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New Procedures for the Synthesis of Mixed-Metal and/or Mixed-Ligand Ruthenium(II) and Osmium(II) Polypyridine Supramolecules and the Use of These Procedures in the Preparation of Hexanuclear Species

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The use of a protection/deprotection procedure within the "complexes-as-ligands/complexes-as-metals" strategy for the synthesis of oligonuclear Ru(II) and Os(II) polypyridine complexes is reported. The preparation of the monochelating cationic ligand 2-[2-(1-methylpyridiniumyl)]-3-(2-pyridyl)pyrazine [(2,3-Medpp)$^+$, **1**] is described, along with the synthesis of the trinuclear building blocks {(2,3-Medpp)Ru[(μ-2,5-dpp)Ru(bpy)$_2$]$_2$}(PF$_6$)$_7$ (**2**), {(2,3-dpp)Ru[(μ-2,5-dpp)Ru(bpy)$_2$]$_2$}(PF$_6$)$_6$ (**3**), {Ru[(μ-2,3-dpp)Ru(biq)$_2$]$_2$Cl}(PF$_6$)$_4$ (**4**), and {Ru[(μ-2,3-dpp)Os(bpy)$_2$]$_2$Cl$_2$}(PF$_6$)$_4$ (**5**) [dpp = bis(2-pyridyl)pyrazine; bpy = 2,2′-bipyridine; biq = 2,2′-biquinoline]. The use of the above building blocks is illustrated in the preparation of four new hexanuclear complexes of general formula {[ML$_2$(μ-2,*m*-dpp)]$_2$Ru(μ-2,3-dpp)Ru[(μ-2,*n*-dpp)M′L′$_2$]$_2$}(PF$_6$)$_{12}$ (**6**, M = M′ = Ru, L = L′ = biq, *m* = *n* = 3; **7**, M = M′ = Ru, L = bpy, L′ = biq, *m* = 5, *n* = 3; **8**, M = M′ = Os, L = L′ = bpy, *m* = *n* = 3; **9**, M = Ru, M′ = Os, L = L′ = bpy, *m* = 5, *n* = 3). The new synthetic procedure is discussed with reference to the design of "made-to-order" luminescent and redox-reactive compounds of unusual composition and topologies.

Introduction

In the last few years our[1-13] and other[14-19] research groups have been interested in the synthesis of oligonuclear Ru(II) and Os(II) polypyridine complexes containing 2,3-bis(2-pyridyl)pyrazine (2,3-dpp) or 2,5-bis(2-pyridyl)pyrazine (2,5-dpp) as bridging ligands and 2,2′-bipyridine (bpy) or 2,2′-biquinoline (biq) as terminal ligands. These compounds constitute a family of supramolecules whose outstanding photophysical and electrochemical properties[8,20] depend on the nature of the components (metal atoms and ancillary ligands) and on the spatial and electronic relationships between them (bridging ligands). Thus the design of effective synthetic procedures to prepare systems having particular compositions and topologies represents a major target in this research field.

A general approach to step-by-step syntheses has been therefore developed, which is based on the so-called "complexes-as-ligands/complexes-as-metals" strategy[11] and consists of reacting "metals" or "complex-metals" with ligands or "complex-ligands" (see Chart I). Adopting this strategy, we have been able to prepare several di-, tri-, tetra-, hexa-, hepta-, deca-, and tridecanuclear species, in some instances rather complicated ones. For example: the heterometallic tetranuclear species {Ru[(μ-2,3-dpp)Ru(bpy)$_2$]$_2$[(μ-2,3-dpp)Os(bpy)$_2$]}$^{8+}$ has been prepared from complexes a and b (see Chart I) (1:1); the heterobridged hexanuclear complex {[Ru(bpy)$_2$(μ-2,5-dpp)]$_2$Ru(μ-2,3-dpp)Ru[(μ-2,5-dpp)Ru(bpy)$_2$]$_2$}$^{12+}$, from c and 2,3-dpp (2:1); hepta-, deca-, and tridecanuclear species from d and e (3:1), from a and f (3:1), and from a and e (3:1), respectively.

As a further enrichment of the number of synthons useful within the above context, we report here the synthesis and characterization of two new trinuclear building blocks belonging to the "complex-metal" class, namely {Ru[(μ-2,3-dpp)Ru(biq)$_2$]$_2$Cl$_2$}(PF$_6$)$_4$ (**4**) and {Ru[(μ-2,3-dpp)Os(bpy)$_2$]$_2$Cl$_2$}(PF$_6$)$_4$ (**5**), and, more interestingly, the synthesis of the new trimetallic heterobridging "complex-ligand" compound {(2,3-dpp)Ru[(μ-2,5-dpp)Ru(bpy)$_2$]$_2$}(PF$_6$)$_6$ (**3**), obtained by a protection/deprotection method. The use of these new synthons is illustrated for the preparation of the four novel hexanuclear species **6**–**9**.

The new compounds are presently under photophysical and electrochemical study.

