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cis-[Ru(2,2′:6′,2″-terpyridine)(DMSO)Cl_2]: Useful Precursor for the Synthesis of Heteroleptic Terpyridine Complexes under Mild Conditions

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[Ru^{II}(terpy)(DMSO)Cl_2] complexes were synthesized as a 5/1 mixture of cis and trans isomers, and their reactivities with CO and with substituted 2,2′:6′,2″-terpyridine (terpy) moieties have been investigated. The structure of a trans isomer and its CO adduct have been unambiguously assigned by spectroscopy and X-ray diffraction. The [Ru(terpy)(terpy-Br)]$^{2+}$ complex prepared either from the *cis*-[Ru^{II}(terpy)(DMSO)Cl_2] or from the *cis*-[Ru^{II}(terpy-Br)-(DMSO)Cl_2] precursor appeared to be reactive in cross-coupling reactions promoted by low-valent palladium(0) and is an attractive target for the stepwise synthesis of polynuclear complexes bearing vacant coordination sites (terpy-Br for 4′-bromo-2,2′:6′,2″-terpyridine). Several bipyridine, phenanthroline, and bipyrimidine complexes were prepared this way and their optical and redox properties determined and discussed.

Introduction

The chemistry of 2,2′:6′,2″-terpyridine complexes has significantly expanded in recent years, and particular attention has been focused on ruthenium(II) complexes because of their attractive photochemical and electrochemical properties.[1,2] Although homo- and heteroleptic Ru complexes could be prepared in classical ways starting from $RuCl_3 \cdot 3H_2O$ or [Ru(terpy)Cl_3] precursors,[3] it appears that the presence of reactive functions on the terpy ligand resulted in the degradation of the complex due to the drastic conditions required. For example, attempts to react [Ru(terpy)Cl_3] with ethynyl-grafted terpy ligands resulted in intractable mixtures of compounds.[4] The in-situ reduction of Ru(III) to Ru(II) requires forcing conditions (boiling ethylene glycol or DMF) to provide the electrons for the metal reduction.[5] In some cases, the use of microwave irradiation facilitates the complexation procedure. These observations led us and other to prepare a mono-terpy ruthenium(II) precursor bearing labile ligands and able to form heteroleptic complexes under mild conditions. After some experimentation we found that [Ru^{II}-(terpy)(DMSO)Cl_2] is a keystone compound able to provide such complexes.[4] At that time the molecular nature (cis or trans; S- or O-bonded DMSO) of this complex was not precisely known due to the absence of a X-ray structure. This complex is now widely used in the preparation of Ru−bis(terpyridine) types of complexes.[6] A few other Ru(II) mono-terpy species have been previously described, but our own experience with [Ru(terpy)(acac)Cl],[7] [Ru(terpy)(CH_3-CN)Cl_2],[8] and [Ru(terpy)(CH_3CN)$_3$](PF_6)$_2$[8] shows them to be very difficult to handle. They do not properly afford heteroleptic bis-terpy complexes under mild conditions.

We have now investigated in detail the reaction of [Ru^{II}(DMSO)$_4Cl_2$] with terpy in chloroform and dichloromethane solutions and have analyzed the structure and spectroscopic properties of the new [Ru^{II}(terpy)(DMSO)Cl_2]

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complexes that resulted. In addition, we have examined their reactivity toward substituted terpy ligands. We have shown, for instance, that the [Ru(terpy)(terpy-Br)]$^{2+}$ complex is a very useful starting material for the preparation of preorganized polynuclear complexes bearing vacant coordination sites. A variety of such complexes were prepared and their optical and redox properties analyzed.

Experimental Section

General Methods. Nuclear magnetic resonance spectra were recorded at room temperature on a Bruker AC-200 spectrometer at 200.1 MHz for ^{1}H NMR and at 50.3 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm) relative to residual protiated solvents (2.50 for DMSO-d_6, 2.17 acetone-d_6, and 1.93 ppm acetonitrile-d_3) and the carbon resonance of the solvent. Fast-atom bombardment (FAB, positive mode) spectra were recorded on a ZAB-HF-VB-analytical apparatus in a *m*-nitrobenzyl alcohol (*m*-NBA) matrix and Ar atoms were used for the bombardment (8 keV). All relevant patterns have the expected isotopic envelopes, as compared with simulated values. Routine absorption spectra were measured in DMSO solutions at room temperature with a Kontron Uvikon 941 spectrophotometer. FT-IR spectra were measured as KBr pellets with an IFS 25 Bruker spectrometer. Electrochemical studies employed cyclic voltammetry with a conventional 3-electrode system using a BAS CV-50W voltammetric analyzer equipped with a Pt microdisk (2 m^2) working electrode and a silver wire counter electrode. Ferrocene was used as an internal standard and was calibrated against a saturated calomel reference electrode (SSCE) separated from the electrolysis cell by a glass frit presoaked with electrolyte solution. Solutions contained the electroactive substrate (ca. $1-1.5 \times 10^{-3}$ mol·dm^{-3}) in deoxygenated and anhydrous acetonitrile containing recrystallized tetra-*n*-butylammonium hexafluorophosphate (0.1 mol·dm^{-3}) as supporting electrolyte. The quoted half-wave potentials were reproducible within ±10 mV.

Materials. [Ru^{II}(DMSO)$_4$Cl$_2$],[9] 4-bromo-2,2′:6′,2″-terpyridine,[10] 4-((diphenylphosphinoyl)methylene)-2,2′:6′,2″-terpyridine,[11] 4-ethynyl-2,2′:6′,2″-terpyridine,[12] ditopic ligands **10**, **11**, **14**, **20**, and **21**, precursors **16** and **17**, and 5,5′-diethynyl-2,2′-bipyrimidine were prepared according to literature procedures.[12,13] RuCl$_3$·3H$_2$O and 2,2′:6′,2″-terpyridine are commercially available and were used as received.

Preparation of the Complexes. Complexes 1 and 2. Method 1. A mixture of [Ru(DMSO)$_4$Cl$_2$] (0.349 g, 0.72 mmol) and 2,2′;6′,2″-terpyridine (0.185 g, 0.72 mmol) in argon-degassed CH_2Cl_2 (30 mL) was heated at 50 °C for 6 h. During this time the solution turned deep-violet and a brown precipitate deposited progressively. After cooling of the mixture to ambient temperature, the brown solid was recovered with a glass frit under argon and washed twice with Et$_2$O affording the cis complex (**2**, 0.185 g, 53%). Single crystals of the trans form (**1**, 0.090 g, 25%) suitable for X-ray diffraction were obtained by slow diffusion of argon-degassed Et$_2$O for a few days into the resulting violet solution.

Method 2. A mixture of [Ru(DMSO)$_4$Cl$_2$] (0.212 g, 0.44 mmol) and 2,2′;6′,2″-terpyridine (0.102 g, 0.44 mmol) in argon-degassed $CHCl_3$ (10 mL) was heated at 80 °C for 7 h. During this time the solution turned brown and a brown precipitate formed slowly. After being cooled to ambient temperature, the solution was concentrated under vacuum to ca. 2 mL and cooled to −20 °C, and the brown solid was recovered via filtration with a glass frit under argon and washed with Et$_2$O (2 × 5 mL) affording the cis complex (**2**, 0.180 g, 85%). Under these experimental conditions the trans form **1** is isolated by Et$_2$O addition (ca. 10%).

