (t), 26 (13 (t), 26.5 (t), 55.7 (q), 55.8 (t), 114.9 (d), 115.0 (d), 125.2 (d), 129.0 (d), 129.3 (d), 129.4 (d), 129.5 (d), 130.1 (d), 131.4 (d), 137.2 (s), 138.9 (s), 142.8 (d), 150.2 (d), 152.1 (d), 155.2 (s), 155.8 (s), 161.0 (s).

X-Ray structure analysis of 14e[48]. [$C_{32}H_{28}N_4OPt$][BF_4]$_2$*2 CH_3CN, M_r = 935.4 g mol^{-1}, crystal size 0.60 × 0.12 × 0.08 mm^3, T = 193(2) K, monoclinic, space group $P2_1/n$, a = 19.275(4), b = 8.415(3), c = 23.953(5) Å, β = 111.90(1)°, V = 3605(1) Å^3, Z = 4, D_c = 1.724 g cm^{-3}, μ = 3.974 mm^{-1}, F(000) = 1840. Data collection was performed on a Bruker AXS P4 diffractometer using graphite monochromated Mo-Kα radiation, ω-scan, 2.5 < θ< 25.0°, index ranges h: −1/22, k: −10/1, l: −28/26; 7818 reflections collected, 6263 unique reflections, LP correction, gaussian absorption correction. Structure solved by direct and conventional Fourier synthesis, full-matrix least-squares refinement based on F^2 and 489 parameters, all but H atoms refined anisotropically, H atoms refined with riding model. Refinement converged at $R1$ ($I > 2\sigma(I)$) = 0.053, w$R2$ (all data) = 0.136, S = 1.025, min./max. height in final ΔF map −0.88/0.93 e Å^{-3}. The structure consists of one cation, two tetrafluoroborate anions and two acetonitrile solvent molecules per asymmetric unit. † Programs used: SHELXTL.[49]

Complex 14f: [Pt(L)4-picoline][BF_4]$_2$ (L =4f). Prepared form $PtCODI_2$ (55 mg, 0.10 mmol), AgBF4 (40 mg, 0.20 mmol), **4f** (29 mg, 0.08 mmol) and 4-picoline (25 μl). Yield: 33 mg (51%), yellow crystals, after crystallization from CH_3CN–Et_2O, mp >250 °C;[46] ν_{max}(KBr)/cm^{-1} 2919, 2852, 1600, 1435, 1057; δ_H(200 MHz, CD_3CN, $SiMe_4$) 2.68 (s, 3 H, CH_3), 3.39 (m_c, 8 H, CH_2), 6.85 (dd, ^3J = 3.5 Hz, ^3J = 1.8 Hz, 1 H), 7.35 (d, ^3J = 3.5 Hz, 1 H), 7.60–7.77 (m, 7 H), 7.93 (d ^3J = 1.8 Hz, 1 H), 8.17 (dd, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 2 H), 8.84 (d, ^3J = 7.2 Hz, 2 H); δ_C(50 MHz, CD_3CN, $SiMe_4$) 21.0 (q), 24.8 (t), 26.1 (t), 112.7 (d), 117.3 (d), 129.1 (d), 129.3 (d), 136.0 (s), 138.9 (s), 141.4 (s), 142.8 (d), 146.0 (s), 146.2 (d), 149.7 (s), 150.1 (d), 152.1 (d), 155.3 (s), 155.6 (s).

† CCDC reference number 152310. See http://www.rsc.org/suppdata/ob/b3/b316633c/ for crystallographic data in.cif or other electronic format.

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49 SHELXTL NT, V5, Bruker Analytical X-ray Systems, Madison, Wisconsin, USA.