Experimental Section

Materials and Methods. 2,3-dpp was prepared as previously reported[4] and purified by recrystallization from ethanol and by sublimation (0.05 Torr, ca. 200 °C). The preparations of the precursor complexes [Ru(bpy)$_2$(2,5-dpp)](PF$_6$)$_2$,[4] [Ru(biq)$_2$(2,3-dpp)](PF$_6$)$_2$,[4] [Os(bpy)$_2$(2,3-

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Chart I. Mono- and Trinuclear Synthons Previously Employed in the Preparation of Supramolecular Systems

"Metals"

$RuCl_3{\cdot}3H_2O$ K_2OsCl_6

"Complex-Metals"

$[Ru(bpy)Cl_3]_n$
$Ru(bpy)_2Cl_2$ (d)
$Ru(biq)_2Cl_2$
$Os(bpy)_2Cl_2$
$Os(biq)_2Cl_2$
$[Ru\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2\}_2Cl_2]^{4+}$ (a)
$[Ru\{(\mu\text{-}2,5\text{-dpp})Ru(bpy)_2\}_2Cl_2]^{4+}$ (c)

Ligands

2,3-dpp 2,5-dpp

"Complex-Ligands"

$[Ru(bpy)_2(2,3\text{-dpp})]^{2+}$
$[Ru(biq)_2(2,3\text{-dpp})]^{2+}$
$[Ru(bpy)_2(2,5\text{-dpp})]^{2+}$
$[Ru(biq)_2(2,5\text{-dpp})]^{2+}$
$[Os(bpy)_2(2,3\text{-dpp})]^{2+}$ (b)
$[Os(biq)_2(2,3\text{-dpp})]^{2+}$
$[Os(bpy)_2(2,5\text{-dpp})]^{2+}$
$[Os(biq)_2(2,5\text{-dpp})]^{2+}$
$[Ru(bpy)(2,3\text{-dpp})_2]^{2+}$
$[Ru(bpy)(2,5\text{-dpp})_2]^{2+}$
$[Ru(2,3\text{-dpp})_3]^{2+}$
$[Os(2,3\text{-dpp})_3]^{2+}$ (f)
$[Os(2,5\text{-dpp})_3]^{2+}$
$[Ru\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2\text{-}(2,3\text{-dpp})\}_3]^{8+}$ (e)

dpp)]$(PF_6)_2$,[7] and $\{Ru[(\mu\text{-}2,5\text{-dpp})Ru(bpy)_2]_2Cl_2\}(PF_6)_4$,[11] as well as the details and procedures[4] for elemental analyses, IR spectra, and conductivity measurements, have been previously reported. All reactions were carried out under argon, using, when appropriate, the needle technique. 1,2-Dichloroethane and acetonitrile employed as reaction solvents were dried and distilled prior to use. All reactions and handlings involving biq derivatives in solution were carried out in light-protected vessels. NMR spectra were recorded on a Bruker AC 200 spectrometer. FAB mass spectra (NBA matrix) were obtained by a Vacuum Generator (VG) ZAB-2F instrument operated at an acceleration potential of 8 kV by using the M-scan steerable FAB gun; a neutral xenon beam of 9.5-keV energy and a neutral current of ca. 10 μA were employed.

Preparation of 2-[2-(1-Methylpyridiniumyl)]-3-(2-pyridyl)pyrazine Hexafluorophosphate [1, (2,3-Medpp)PF_6]. To a suspension of trimethyloxonium tetrafluoroborate (0.410 g, 2.77 mmol) in 1,2-dichloroethane (20 mL) was slowly added a solution of 2,3-dpp (0.607 g, 2.59 mmol) in the same solvent (40 mL). The mixture was refluxed for 30 min and then cooled to room temperature, and the green solid that formed was filtered off. The solution was taken to dryness by rotary evaporation in vacuo. To the residue dissolved in warm ethanol was added a saturated solution of NH_4PF_6. After the mixture was cooled at −18 °C, the white crystalline precipitate that formed was recovered by filtration (0.659 g, 64% yield). ^1H NMR (acetonitrile-d_3 solvent, room temperature, TMS internal reference, ppm): 8.98 (d, 1 H), 8.85 (d, 1 H), 8.80 (m, 1 H), 8.43 (m, 1 H), 8.41 (m, 1 H), 8.14 (m, 1 H), 7.96 (m, 1 H), 7.70 (m, 1 H), 7.35 (m, 1 H), 4.08 (s, 3 H). (See Figure 1.)