Trans isomer 1: ^{1}H NMR (DMSO-d_6) (violet solution) $\delta = 9.36$ ppm (d, 2H, $^3J = 4.8$ Hz), 8.67 (d, 2H, $^3J = 8.0$ Hz), 8.59 (d, 2H, $^3J = 7.2$ Hz), 8.18 (t, 1H, $^3J = 8.0$ Hz), 7.99 (dt, 2H, $^3J = 6.5$ Hz, $^4J = 1.4$ Hz), 7.53 (ddd, 2H, $^3J = 6.5$ Hz, $^3J = 6.5$ Hz, $^4J = 1.3$ Hz), 3.58 (s, 6H); ^{13}C{^{1}H} NMR (DMSO-d_6) $\delta = 159.6$, 157.8, 156.6, 137.7, 137.0, 127.3, 123.9, 122.3, 45.4; IR (KBr, cm^{-1}) 3438, 1601, 1448, 1384, 1064, 1011, 775; FAB$^+$-MS (*m*-NBA) *m*/*z* (nature of the peak, rel inten %) 484.2/486.2 ([M + H]$^+$, 100), 448.2 ([M − Cl], 40), 405.3 ([M − DMSO], 20), 370.5 ([M − Cl − DMSO], 20); UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 630 (1500), 517 (3800), 386 (3700), 330 (23 900), 276 (14 400). Anal. Calcd for $C_{17}H_{17}N_3OSCl_2Ru$ ($M_r = 483.37$): C, 42.24; H, 3.55; N, 8.69. Found: C, 41.94; H, 3.27; N, 8.46.

Cis isomer 2: ^{1}H NMR (DMSO-d_6) (brown solution) $\delta = 9.03$ ppm (d, 2H, $^3J = 5.0$ Hz), 8.54 (m, 4H), 8.15 (dt, 2H, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz), 8.02 (t, 1H, $^3J = 8.0$ Hz), 7.79 (t, 2H, $^3J = 8.0$ Hz), 3.59 (s, 6H); ^{13}C{^{1}H} NMR (DMSO-d_6) $\delta = 159.8$, 158.2, 157.0, 136.9, 136.5, 127.8, 123.5, 122.6, 45.7; IR (KBr, cm^{-1}) 3428, 2992, 1449, 1384, 1082, 1010, 776, 426; FAB$^+$-MS (*m*-NBA) *m*/*z* (nature of the peak, rel inten %) 448.2 ([M − Cl]$^+$, 100), 405.3 ([M − DMSO], 30), 370.5 ([M − Cl −DMSO], 15), 335.2 ([M − 2Cl − DMSO], <5); UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 481 (4800), 330 (14 900), 314 (22 900), 271 (15 200). Anal. Calcd for $C_{17}H_{17}N_3OSCl_2Ru$ ($M_r = 483.37$): C, 42.24; H, 3.55; N, 8.69. Found: C, 42.13; H, 3.44; N, 8.73.

Complex 3. A mixture of [Ru(DMSO)$_4$Cl$_2$] (0.143 g, 0.29 mmol) and 4′-bromo-2,2′;6′,2″-terpyridine (0.092 g, 0.29 mmol) in argon-degassed $CHCl_3$ (20 mL) was heated at 80 °C during 7 h. After cooling of the mixture to room temperature, the brown solid was recovered with a glass frit under argon and washed with Et$_2$O (2 × 15 mL) affording complex **3** (0.125 g, 80%): ^{1}H NMR (DMSO-d_6) $\delta = 9.03$ ppm (d, 2H, $^3J = 6.0$ Hz), 8.92 (s, 2H), 8.67 (d, 2H, $^3J = 8.0$ Hz), 7.17 (dt, 2H, $^3J = 7.6$ Hz, $^4J = 1.2$ Hz), 7.83 (t, 2H, $^3J = 6.0$ Hz), 3.62 (s, 6H); FAB$^+$-MS (*m*-NBA) *m*/*z* (nature of the peak, rel inten %) 528.2 ([M − Cl]$^+$, 100), 493.5 ([M − 2Cl], 50), 415.2 ([M − 2Cl − DMSO], 10); IR (KBr, cm^{-1}) 3429, 1605, 1453, 1455, 1387, 1078, 1015; UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 478 (5100), 328 (16 500), 310 (23 600), 270 (17 800). Anal. Calcd for $C_{17}H_{16}N_3OSCl_2BrRu$ ($M_r = 562.27$): C, 36.31; H, 2.87; 7.47. Found: C, 36.29; H, 2.49; N, 7.21.

Complex 4. A solution of freshly distilled 1,2-dichloroethane (50 mL) containing complex **1 (**0.100 g, 0.20 mmol) was gently heated at 80 °C under a stream of carbon monoxide at atmospheric pressure. During this reaction time a bright-red solid progressively deposited in the solution. After 5 h the precipitate was filtered on a glass frit and successively washed with cold 1,2-dichloroethane (3 × 10 mL) and diethyl ether (2 × 10 mL), affording the analytically pure complex **4** (0.083 g, 95%): ^{1}H NMR (DMSO-d_6) $\delta = 8.85$ (d, 2H, $^3J = 4.8$ Hz), 8.72 (d, 2H, $^3J = 8.0$ Hz), 8.62 (d, 2H, $^3J = 8.4$ Hz), 8.43 (t, 1H, $^3J = 8.0$ Hz), 8.07 (td, 2H, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz), 7.56 (td, 2H, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz); IR (KBr) $\nu = 3450$, 3068, 1950 (ν_{CO}), 1596, 1568, 1443, 1396, 1238, 779 cm^{-1}; UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 570 (1000), 450 (1900), 360 (1700), 320 (20 200), 282 (14 500), 270 (12 400), 230 (27 000); FAB$^+$ (*m*-NBA) *m*/*z* (nature of the peak, rel inten

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%) 398.3 [M − Cl]$^+$, 363.3 [M − 2Cl], 335.2 [M − 2Cl − CO]. Anal. Calcd for $C_{16}H_{11}N_3OCl_2Ru$ (M_r = 433.261): C, 44.36; H, 2.56; N, 9.70. Found: C, 44.03; H, 2.33; N, 9.56.

Complex 5. A solution of freshly distilled 1,2-dichloroethane (50 mL) containing complex **2** (0.100 g, 0.20 mmol) was heated at 80 °C under a stream of carbon monoxide at atmospheric pressure for 6 h. During this reaction time an orange-red solid progressively formed in the solution. The precipitate was recovered by filtration on a glass frit and successively washed with cold 1,2-dichloroethane (3 × 10 mL) and diethyl ether (2 × 10 mL), affording the analytically pure title compound **5** (0.082 g, 92%): ^{1}H NMR (DMSO-d_6) δ = 8.91 (d, 2H, ^3J = 5.4 Hz), 8.66 (m, 4H), 8.33 (t, 1H, ^3J = 8.2 Hz), 8.27 (td, 2H, ^3J = 8.2 Hz, ^4J = 1.6 Hz), 7.83 (t, 2H, ^3J = 6.7 Hz); IR (KBr) ν = 3504, 3061, 3029, 1948 (ν_{CO}), 1596, 1558, 1443, 1389, 1240, 1107, 783 cm^{-1}; UV−vis (CH_3-CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 408 (2600), 324 (21 400), 312 (15 000), 270 (16 300), 238 (24 500); FAB$^+$ (*m*-NBA) *m*/*z* (nature of the peak, rel inten %) 398.3 ([M − Cl]$^+$, 100), 335.2 ([M − 2Cl − CO], 20). Anal. Calcd for $C_{16}H_{11}N_3OCl_2Ru$ (M_r = 433.261): C, 44.36; H, 2.56; N, 9.70. Found: C, 44.19; H, 2.17; N, 9.39.