Preparation of $\{(2,3\text{-Medpp})Ru[(\mu\text{-}2,5\text{-dpp})Ru(bpy)_2]_2\}(PF_6)_7$ (2). $\{Ru[(\mu\text{-}2,5\text{-dpp})Ru(bpy)_2]_2Cl_2\}(PF_6)_4$ (0.137 mg, 0.067 mmol) in 1:1 (v/v) water/ethanol (6 mL) was treated with silver nitrate (0.023 g, 0.133 mmol). After 3 h of stirring at room temperature, (2,3-Medpp)-PF_6 (0.026 g, 0.067 mmol) was added to the mixture, which was then refluxed for 72 h. AgCl was separated from the mixture cooled to room temperature by repeated centrifugations, and to the mother liquor was added an excess of solid NH_4PF_6. The blue-green solid that formed was filtered off, dissolved in acetonitrile, and purified by flash chromatography on Sephadex G-10. After addition of ethanol, the solution was rotary-evaporated until a substantial amount of precipitate was obtained; this was filtered off, washed with small portions of cold ethanol and then with diethyl ether, and dried in vacuo (0.110 g, 65% yield). ^1H NMR (acetonitrile-d_3 solvent, room temperature, TMS internal reference): at least five singlets of different intensities between 5.44 and 5.43 ppm, attributable to the methyl group bound to a pyridyl nitrogen in different isomers (see Results and Discussion). Selected peaks in the FAB mass spectrum for $m/z > 1000$ (m/z of most abundant peak in the isotopic cluster, ion composition, and intensity relative to $m/z = 1113$): 2371, $[M - 2PF_6 + e]^+$, 78%; 2225, $[M - 3PF_6 + 2e]^+$, 60%; 2080, $[M - 4PF_6 + 3e]^+$, 41%; 1935, $[M - 5PF_6 + 4e]^+$, 27%; 1185, $[M - 2PF_6]^{2+}$, 55%; 1113, $[M - 3PF_6 + e]^{2+}$, 100%; 1040, $[M - 4PF_6 + 2e]^{2+}$, 64%.

Preparation of $\{(2,3\text{-dpp})Ru[(\mu\text{-}2,5\text{-dpp})Ru(bpy)_2]_2\}(PF_6)_6$ (3). A solution of complex **2** (0.056 g, 0.021 mmol) and of a very large excess (ca. 30:1) of 1,4-diazabicyclo[2.2.2]octane (DABCO) in acetonitrile (6 mL) was refluxed for 72 h. After cooling of the solution to room temperature and addition of ethanol, the reaction mixture was rotary-evaporated in vacuo until a substantial amount of green precipitate was obtained. This was filtered off, dissolved in acetonitrile, and purified by flash chromatography on Sephadex G-10. After addition of ethanol, the solution was partially evaporated, and the precipitate so obtained was filtered off, washed with small portions of cold ethanol and then with diethyl ether, and dried in vacuo (0.046 g, 87% yield).

Preparation of $\{Ru[(\mu\text{-}2,3\text{-dpp})Ru(biq)_2]_2Cl_2\}(PF_6)_4$ (4). A mixture of $RuCl_3{\cdot}3H_2O$ (0.0185 g, 0.071 mmol), $[Ru(biq)_2(2,3\text{-dpp})](PF_6)_2$ (0.162 g, 0.142 mmol), and LiCl (0.020 g, 0.472 mmol) in ethylene glycol (6 mL) was refluxed for 48 h, cooled to room temperature, and treated with an excess of NH_4PF_6 in methanol (6 mL). On addition of diethyl ether, a violet precipitate was obtained; it was filtered off, dissolved in acetonitrile, and purified by flash chromatography on Sephadex G-10 and treated as above (0.120 g, 72% yield). Selected peaks in the FAB mass spectrum for $m/z > 1500$ (m/z of most abundant peak in the isotopic cluster, ion composition, and intensity relative to $m/z = 2158$): 2303, $[M - PF_6]^+$, 40%; 2158, $[M - 2PF_6 + e]^+$, 100%; 2013, $[M - 3PF_6 + 2e]^+$, 60%.

Preparation of $\{Ru[(\mu\text{-}2,3\text{-dpp})Os(bpy)_2]_2Cl_2\}(PF_6)_4$ (5). A mixture of $RuCl_3{\cdot}3H_2O$ (0.0146 g, 0.056 mmol), $[Os(bpy)_2(2,3\text{-dpp})](PF_6)_2$ (0.115 g, 0.112 mmol), and LiCl (0.016 g, 0.373 mmol) in 2:1 (v/v) ethylene glycol/methanol (15 mL) was refluxed for 36 h. The mixture was cooled to room temperature, and an excess of NH_4PF_6 in methanol (3 mL) was added. Upon addition of diethyl ether, a solid precipitated; it was dissolved in acetonitrile and purified by flash chromatography on Sephadex G-15. The deep greenish blue product was recovered from the acetonitrile solution by addition of ethanol, filtration, washings with cold ethanol and diethyl ether, and vacuum-drying (0.100 g, 80% yield). Selected peaks in the FAB mass spectrum for $m/z > 1500$ (m/z of most abundant peak in the isotopic cluster, ion composition, and intensity relative to $m/z = 1935$): 2080, $[M - PF_6]^+$, 60%; 1935, $[M - 2PF_6 + e]^+$, 100%; 1790, $[M - 3PF_6 + 2e]^+$, 50%.