Complex 6. A mixture of *cis*-[Ru(terpy)(DMSO)Cl$_2$] (**2**) (0.142 g, 0.29 mmol) and $AgBF_4$ (0.130 g, 0.64 mmol) in degassed methanol (60 mL) was heated at 80 °C for 8 h. After cooling of the mixture to ambient temperature, the precipitate (AgCl) was separated by filtration and the red solution was allowed to react with 4′-bromo-2,2′;6′,2″-terpyridine (0.093 g, 0.29 mmol) for 20 h at 80 °C. After this period, water (2 mL) containing KPF_6 (0.270 g, 1.45 mmol) was added and the organic solvent smoothly evaporated under vacuum until a precipitate was formed. The resulting solid was recovered by centrifugation and washed with water (3 × 10 mL). Purification by chromatography on alumina using a mixture of 1/1 toluene/acetonitrile afforded the analytically pure complex **6** (0.155 g, 56%): ^{1}H NMR (acetone-d_6) δ = 9.33 ppm (s, 2H), 9.09 (d, 2H, ^3J = 8.0 Hz), 8.86 (m, 4H), 8.60 (t, 1H, ^3J = 8.0 Hz), 8.09 (m, 4H), 7.78 (m, 4H), 7.34 (m, 4H); MALDI-TOF *m*/*z* (nature of the peak, rel inten %) 324.0 ([M − 2PF$_6$]$^{2+}$, 100); UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 478 (19 400), 324 (43 800), 308 (90 700), 272 (62 900), 240 (55 300). Anal. Calcd for $C_{30}H_{21}N_6BrP_2F_{12}Ru$ (M_r = 936.44): C, 38.48; H, 2.26; N, 8.97. Found: C, 38.24; H, 1.91; N, 8.63.

General Procedure for the Preparation of Complexes 7−9, 12, and 13. A stirred solution of *cis*-[Ru(terpy)(DMSO)Cl$_2$] (1 equiv for the mononuclear complexes and 2 equiv for the dinuclear complexes) and $AgBF_4$ (1.1 or 2.2 equiv, respectively) in argon-degassed methanol was heated at 80 °C for 6 h in a Schlenk round-bottom flask. After cooling of the mixture to ambient temperature, the precipitate (AgCl) was separated by filtration under argon over cotton wool and the deep-red solution quantitatively transferred via cannula to a methanol (20 mL) solution containing the corresponding ligand (100 mg, 1 equiv). During heating at 60 °C the deep-red solution progressively turned orange, a color characteristic of Ru bis-terpy complexes. The progression of the complexation reaction was followed by thin-layer chromatography (TLC), which clearly showed the consumption of the free ligand and the formation of the desired complexes. After a few hours, the clear orange solution was cooled to ambient temperature and filtered over Celite and an aqueous solution (2 mL) of NH_4PF_6 (10 equiv) was added. Slow evaporation of the organic solvent led to the precipitation of a deep-red solid, which was recovered by centrifugation and washed three times with water (3 × 20 mL) and diethyl ether (2 × 10 mL). The crude material was dried under high vacuum and ultimately purified by chromatography over alumina using dichloromethane as solvent and an increasing gradient of methanol (3−10%). Finally, the purified complexes were recrystallized from a 1/1 mixture of acetonitrile/toluene affording the analytically pure complexes.

Mononuclear complex 7: isolated yield 66%; ^{1}H NMR (acetonitrile-d_3) δ = 8.55 (d, 4H, ^3J = 7.6 Hz), 8.43 (dd, 2H, ^3J = 8.2 Hz, ^4J = 4.2 Hz), 8.25 (t, 4H, ^3J = 7.6 Hz), 7.84 (m, 11H), 2.45 (s, 3H); ESI-MS *m*/*z* (nature of the peak, rel inten %) 727.2 ([M − PF$_6$]$^+$, 100), 291.3 ([(M − 2PF$_6$)]$^{2+}$, 30); UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 470 (15 800), 303 (57 200), 268 (43 600). Anal. Calcd for $C_{31}H_{24}F_{12}N_6P_2Ru$ (M_r = 871.57): C, 42.72; H, 2.78; N, 9.64. Found: C, 42.49; H, 2.54; N, 9.35.

Mononuclear complex 8: isolated yield 75%; ^{1}H NMR (acetonitrile-d_3) δ = 8.74 (d, 2H, ^3J = 8.1 Hz), 8.44 (m, 5H), 8.25 (d, 2H, ^3J = 8.1 Hz), 7.91 (m, 8H),7.61 (m, 6H), 7.16 (m, 8H), 4.33 (d, 2H, $^2J_{HP}$ = 14 Hz); ^{31}P{H} NMR (acetonitrile-d_3) δ = 30.6 ppm; ESI-MS *m*/*z* (nature of the peak, rel inten %) 927.3 ([M − PF$_6$]$^+$, 100), 391.3 ([(M − 2PF$_6$)]$^{2+}$, 40); UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 471 (15 200), 301 (53 700), 265 (41 200). Anal. Calcd for $C_{43}H_{33}F_{12}N_6P_3ORu$ (M_r = 1071.754): C, 48.19; H, 3.10; N, 7.84. Found: C, 47.85; H, 2.89; N, 7.66.

Mononuclear complex 9: isolated yield 58%; ^{1}H NMR (acetonitrile-d_3) δ = 8.47 (d, 4H, ^3J = 7.1 Hz), 8.32 (dd, 2H, ^3J = 8.5 Hz, ^4J = 5.0 Hz), 8.03 (t, 4H, ^3J = 7.6 Hz), 7.79 (m, 11H), 4.16 (s, 1H); FT-IR (KBr pellets, cm^{-1}) 3239 (m, $\nu_{C\equiv C-H}$), 2975 (m), 2920 (m), 1640 (m), 1453 (m), 1389 (m), 1247 (m), 1090 (m), 1049 (s), 836 (s); ESI-MS *m*/*z* (nature of the peak, rel inten %) 736.9 ([M − PF$_6$]$^+$, 100), 295.9 ([(M − 2PF$_6$]$^{2+}$, 25); UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 486 (20 200), 308 (63 200), 272 (48 500). Anal. Calcd for $C_{32}H_{22}F_{12}N_6P_2Ru$ (M_r = 881.57): C, 43.60; H, 2.52; N, 9.53. Found: C, 43.29; H, 2.29; N, 9.34.

Dinuclear complex 12: isolated yield 85%; ^{1}H NMR (acetone-d_6) δ = 9.23 (s, 4H), 8.96 (d, 4H, ^3J = 8.5 Hz), 8.64−8.43 (m, 6H), 8.27 (t, 4H, ^3J = 7.0 Hz), 8.18 (dd, 4H, ^3J = 8.5 Hz, ^4J = 1.9 Hz), 8.02−7.90 (m, 8H), 7.63−7.57 (m, 8H), 7.32−7.21 (m, 4H); ESI-MS *m*/*z* (nature of the peak, rel inten %) 1593.2 ([M − PF$_6$]$^+$, 100), 724.1 ([M − 2PF$_6$]$^{2+}$, 30), 434.4 ([M − 3PF$_6$]$^{3+}$, 20), 289.6 ([M − 4PF$_6$]$^{4+}$, 15); UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 515 (32 800), 306 (69 800), 272 (53 900). Anal. Calcd for $C_{62}H_{42}F_{24}N_{12}P_4Ru_2$ (M_r = 1737.10): C, 42.87; H, 2.44; N, 9.68. Found: C, 42.53; H, 2.15; N, 9.39.

Dinuclear complex 13: isolated yield 88%; ^{1}H NMR (acetone-d_6) δ = 9.27 (s, 4H), 9.02(d, 4H, ^3J = 8.6 Hz), 8.64−8.48 (m, 6H), 8.32 (t, 4H, ^3J = 7.2 Hz), 8.24 (dd, 4H, ^3J = 8.6 Hz, ^4J = 2.0 Hz), 8.12−7.99 (m, 8H), 7.65−7.52 (m, 8H), 7.36−7.28 (m, 4H); ESI-MS *m*/*z* (nature of the peak, rel inten %) 1617.3 ([M − PF$_6$]$^+$, 100), 724.1 ([M − 2PF$_6$]$^{2+}$, 50), 442.4 ([M − 3PF$_6$]$^{3+}$, 20); UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 512 (39 300), 308 (95 700), 272 (69 500). Anal. Calcd for $C_{64}H_{42}F_{24}N_{12}P_4Ru_2$ (M_r = 1761.12): C, 43.65; H, 2.40; N, 9.54. Found: C, 43.53; H, 2.11; N, 9.32.

General Procedure for the Preparation of Complexes 15 and 19. A Schlenk flask was charged with 5,5′-diethynyl-2,2′-bipyridine (0.100 g, 0.49 mmol), [Ru(terpy)(terpy-Br)](PF$_6$)$_2$ (0.091 g, 0.98 mmol), 10 mL of degassed CH_3CN, [Pd(PPh$_3$)$_2$Cl$_2$] (0.004 g, 6 mol %), and CuI (0.002 g, 10 mol %). After purging of the solution with argon, (^{i}Pr)$_2$NH (5 mL) was added. The solution was stirred at room temperature for 6 days, and then KPF_6 (0.018 g, 4 equiv) in water (5 mL) was added and the solvent was removed. The crude product was subjected to chromatography on alumina using a mixture of CH_3CN/H_2O with a gradient of water increasing from 0 to 25%. The analytically pure compound was obtained by recrystallization from CH_3CN/diethyl ether.

Dinuclear complex 15: isolated yield 32%; ^{1}H NMR (acetonitrile-d_3) δ = 9.39 (s, 4H), 8.96 (s, 4H), 8.78 (d, 4H, ^3J = 8.0 Hz),

Table 1. X-ray Data for *trans*-[Ru(terpy)(DMSO)Cl_2] (**1**)

formula	$2(C_{17}H_{17}Cl_2N_3ORuS)\cdot 3CH_2Cl_2 2H_2O$
MW	1257.60
cryst system	monoclinic
space group	*C*12/*m*1
a (Å)	10.9878(4)
b (Å)	29.844(1)
c (Å)	8.6903(5)
β (deg)	118.496(5)
V (Å^3)	2504.5(2)
Z	2
color	violet
cryst dimens (mm^3)	0.10 × 0.08 × 0.06
D_{calcd} (g cm^{-3})	1.67
F_{000}	1260
μ (mm^{-1})	1.264
hkl limits	−14, 14/−29, 30/−11, 11
θ limits (deg)	2.5/27.40
no. of data measd	4851
no. of data with $I > 3\sigma(I)$	1772
no. of variables	151
GOF[a]	1.699
$R(F_o)$[b]	0.057
$R_w(F_o)$[c]	0.095
largest peak in final diff (e Å^{-3})	0.885

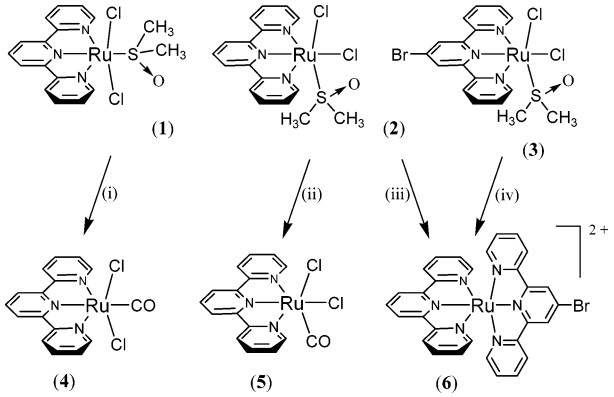
[a] GOF = $[\sum w(|F_o|^2 - |F_c|^2)^2/(n-p)]^{1/2}$. [b] $R(F_o) = \sum(|F_o| - |F_c|)/\sum|F_o|$. [c] $R_w(F_o) = \sum(w^{1/2}|F_o| - |F_c|)/\sum w^{1/2}|F_o|$.

8.49 (m, 10H), 7.95 (m, 8H), 7.39 (m, 8H), 7.19 (m, 8H); $^{13}C\{^1H\}$ NMR (acetonitrile-d_3) δ = 161.3, 160.6, 158.3, 157.8, 156.1, 155.5, 153.0, 138.7, 136.8, 128.7, 128.2, 127.9, 125.8, 125.1, 125.0, 124.2, 118.8, 94.0, 90.1, 72.6, 61.4; MALDI-TOF *m*/*z* (nature of the peak, rel inten %) 494.5 ([M − 3PF_6]$^{3+}$, 23), 334.3 ([M − 4PF_6]$^{4+}$, 100); IR (KBr, cm^{-1}) 3421, 2924, 821, 558; UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 498.0 (68 600), 309.0 (141 700), 272.0 (92 600). Anal. Calcd for $C_{72}H_{46}N_{16}P_4F_{24}Ru_2$ (*M* = 1917.27): C, 45.11; H, 2.42; N, 11.69. Found: C, 44.92; H, 2.13; N, 11.35.

Dinuclear complex 19: isolated yield 51%; ^1H NMR (acetonitrile-d_3) δ = 9.49 (d, 2H, ^3J = 2,0 Hz), 8.99 (s, 4H), 8.84 (d, 2H, ^4J = 2.0), 8.78 (d, 4H, ^3J = 8.4), 8.41−8.59 (m, 10 H), 8.19 (s, 2H), 7.90−8.02 (m, 8H), 7.38−7.43 (m, 8H), 7.15−7.25 (m, 8H); ESI-MS *m*/*z* (nature of the peak, rel inten %) 1795.2 ([M − PF_6]$^+$, 100), 825.2 ([M − 2PF_6]$^{2+}$, 40), 501.8 ([M − 3PF_6]$^{3+}$, 10); IR (KBr, cm^{-1}) 3420, 1604, 1449, 1424, 840, 788, 768, 557; UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 495.0 (94 500), 307.0 (16 900), 272.0 (14 900). Anal. Calcd for $C_{76}H_{48}N_{14}P_4F_{24}Ru_2$ (*M* = 1939.32): C, 47.07; H, 2.49; N, 10.11. Found: C, 47.09; H, 2.43; N, 10.49.

X-ray Crystal Structure Analysis. The intensity data were collected in the ϕ scan mode at 173 K for complexes **1** and **4** on a KappaCCD diffractometer equipped with a graphite monochromator for Mo Kα radiation (wavelength 0.710 73 Å). Cell constants were derived from a least-squares fit of the setting angles for 25 selected reflections with 10° < θ < 15°. The intensities were corrected for Lorentz and polarization effects but not for absorption. The atoms were located in a succession of difference Fourier syntheses and were refined with anisotropic thermal parameters using the SHELX76 and SHELX85 packages.[14] The hydrogen atoms were included in the final refinement model in calculated and fixed positions with isotropic thermal parameters. Crystal structure and refinement data are summarized in Table 1.

Scheme 1[a]



[a] Key: (i) CO flow, 1 atm, 60 °C, $CHCl_3$; (ii) CO flow, 1 atm, 80 °C, 1,2-dichloroethane; (iii) (a) $AgBF_4$, CH_3OH, 80 °C, (b) 4′-bromo-2,2′:6′,2"-terpyridine; (iv) (a) $AgBF_4$, CH_3OH, 80 °C, (b) 2,2′:6′,2"-terpyridine. Counteranions resulting from anion exchange are PF_6^-.

Results and Discussion

[$Ru^{II}(DMSO)_4Cl_2$] reacts readily with terpy in degassed $CHCl_3$ or CH_2Cl_2 to yield [Ru^{II}(terpy)(DMSO)Cl_2] as a mixture of two isomers (**1** and **2**) (Scheme 1).