Preparation of $\{[Ru(biq)_2(\mu\text{-}2,3\text{-dpp})]_2Ru(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(biq)_2]_2\}(PF_6)_{12}$ (6). A suspension of complex **4** (0.040 g, 0.016 mmol) in 95% ethanol (3 mL) was treated with silver nitrate (0.005 g, 0.032 mmol) and the mixture stirred for 3 h at room temperature. 2,3-dpp (0.0019 g, 0.008 mmol) and ethylene glycol (3 mL) were added. The reaction mixture was refluxed for 40 h and then cooled to room temperature. AgCl was separated by repeated centrifugations, the mother liquor was concentrated by rotary evaporation in vacuo, and a saturated solution of NH_4PF_6 in methanol (3 mL) was added. Upon addition of diethyl ether, a violet precipitate formed; it was filtered off, dissolved in acetonitrile, and chromatographed on Sephadex G-25 (acetonitrile eluant). After addition of ethanol, the solution was partially evaporated until precipitation of the product was apparently complete. The solid was filtered off, washed with cold ethanol and diethyl ether, and vacuum-dried (0.025 g, 55% yield).

Preparation of $\{[Ru(bpy)_2(\mu\text{-}2,5\text{-dpp})]_2Ru(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(biq)_2]_2\}(PF_6)_{12}$ (7). A solution of complex **4** (0.020 g, 0.008 mmol) in ethanol (3 mL) was treated with a solution of silver nitrate (0.0027 g, 0.016 mmol) in water (2 mL). After 3 h of stirring at room temperature, complex **3** (0.0020 g, 0.008 mmol) in ethylene glycol (3 mL) was added to the solution. The reaction mixture was refluxed for 48 h and then cooled to room temperature. AgCl was separated from the mixture by repeated centrifugations, the mother liquor was concentrated by rotary evaporation in vacuo, and an excess of solid NH_4PF_6 was added. The violet precipitate that formed was filtered off, dissolved in acetonitrile, and flash-chromatographed on Sephadex G-25. After addition of ethanol, the solution was partially evaporated until precipitation of the product was apparently complete. The solid was filtered off, washed with ethanol and diethyl ether, and vacuum-dried (0.032 g, 78% yield).

Preparation of $\{[Os(bpy)_2(\mu\text{-}2,3\text{-dpp})]_2Ru(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Os(bpy)_2]_2\}(PF_6)_{12}$ (8). A solution of complex **5** (0.040 g, 0.018 mmol) in ethanol (3 mL) was treated with a solution of silver nitrate (0.0062 g, 0.036 mmol) in water (2 mL), and the mixture was stirred for 3 h at room temperature. To the resulting violet solution was added 2,3-dpp (0.0021 g, 0.009 mmol) in ethylene glycol (3 mL). The reaction mixture was refluxed for 48 h and then cooled to room temperature. AgCl was separated from the mixture by repeated centrifugations, the mother liquor was concentrated by rotary evaporation in vacuo, and an excess of solid NH_4PF_6 was added. The violet precipitate that formed was filtered off, dissolved in acetonitrile, and flash-chromatographed on Sephadex G-25. After addition of ethanol, the solution was partially evaporated until precipitation of the product was apparently complete. The solid was filtered off, washed with ethanol and diethyl ether, and vacuum-dried (0.033 g, 70% yield).

Table I. Analytical Data[a] for the Novel Compounds

no.		%C	%H	%N
1[b]	(2,3-Medpp)PF$_6$	41.22 (41.87)	3.55 (3.98)	13.46 (13.02)
2	{(2,3-Medpp)Ru[(μ-2,5-dpp)Ru(bpy)$_2$]$_2$}(PF$_6$)$_7$	37.68 (37.47)	2.60 (2.46)	10.61 (10.52)
3	{(2,3-dpp)Ru[(μ-2,5-dpp)Ru(bpy)$_2$]$_2$}(PF$_6$)$_6$	39.55 (39.39)	2.28 (2.50)	11.08 (11.20)
4[c]	{Ru[(μ-2,3-dpp)Ru(biq)$_2$]$_2$Cl$_2$}(PF$_6$)$_4$	46.96 (46.99)	2.73 (3.15)	8.72 (8.77)
5[c]	{Ru[(μ-2,3-dpp)Os(bpy)$_2$]$_2$Cl$_2$}(PF$_6$)$_4$	34.83 (34.99)	2.70 (2.76)	9.45 (9.60)
6[d]	{[Ru(biq)$_2$(μ-2,3-dpp)]$_2$Ru(μ-2,3-dpp)Ru[(μ-2,3-dpp)Ru(biq)$_2$]$_2$}(PF$_6$)$_{12}$	44.14 (44.16)	3.00 (3.01)	8.91 (8.66)
7[e]	{[Ru(bpy)$_2$(μ-2,5-dpp)]$_2$Ru(μ-2,3-dpp)Ru[(μ-2,3-dpp)Ru(biq)$_2$]$_2$}(PF$_6$)$_{12}$	40.20 (40.88)	2.63 (2.82)	9.48 (9.42)
8[f]	{[Os(bpy)$_2$(μ-2,3-dpp)]$_2$Ru(μ-2,3-dpp)Ru[(μ-2,3-dpp)Os(bpy)$_2$]$_2$}(PF$_6$)$_{12}$	34.11 (34.68)	2.35 (2.37)	9.72 (9.70)
9	{[Ru(bpy)$_2$(μ-2,5-dpp)]$_2$Ru(μ-2,3-dpp)Ru[(μ-2,3-dpp)Os(bpy)$_2$]$_2$}(PF$_6$)$_{12}$	36.42 (36.43)	2.27 (2.32)	10.25 (10.20)

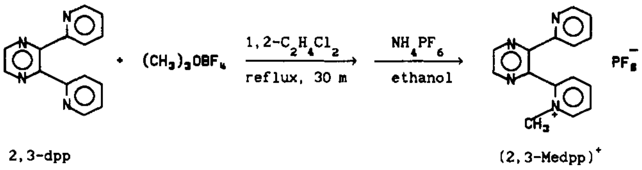
[a] Found (calcd). [b-f] Formulated with nH$_2$O: (*b*) $n = 2$; (*c*) $n = 6$; (*d*) $n = 14$; (*e*) $n = 10$; (*f*) $n = 4$.