The isomers were separated by crystallization and exhibit different NMR patterns (Figure 1). On the basis of spectroscopic analysis (NMR and FT-IR), it was not possible to properly assigned the nature of each isomer.[4,6] Thanks to a crystal structure of one of the isomers (vide infra), it was possible to deduce that the less soluble brownish compound is the cis isomer (**2**), while the violet derivative is the trans isomer (**1**) isolated respectively with 85% and 10% yields in $CHCl_3$. Both isomers exhibit markedly different proton NMR spectra, with each spectrum having the expected six protons pattern corresponding to the terpy ligand. The characteristic fingerprint for the trans isomer, compared to the cis, is the deshielding (Δ = 0.33 ppm) of the 6,6″ protons and the shielding of the 5,5″ protons (Δ = 0.26 ppm), probably induced by the stereoelectronic effect of the DMSO and/or Cl ligands, as compared to the free ligand. For the cis isomer the proton NMR is more compact and no such significant shifts are found. For both complexes the methyl groups of the bonded DMSO resonate at ca. 3.5 and 45 ppm, respectively, in the proton and carbon NMR spectra.

For both isomers the FT-IR spectra are similar with a ν_{SO} stretching vibration at 1064 and 1082 cm^{-1}, respectively, for **1** and **2**. The absence of any significant vibration in the 920−930 cm^{-1} ranges indicates a S-bonded DMSO molecule.[15] Interestingly, both isomers are thermodynamically stable in solution, even when exposed to DMSO-d_6 solutions in sunlight. This demonstrates that the cis and trans photoinduced isomerization or desolvation is not feasible under standard experimental conditions, as previously discovered in other Ru(II) complexes.[16,17] Furthermore, heating the trans isomer in refluxing $CHCl_3$ does not afford the cis isomer and suggests that the cis isomer is not the thermodynamic product of the reaction.

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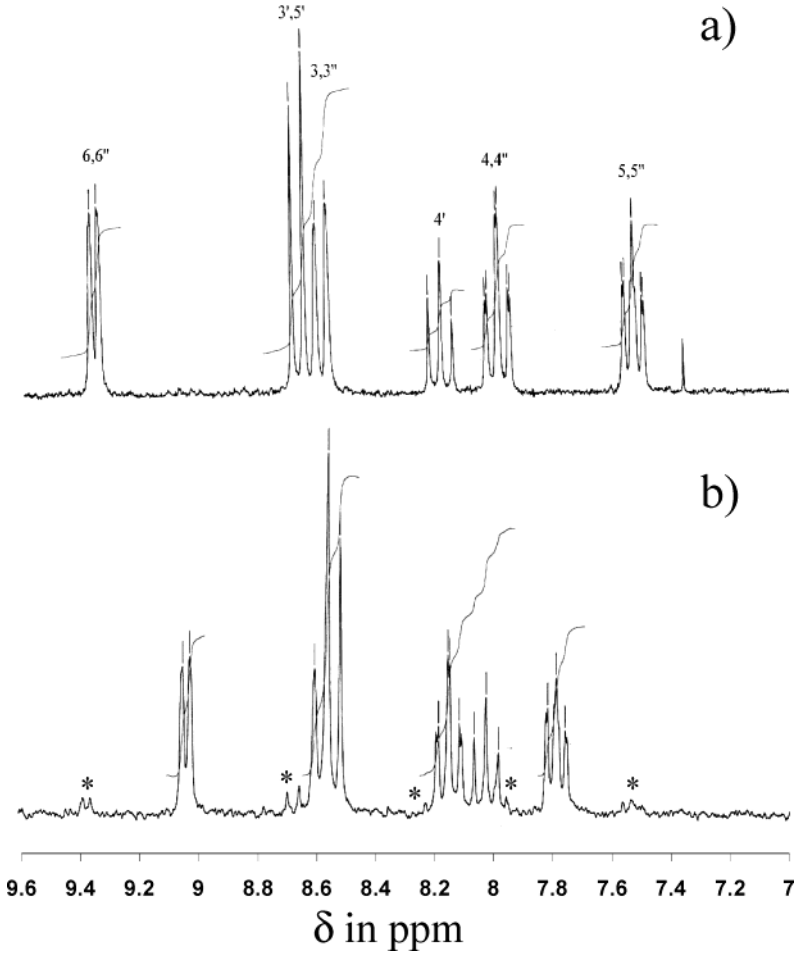

Figure 1. Proton NMR of the purified trans complex **1** (a) and crude cis complex **2** (b) in argon-degassed DMSO-d_6. In spectrum b the asterisk label corresponds to the presence of traces of the trans complex which could be eliminated by a single recrystallization procedure.

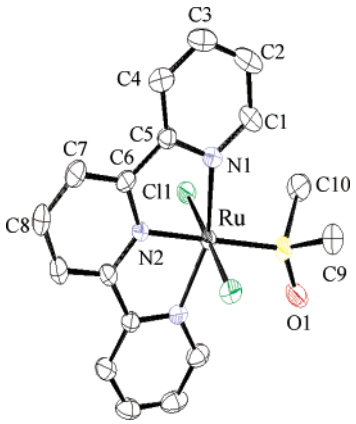

Figure 2. ORTEP views for complex **1**.

The X-ray molecular structure of complex **1** confirms that the coordination geometry is octahedral (Figure 2). This complex crystallizes in the *C*2/*m* space group with a crystallographically imposed C_2 axis containing the Ru and S atoms bisecting the central pyridine ring. As a consequence, the two Ru−Cl 2.404(2) Å and Ru−N1 2.081(6) Å bond lengths are identical. The central Ru−N2 1.980(8) Å is the shortest bond, and the terpy bites angle are typical of those for Ru−terpy complexes reported earlier.[18] The tridentate terpy ligand is almost planar with a slight tilt angle of 1.6° between the external and central pyridine ring. The Cl ligands are coordinated trans to the terpy plane confirming the chemical equivalence of the external pyridine rings, as suggested by NMR studies. As anticipated by FT-IR, the DMSO molecule is coordinated to the metal center via the sulfur atom Ru−S 2.268(3) Å. This Ru−S bond length is short compared to Ru(II) thiourea[19] or thiocyanato complexes[20] but in the expected range (2.262−2.393 Å) when compared to other Ru(II)−sulfur- bonded compounds.[21,22] In the crystal structure the DMSO molecule occupied two positions on each side of the C_2 axis bisecting the basal plane of the octahedron.

Both isomers **1** and **2** react with CO to provide the corresponding carbonyl complexes **4** and **5** in excellent yields (Scheme 1). The exchange reaction of DMSO for CO is stereoselective, and cis/trans isomerization could not be detected on the basis of NMR spectroscopy. To unambiguously establish the isomeric nature of complex **4**, we have undertaken an X-ray crystal determination (see Supporting

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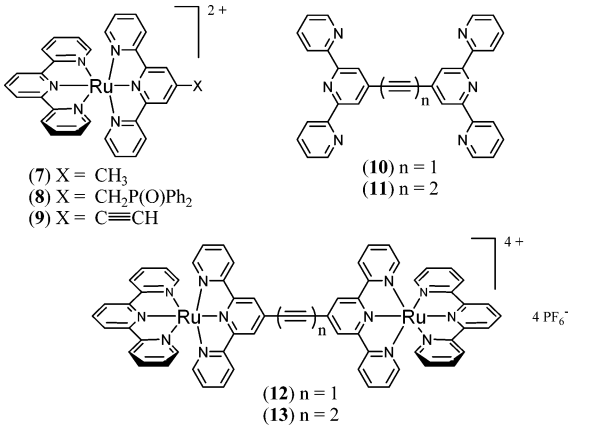
Scheme 2[a]



[a] Key: (i) (a) complex **6** (2 equiv), $AgBF_4$, CH_3OH, 80 °C, (b) ligand addition; (ii) 5,5′-diethynyl-2,2′-bipyrimidine, [$Pd(PPh_3)_2Cl_2$] 6 mol %, CuI 10 mol %, CH_3CN, $^iPr_2NH$, room temperature. Counteranions resulting from anion exchange are PF_6^-.

Information Figure S1). The coordination sphere is again octahedral, and both Cl ligands (Ru−Cl1 2.413(1) and Ru−Cl2 2.414(1) Å) lie apart from the plane defined by the terpy ligand and the carbonyl. The shortest Ru−N2 2.024(2) Å is found within the central pyridine ring while the other two lie at Ru−N1 2.084(2) and Ru−N3 2.087(2) Å. The terpy ligand is almost planar with the largest deviation from planarity of about 4.9°. The Ru−CO bond is 1.882(3) Å. This X-ray structure is similar to the one reported by White at al.[18] At that time complex **4** was prepared by reaction of polymeric ruthenium(II)−carbonyl−halides with terpyridine, followed by a subsequent oxidation of one carbonyl ligand with trimethylamine *N*-oxide.

The unique protocol used to prepare mono-terpy Ru(II) complexes has been extended to the synthesis of complexes bearing an additional reactive function. These building blocks should be very useful for the construction of sophisticated multinuclear complexes.[23] We succeed in preparing complex **3** as the cis isomer under similar conditions (Scheme 1). At this stage it was very interesting to test the reactivity of both cis isomers **2** and **3** toward the preparation of heteroleptic bis-terpy complexes. We were pleased to find that both compounds smoothly react, after silver dehalogenation, under mild conditions (60 °C in methanol) respectively with 4′-bromo-terpy and terpy affording complex **6** in fair yield (Scheme 1). To demonstrate the synthetic potential of complex **2** we have prepared the mononuclear complexes **7**−**9** under similar conditions. These complexes are grafted respectively with a methyl group, a phosphine oxide fragment, and an ethynyl function (Scheme 2). In addition, by using a similar synthetic approach, it was easy to isolate the dinuclear complexes **12** and **13** by reacting 2 equiv of complex **2** with the ditopic ligands **10** and **11**.[12] At this stage it should be interesting to point out that these complexes bearing alkyne functions (i.e. **9**, **12**, and **13**) could not be prepared using the standard Ru(II)−terpy chemistry, which requires harsh experimental conditions. In our hands boiling 4-ethynyl-terpy or ligands **10** and **11** with [Ru(terpy)Cl_3] in DMF or ethylene glycol, even in the presence of reducing agents such as *N*-ethylmorpholine, produced only polymeric and intractable materials.[4] Similarly, the use of Ru(terpy)(acac)Cl][7] or[Ru(terpy)$(CH_3CN)_3$]$(PF_6)_2$[8] precursors did not provide a reliable synthetic procedure.

From a general point of view it was disappointing to find that the preparation of advanced multicomponent complexes, where free coordination sites are inserted in the spacer, failed using starting material **2**. No complexation selectivity for **2** is observed with a 2,2′:6′,2″-terpyridine, a 2,2′-bipyrimidine, a 2,2′-bipyridine, or a 1,10-phenanthroline fragment respectively present in ligands **14**, **20**, and **21**. After some experimentation, we were pleased to discover that complex **6** bearing a bromine function is a convenient starting material for cross-coupling reactions, under Sonogashira conditions,[24] with uncomplexed oligopyridino building blocks grafted with the adequate alkyne groups such as 5,5′-diethynyl-2,2′-bipyrimidine, 3,8-diethynyl-1,10-phenanthroline, or 5,5′-diethynyl-2,2′-bipyridine. This strategy provides access to the target dinuclear complexes **15**, **18**, and **19** without any noticeable side reactions (Schemes 3 and 4). Complex **18** has been previously prepared using a similar synthetic strategy.[25]

The cross-coupling reactions proceed at ambient temperature and are promoted by low-valent Pd(0) [prepared in situ from Pd(II) (6 mol %) and CuI (10 mol %)] and a secondary amine required to quench the nascent HBr. It is worth noting that the presence of CH_3CN, needed to dissolve the starting complex **6**, does not significantly perturb the catalytic reaction. Similar observations were previously noted during the stepwise construction of ordered networks[26] or conjugated organic molecules.[27]

It is noteworthy that when the violet trans precursor **1** is used as starting material in the complexation of mono- or ditopic ligands (i.e. **10** and **11**), the isolated yields for the mono- or dinuclear complexes are very low, while under similar conditions the brown cis complex **2** provides fair yields. It is surmised that the decoordination of DMSO in the trans position of the terpy ligand is more difficult than in the cis isomer. It thus becomes more difficult to efficiently chelate a second tridentate terpy ligand. The electrochemistry of these monomers is also in keeping with a greater lability of the coordinated DMSO molecule in the cis isomer versus the trans isomer when those experiments were carried out in a competitive solvent such as DMF (vide infra).

UV−Visible Absorption Spectroscopy. Figure 3 illustrates the absorption spectra of the *cis*- and *trans*-[Ru(terpy)(DMSO)Cl_2] complexes in DMSO solutions, and the band maxima and molar extinction coefficient are listed in Table 2. Both complexes display two strong and narrow absorption band in the UV region at approximately 274 and 320 nm, assigned to the π,π^* transition of the terpy ligand.

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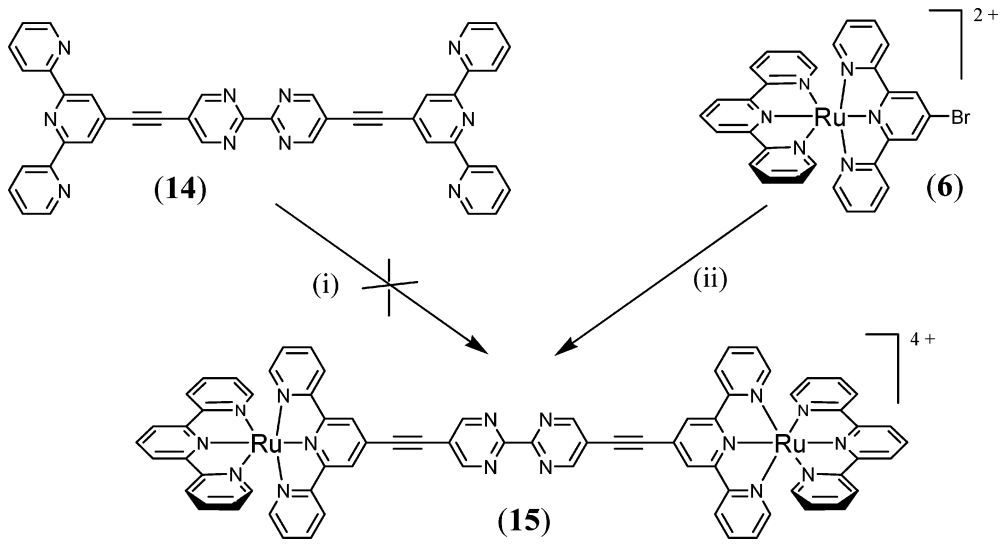
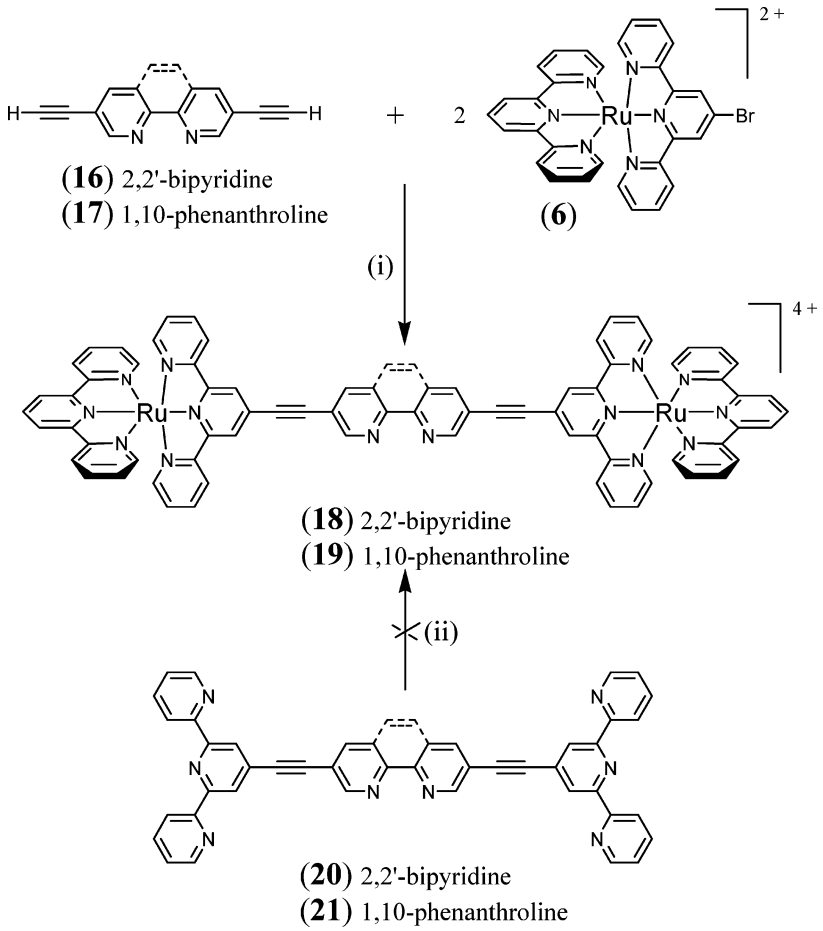
Scheme 3