Table II. Selected IR Absorption Maxima and Conductivity Values for the Novel Compounds

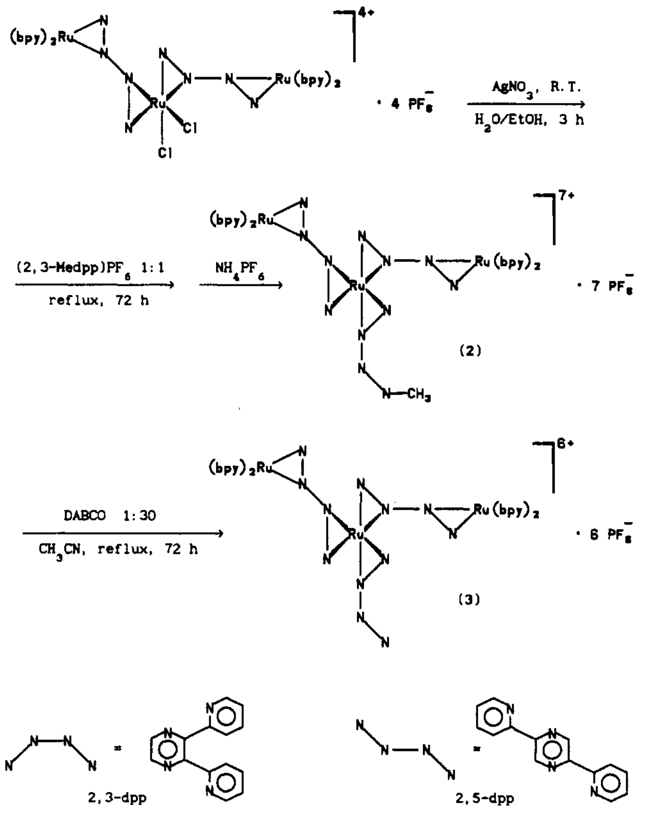
no.	IR data[a]	Λ[b]
1	1632 (s), 1589 (s), 1550 (w), 1532 (w), 1519 (m), 1479 (w), 1465 (w), 1455 (w), 1440 (m), 1412 (sh), 1398 (s), 999 (w)	89.5
2	1626 (m), 1606 (s), 1565 (w, br), 1505 (w), 1462 (s), 1448 (s), 1425 (m), 1386 (vs), 1370 (s, sh)	372.2
3	1606 (m), 1558 (w, sh), 1505 (w), 1465 (s), 1449 (s), 1425 (m), 1388 (vs), 1370 (m, sh), 990 (vw)	354.3
4	1617 (w), 1595 (s), 1588 (w, sh), 1550 (w), 1510 (s), 1460 (w, br), 1432 (m), 1420 (m), 1390 (s), 1370 (m)	304.7
5	1605 (m), 1560 (w, br), 1485 (w), 1466 (s), 1449 (m), 1423 (m), 1387 (s)	303.5
6	1599 (s), 1578 (w, sh), 1560 (w), 1510 (s), 1470 (m), 1460 (m, sh), 1435 (m), 1420 (m, sh), 1391 (m), 1370 (m, sh)	597.4
7	1596 (s), 1579 (w, sh), 1560 (w, br), 1511 (s), 1462 (s), 1449 (s), 1422 (m), 1395 (m), 1370 (m)	677.2
8	1606 (m), 1560 (w, br), 1469 (s), 1450 (m), 1423 (m), 1390 (m)	633.9
9	1606 (m), 1560 (w, br), 1465 (s), 1449 (s), 1425 (m), 1388 (m), 1370 (w)	671.4

[a] cm^{-1}; KBr pellets. [b] Ω^{-1} cm^2 mol^{-1}. Approximately 1 × 10^{-3} M solutions in nitromethane; 20 °C.

Scheme I



Scheme II



Preparation of {[Ru(bpy)$_2$(μ-2,5-dpp)]$_2$Ru(μ-2,3-dpp)Ru[(μ-2,3-dpp)Os(bpy)$_2$]$_2$}(PF$_6$)$_{12}$ (9). A solution of complex **5** (0.018 g, 0.008 mmol) in ethanol (3 mL) was treated with a solution of silver nitrate (0.0027 g, 0.016 mmol) in water (2 mL), and the mixture was stirred for 3 h at room temperature. To the resulting solution was added complex **3** (0.0020 g, 0.008 mmol) in ethylene glycol (3 mL). The reaction mixture was refluxed for 48 h and then cooled to room temperature. AgCl was separated from the mixture by repeated centrifugations, the mother liquor was concentrated by rotary evaporation in vacuo, and an excess of solid NH$_4$PF$_6$ was added. The Prussian blue precipitate that formed was filtered off, dissolved in acetonitrile, and flash-chromatographed on Sephadex G-25. After addition of ethanol, the solution was partially evaporated until precipitation of the product was apparently complete. The solid was filtered off, washed with ethanol and diethyl ether, and vacuum-dried (0.030 g, 75% yield).