Scheme 4[a]



[a] Key: (i) compounds **16** or **17**, $[Pd(PPh_3)_2Cl_2]$ 6 mol %, CuI 10 mol %, CH_3CN, $^iPr_2NH$, room temperatrure; (ii) (a) complex **6** (2 equiv), $AgBF_4$, CH_3OH, 80 °C, (b) ligand addition. All counteranions resulting from anion exchange are PF_6^-.

Note that all transition are bathochromically shifted for the trans complex versus the cis complex. In the low-energy region the spectra display weaker absorption between 450 and 550 nm assigned to a metal-to-ligand charge transfer state (MLCT). For the violet trans complex **1** the absorption band presents a shoulder at low energy (ca 630 nm) versus the cis complex **2**. It is likely that the bathochromic shift found for the trans complex is related to a significant decrease of the HOMO/LUMO gap which is also evident from the electrochemical data described below (Table 2). An assignment to direct singlet−triplet absorption could not be excluded for the trans isomer.

All other complexes similarly display strong and narrow absorption bands in the UV around 272 and 308 nm, likely

Table 2. Absorption[a] and Electrochemical Properties of Complexes in Solution[b]

complex	λ_{abs}, nm (ϵ, $M^{-1}\,cm^{-1}$)	$E°$(oxdn, soln), V (ΔE_p, mV)[c]	$E°$(redn, soln), V (ΔE_p, mV)[d]
1	630 (sh), 517 (3800), 386 (3700), 330 (23 900), 276 (14 400)	+0.59 (70)	−1.63[e]
2	481 (4800), 330 (14 900), 314 (22 900), 271 (15 200)	+0.68 (70)	−1.62[e]
7	470 (15 800), 303 (57 200), 268 (43 600)	+1.21 (60)	−1.30 (60), −1.54 (60)
8	471 (15 200), 301 (53 700), 265 (41 200)	+1.23 (60)	−1.29 (60), −1.52 (70)
9	486 (20 200), 308 (63 200), 272 (48 500)	+1.32 (70)	−1.16 (70), −1.42 (70)
12	515 (32 800), 306 (69 800), 272 (53 900)[e]	+1.33 (80, 2e)	−0.97 (60, 1e), −1.19 (70, 1e), −1.44 (70, 2e)
13	512 (39 300), 308 (95 700), 272 (69 500)[e]	+1.30 (80, 2e)	−0.92 (70, 1e), −1.02 (70, 1e), −1.37 (80, 2e)
15	498 (68 600), 309 (141 700), 272 (92 600)	+1.27 (60, 2e)	−1.11 (60, 2e), −1.33 (70, 1e), −1.44 (80, 1e), −1.77 (90, 2e)[e]
18	495 (41 400), 258 (45 000), 332 (56 000), 308 (69 400), 272 (58 400)[f]	+1.36 (80, 2e)	−1.06 (70, 2e), −1.42 (80, 2e), −1.57 (70, 1e)
19	495 (94 500), 307 (16 900), 272 (14 900)	+1.30 (70, 2e)	−1.15 (60, 2e), −1.48 (70, 2e), −1.62 (70, 1e)

[a] Data were obtained in anhydrous DMSO (**1** and **2**) or in anhydrous acetonitrile solutions at room temperature. [b] The electrolyte was 0.1 M $(TBA)PF_6$/anhydrous CH_3CN, complex concentration 1−1.5 mM, at room temperature. All potentials (±10 mV) are reported in volts vs a Pt^0 pseudo reference electrode and using Fc^+/Fc as an internal reference 0.38 V (ΔE_p = 70 mV). Under these experimental conditions the Fc^+/Fc is quoted at 0.39 V (ΔE_p = 80 mV) versus the SSCE electrode. Data for an authentic sample of $[Ru(terpy)_2]^{2+}$: +1.27 (60), −1.27 (60), −1.51 V (60 mV). [c] Metal-based oxidation. [d] Successive ligand-localized reductions; number of electron involved are indicated as *n*e. The number of involved electrons is estimated by integration of the reversible processes. For the irreversible wave, the peak potential E_{pc} is quoted. [e] From ref 38. [f] From ref 25.

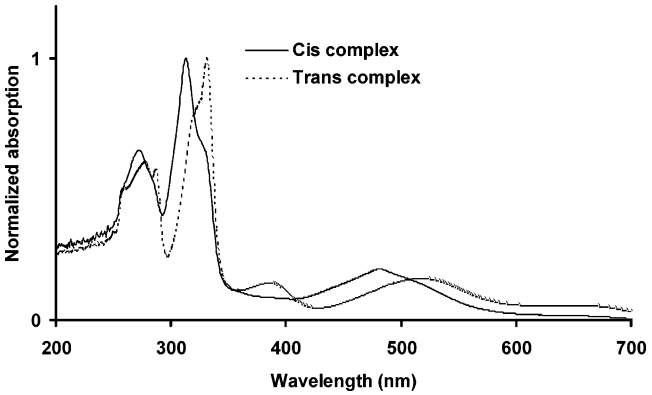


Figure 3. UV−vis absorption spectra of the trans complex **1** (---) and cis complex **2** (−) in argon-degassed anhydrous DMSO.

assignable to spin-allowed $\pi-\pi^*$ transitions centered on the polypyridine part of the ligand.[28] The shoulders around 320 nm are tentatively assigned to $n-\pi^*$ transitions also involving the polypyridine sites.[29] It is worth noting that for complexes **12** and **13**, bearing respectively a single alkyne and a butadiyne linker, a significative bathochromic shift (45 nm) of the MLCT[30] is found, owing to a better delocalization between both metal centers as compared to complexes **15, 18**, and **19**, in which the shift is only 25 nm. The weakening of this delocalization results from the folding of the central bipyridine or phenanthroline fragments. Note that the molar absorptivity of the MLCT band is approximately two times greater in dinuclear complexes **12** and **13** than in the mononuclear one, while a hyperchromic shift is found for the bipyrimidine-, bipyridine-, and phenanthroline-bridged back-to-back terpyridines. This is likely due to a contribution of Laporte forbidden $n \rightarrow \pi^*$ transitions induced by the increasing number of nitrogen lone pairs.