Results and Discussion

The formulas of the novel compounds reported in this paper are listed in Table I, together with analytical data. The IR data and the conductivity values (Table II) are in agreement with those observed for strictly related compounds.[4]

The reaction between 2,3-dpp and trimethyloxonium tetrafluoroborate in 1,2-dichloroethane[21] (Scheme I) gives rise to the monoprotected ligand **1** that was recovered as hexafluorophosphate salt in satisfactory yield and purity. Its assigned ^{1}H NMR spectrum (Figure 1) clearly demonstrates that the methylation takes place at the pyridyl nitrogen, as expected on the basis of its greater nucleophilicity in comparison to that of the pyrazine nitrogens.

Ligand **1** was proved to be sufficiently stable under rather drastic conditions: demethylation was not observed after a 24-h reflux in 2:1 ethanol/water and was remarkably slow even in refluxing diethylene glycol (50% after 5 h).

The preparation of the trimetallic "protected" species {(2,3-Medpp)Ru[(μ-2,5-dpp)Ru(bpy)$_2$]$_2$}(PF$_6$)$_7$ (**2**) (Scheme II, first reactions) was readily accomplished by reacting, at room temperature in water/ethanol, {Ru[(μ-2,5-dpp)Ru(bpy)$_2$]$_2$Cl$_2$}(PF$_6$)$_4$ with silver nitrate, in order to obtain the intermediate diaquo species under the mildest conditions, and then adding ligand **1** and refluxing for 72 h. This reaction time, necessary for obtaining fair yields, is substantially longer than that sufficient, for instance, in the preparation[4] of [Ru(bpy)$_2$(2,3-dpp)](PF$_6$)$_2$ from [Ru(bpy)$_2$Cl$_2$] and 2,3-dpp (8 h). This fact can be easily accounted for, considering that the reaction kinetics is negatively affected by a statistical factor (one chelating site instead of two), by a steric factor (greater hindrance at the reaction center), and by an activity factor (reduced nucleophilicity of the monopositively charged ligand). Nevertheless the procedure is effective and does not

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(21) Curphey, T. J.; Prasad, K. S. *J. Org. Chem.* **1972**, *37*, 2259.

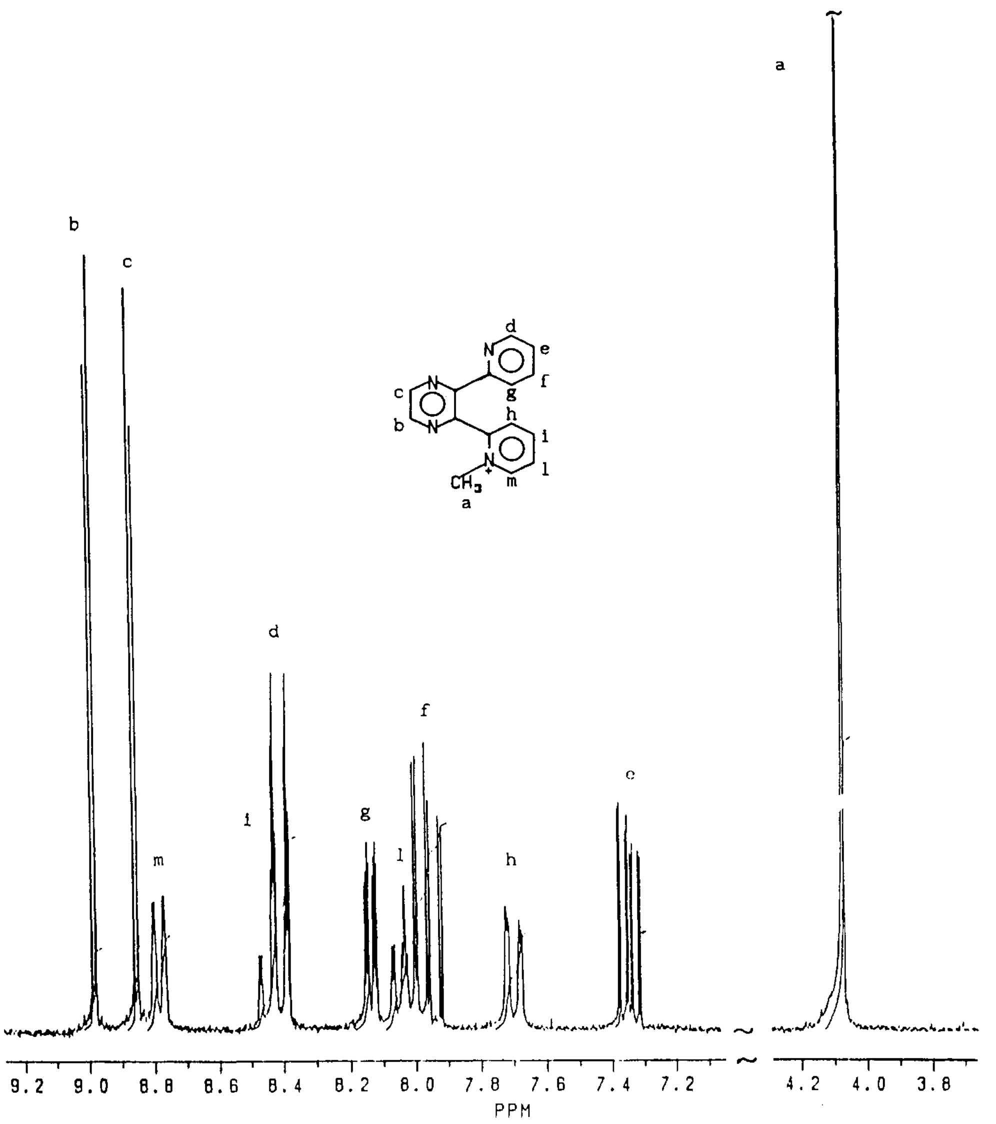


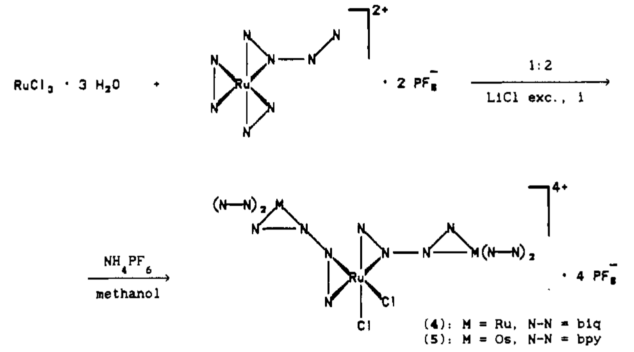
Figure 1. Assigned ^{1}H NMR spectrum of (2,3-Medpp)PF_6 in CD_3CN.

lead to the hexanuclear side product that results when {Ru[(μ-2,5-dpp)Ru(bpy)$_2$]$_2$$Cl_2$}($PF_6$)$_4$ is directly reacted with even very large excesses of 2,3-dpp.

In order to obtain the deprotected trinuclear "complex-ligand" species {(2,3-dpp)Ru[(μ-2,5-dpp)Ru(bpy)$_2$]$_2$}(PF_6)$_6$ (**3**), compound **2** was treated with 1,4-diazabicyclo[2.2.2]octane (DABCO) as demethylating agent[22] in refluxing acetonitrile (Scheme II, last reaction). The choice of this solvent was made in order to avoid decomposition because of too high reaction temperatures, but as a consequence, long reaction times and substantial excesses of DABCO (see Experimental Section) were necessary. It is noteworthy that free alkylpyridinium derivatives treated with a 2-fold excess of DABCO are reported to undergo dealkylation in refluxing DMF (3 h) but none at all in refluxing ethanol (18 h). In our case, due to complexation of the other chelating site of the molecule, the methyl group is more activated toward nucleophilic attack, as the proton chemical shift (5.44 ppm vs 4.08 ppm of the free ligand) would suggest.

The synthesis of the trinuclear "complex-metal" species {Ru[(μ-2,3-dpp)Ru(biq)$_2$]$_2$$Cl_2$}($PF_6$)$_4$ (**4**) and {Ru[(μ-2,3-dpp)Os(bpy)$_2$]$_2$$Cl_2$}($PF_6$)$_4$ (**5**) was readily achieved by following Scheme III. The method is the same as that already used[11] in the preparation of other homometallic trinuclear synthons based on Ru and bpy, the more relevant differences being longer reaction times and higher temperatures, due to the lower reactivity[4,7] of Ru–biq and Os precursors, respectively. The presence of an excess of LiCl in solution prevents the formation of unwanted species trischelated at the central metal.

Scheme III



i) Reaction conditions. For **4**: ethylene glycol, reflux, 48 h. For **5**: 2:1 (v/v) ethylene glycol/methanol, reflux, 36 h.

The novel hexanuclear species were synthesized by following two different routes, depending on the required geometry, "symmetrical" (supramolecules **6** and **8**) or "unsymmetrical" (supramolecules **7** and **9**) with respect to the central bridge. In the former case, it was sufficient to react the appropriate trinuclear "complex-metal" with the free binucleating ligand in a 2:1 ratio (Scheme IV). In the latter case, an appropriate "complex-metal"