Electrochemistry Discussion. The electrochemical properties of the complexes were measured by cyclic voltammetry in CH_3CN solution. Table 2 lists the potentials (relative to the SSCE reference electrode) for the waves that were observed in the +1.9 to −2.1 V windows. First, for the bis-terpy complexes a single reversible anodic wave was observed around +1.32 V that is due to the Ru(III/II) couple. Note that for the polynuclear complexes the Ru(III/II) wave is notably enlarged versus the mononuclear complexes due to the fact that the two metal centers are oxidized approximately at the same potential. The observation of a single wave support the idea that these metal centers are not in electronic interaction. The shift in the metal-centered oxidation versus $[Ru(terpy)_2]^{2+}$ (E'^0 = +1.27 V) likely reflects the fact that by adding donating group such as CH_3 or $CH_2P(O)Ph_2$ the oxidation is facilitated by ca. 40−60 mV whereas the presence of ethynyl functions, considered as electron withdrawing, renders the oxidation of the metal center more difficult by ca. 30−90 mV. The mono-terpy complexes **1** and **2** are much easier to oxidize, as anticipated from their sensitivity toward air oxidation in solution, than the air stable bis-terpy analogues, whereas the oxidation of the trans complex is more easy by 90 mV, compared to the cis isomer. Both isomers exhibits a single oxidation wave in anhydrous DMSO likely to be metal centered and an irreversible terpy centered reduction at negative potential. Interestingly, when the cis complex is dissolved in anhydrous DMF, two oxidation waves at +0.66 V (ΔE_p = 70 mV) and +1.01 V (ΔE_p = 80 mV) and a single reduction wave are observed. The first oxidation wave is close to the potential found in DMSO and is likely attributed to the reversible Ru(III)/Ru(II) couple of the S-bonded cis isomer. The second oxidation wave having a current intensity 1.9 times greater than the first one could not be attributed to a Ru(IV)/Ru(III) couple due to the fact that such oxidation potentials are typically found near +2.0 V versus SSCE (e.g. in [Ru(TMEDA)(DMSO)Cl_3] complexes).[31] Here we would expect this second potential shift to even more anodic potential due to the π-acidic character of the terpy. The possible solvation of the complex by DMF in the cis case would certainly not result in such a strong difference in potential. Usually, the potential shift for the Ru(III)/Ru(II) couple is between 10 and 40 mV when DMSO molecules are replaced by DMF in the first coordination sphere of dinuclear ruthenium

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(31) Rack, J. J.; Gray, H. B. *Inorg. Chem.* **1999**, *38*, 2.

complexes.[32,33] Here it is plausible that, in DMF, a Ru−SO to Ru−OS isomerization process could occur with a ratio of 30% and 70%, respectively, for each form. Infrared spectra in DMF using a CaF_2 cell reveal a weak but significant ν(SO) stretching frequency at 936 cm^{-1} typical of O-bonded DMSO solvates. A remaining ν(SO) stretching frequency at 1083 cm^{-1} of the S-bonded species is also present confirming the presence of a mixture of cis Ru−SO and cis Ru−OS complexes.[15]

Along theses lines the carbonyl complexes **4** and **5** display each a single monoelectronic reversible oxidation wave and a single irreversible reduction wave in acetonitrile.[34] It is likely that the peculiar electrochemical response of the cis complex **2** in DMF is due to the presence of DMSO in the first coordination sphere.

The mononuclear complexes exhibit two well-defined and reversible reductions corresponding to the successive reduction of the ligands. Again when alkyne substituents are present, the first reduction is lowered by ca. 100 mV versus $[Ru(terpy)_2]^{2+}$ ($E'^0 = -1.27$ and -1.51 V).[35] Interestingly, all dinuclear complexes exhibit three well-resolved reversible waves in the cathodic branch of the voltamograms, which are due to the successive reductions centered on the substituted and unsubstituted terpy ligands. For all of these complexes the first reduction is shifted to a more positive potential than the first reduction of $[Ru(terpy)_2]^{2+}$.[35] This feature clearly indicates that the first reduction is localized on the bridging ligands. Moreover, there are significant differences between the first and second reduction potentials for the dinuclear complexes. These interesting features reflect the different electronic environments of terpyridine connected either to a second terpyridine via an additional alkyne bond or to a chelating platform at its center.

The first reduction of **13** is shifted by +50 mV compared to that of **12**, while the latter complex features a first reduction potential that is shifted by +300 mV relative to that of the parent $[Ru(terpy)_2]^{2+}$ complex. The anodic shifts for the first reduction potentials of **13** and **12** clearly reflect the combined effects of electron withdrawing and charge delocalization over the entire space. Similar effects were observed in bipyridine-, bipyrimidine-, and phenanthroline-bridged complexes **18**, **15**, and **19**, respectively. The first reduction appears as a single dielectronic wave at a potential located between the one observed in complex **13** and $[Ru(terpy)_2]^{2+}$. This similarity reflects the fact that in these dinuclear complexes the first reductions are localized on the bridging ligands and likely on the terpy's. The fact that the reduction appears as a single wave indicates that the electronic interactions between the two terpyridines bridged by a bipyridine, bipyrimidine, or phenanthroline are weak in contrast to complexes **12** and **13**.

Furthermore, the single two electron wave in the potential range −1.42 to −1.48 V for complexes **18** and **19** is close to the reductions found in **12** and **13** and may be safely assigned to the reduction of the external nonsubstituted terpy ligands. Interestingly, a third reversible monoelectronic reduction is observed in complexes **18** and **19** at a more cathodic potential: this is attributed to the reduction of the bipyridine and phenanthroline fragments.

The situation is more interesting with complex **15** where four separate quasi-reversible reductive steps could be discerned (Table 2). It is likely that the first reduction step concerns the two electron reduction of the bipyrimidine fragment[36] which is easier to reduce here than in unsubstituted bipyrimidine due to the pronounced withdrawing features of the ethynyl groups in the 5,5′-substitution positions.[37] As might be expected this first derived $E_{1/2}$ value is somewhat sensitive to the presence of Zn^{2+} cations added in solution and is in keeping with strong coordination with the nitrogen sites of the vacant bipyrimidine. Furthermore, the additional single electron waves located at −1.33 and −1.44 V can safely be attributed to the successive reduction of the ethynylated terpy fragments. The fact that the two processes are distinguished compared to complexes **18** and **19** is probably due to the presence of the two electrons on the central bipyrimidine subunit. The residual signal at −1.77 V is poorly resolved owing to the large electron density present on the complex but can be assigned to the reduction of both unsubstituted terpy ligands. It is interesting to notice that the three waves at −1.33, −1.44, and −1.77 V are not sensitive to the presence of incoming zinc cations contrary to the first reduction wave.

The reduction sequence of the various chelating fragments is in keeping with literature data.[36] The bipy moiety is easier to reduce than the other ligands (bipy < bipyrm < phen) reflecting the increase of electronegativity imported by the nitrogen atoms and the higher electronic density of phenanthroline versus bipyridine itself.

Conclusion

Novel ruthenium(II) mono(terpyridine) complexes were prepared and characterized. The *cis*-$[Ru(terpy)(DMSO)Cl_2]$ complex is a keystone precursor for the preparation, under mild conditions, of heteroleptic mononuclear and dinuclear complexes. Both precursors reacted with CO to stereoselectively give the corresponding carbonyl complexes. This protocol also allows access to a *cis*-$[Ru(terpy)(terpy\text{-}Br)]^{2+}$complex that is demonstrated to be a useful building block in cross-coupling reactions with ethynylated but metal-free bipy, phen, and bipyrm fragments. The new complexes retaining a vacant coordination sites are interesting targets for the spectrofluorometric detection of trace amount of cations present in solution. Work along theses lines is currently under investigation. Finally, NMR, UV−vis spec-

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troscopy, and cyclic voltammetry were used to characterize this series of complexes in which each redox couple can be assigned to a specific site.

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Supporting Information Available: Complete characterization data for complex **18**, CIF files for X-ray structures of complexes **1** and **4**, and an ORTEP view and X-ray crystallographic data for complex **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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