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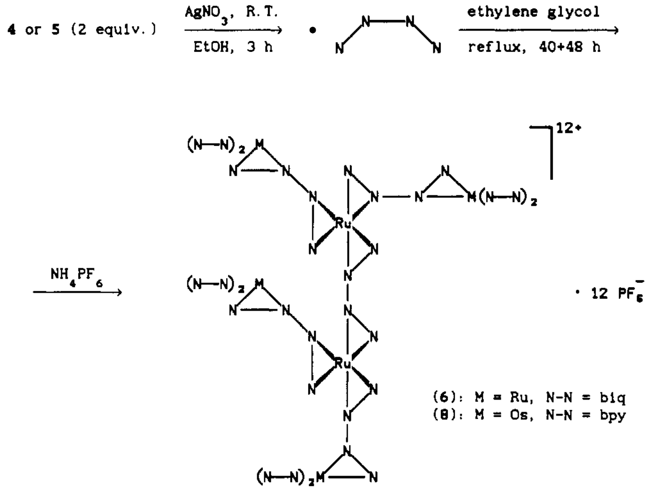
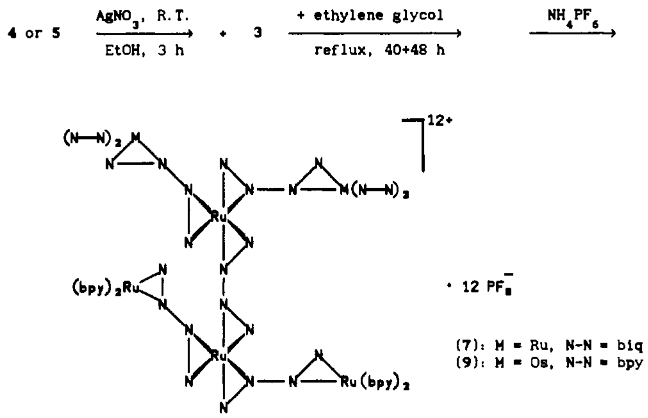
(22) Ho, T.-L. *Synthesis* **1972**, 702.

Scheme IV



(6): M = Ru, N-N = biq
(8): M = Os, N-N = bpy

Scheme V



(7): M = Ru, N-N = biq
(9): M = Os, N-N = bpy

was reacted with the "complex-ligand" species **3** in a 1:1 ratio (Scheme V). With the exception of compound **6**, whose preparation involves the use of a rather inert biq derivative, all yields of hexanuclear species were quite satisfactory, being at least 70% in the purified product.

The structural characterization of oligonuclear Ru and Os polypyridine complexes, as already discussed in previous papers, represents a very complicated problem[13] because of the possibility of many different geometrical and stereochemical isomerisms around each metal center. In general, when a particular metal center is bound to three equivalent bridging ligands, two geometrical isomers (*fac* and *mer*) can exist. When one of these ligands is not equivalent to the others, four different geometrical isomers are, in principle, possible. If two equivalent bridging ligands and two equivalent monodentate ligands are present, the number of possible isomers becomes 3. Furthermore, in all the described situations, the metal is also a chiral center. Thus the trimetallic species **2** and **3** reported in this paper can exist as four different geometrical isomers, each one of which can exist as four diastereomeric couples of enantiomers. For compounds **4** and **5**, the above figures become 3 and 4, respectively. The situation for the hexanuclear complexes can be much more complicated not only in view of the presence of six chiral centers (but **6**–**8** can have a mirror plane) but also because of the possibility that the two trimetallic subunits in the same molecule can have different geometries. For these reasons, structural investigations on supramolecular systems of this type are difficult and would require much more sophisticated preparative approaches in order to obtain at least much simpler isomeric mixtures suitable for NMR analysis (also using perdeuterio ancillary ligands[23]) and for growing crystals from which X-ray structures can be obtained. On the other hand, this route, while stimulating and interesting from a speculative point of view, does not represent the only choice when, as in our case, the aim of the preparative work is to obtain chemically pure samples of new supramolecular compounds, suitable for photophysical and electrochemical studies, in which differences arising from the possible presence of isomeric species are not expected to be sizable.[24]

Conclusion

The new procedure reported in this paper, based on a protection/deprotection method, was used to prepare new building blocks for the synthesis of supramolecular systems based on Ru(II) and/or Os(II), 2,3- and/or 2,5-dpp as bridging ligands, and bpy and/or biq as ancillary ligands.

We have shown some examples of the use of a particular "complex-ligand" species (**3**) in conjunction with new "complex-metal" species (**4** and **5**) to obtain novel hexanuclear systems of photochemical and electrochemical interest.

In view of the effectiveness of the method reported here, the preparation of further "protected" building blocks, such as $[RuL(MeBL)Cl_2]^+$ and $[Ru(MeBL)_2Cl_2]^{2+}$ (L = bpy or biq; MeBL = 2,3- or 2,5-Medpp) is presently under investigation. These synthons could act first as "complex-metals" and then—after deprotection—as "complex-ligands" not only in reaction with the species reported in Chart I but also in the preparation of more complicated synthons belonging to the "complex-ligand" class; therefore, they could be very usefully employed in step by step tailoring of supramolecular species having particular compositions *and* unusual topologies.

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(23) Chirayil, S.; Thummel, R. P. *Inorg. Chem.* **1989**, *28*, 85.

(24) Hage, R.; Dijkhuis, A. H. J.; Haasnot, J. G.; Prins, R.; Reedijk, J.; Buchanan, B. E.; Vos, J. G. *Inorg. Chem.* **1988**, *27*, 2185.