Direct Synthesis of Rigid Ligand-Bridged Homo- and Heterodinuclear Complexes via Stereoselective 1,3-Dipolar Coupling of Mononuclear Ruthenium(II) and Osmium(II) Precursors

**Austin C. Schultz,[1] Laurence S. Kelso,[2]
Martin R. Johnston,[1] Ronald N. Warrener,*,[1] and
F. Richard Keene*,[2]**

School of Biomedical and Molecular Sciences, James Cook
University, Townsville, Queensland 4811, Australia, and
Center for Molecular Architecture, Central Queensland
University, Rockhampton, Queensland 4702, Australia

Received February 25, 1999

Introduction

Polymetallic supramolecular assemblies have been the subject of attention because of their potential application to light-harvesting and light-activated devices.[3] However, the electronic and spatial requirements for effective intercomponent energy transfer within these assemblies are not well understood,[4] and ligand design becomes pivotal to any study addressing such issues.

We have recently reported the synthesis of a variety of bifunctional ligands incorporating rigid alicyclic spacers[5,6] and their reaction with appropriate metal centers to provide homodinuclear complexes.[5] The synthesis of analogous heterodinuclear complexes presents a significant challenge due to the preferential formation of homodinuclear byproducts, and examples of coupling procedures for selective formation of mixed-metal systems are limited and relatively recent.[7,8]

This report deals with an entirely new approach to the synthesis of mixed-metal ligand-bridged dinuclear complexes. Individual preformed mononuclear norbornene-bearing A-BLOCKs (e.g. **1**−**3**) and epoxide-bearing B-BLOCKs (e.g. **4** and **5**), both incorporating 1,10-phenanthroline ligating groups which are coordinated to d^6 octahedral Ru(II) or Os(II) metal centers (E = CO_2Me), are stereoselectively coupled together through their attached carbocyclic components to form rigidly linked [ML_2-(rigid spacer)-$M'L_2$] compounds. The technique builds on the convergent approach developed for linking of uncoordinated BLOCKs to realize the free bifunctional ligands, which we reported recently.[9]

This A+B methodology is able to accommodate a range of different metal centers, whose stereochemistries may be precontrolled in relation to the carbocyclic frame of the participating BLOCKs. Additionally, the relative spatial orientations of the coupled chromophores may be varied from a rodlike topology (e.g. **14** or **15**) to a curved framework (e.g. **12** or **13**).[10] In the rodlike systems, the separation of the chromophores can be varied while maintaining the relative orientation of the metal centers; with curved frameworks, the relative orientation changes with distance.

Results and Discussion

The synthesis (Scheme 1) of ligand **8**, which is used to prepare BLOCK **3** and contains a σ-linked sesquinorbornane subunit in the alicyclic frame, was achieved by the stoichiometrically controlled reaction of 7,8-diazaphencyclone (DAPC; **6**)[6,11] with the bis-alkene **7**.[12] The synthesis of ligand **11** (used to prepare BLOCK **4**) was achieved in a two-step process, the first analogous to that used for **8** but involving the bis-cyclobutene-1,2-diester **9**[10] to form the 1:1-adduct **10**, followed by low-temperature nucleophilic epoxidation of the remaining cyclobutene-1,2-diester group in **10**.

The required BLOCK complexes **1**−**4** were prepared by reaction of the respective ligands with excess [$M(bpy)_2(CF_3SO_3)_2$] (M = Ru or Os, bpy = 2,2′-bipyridine)[11,13] in chloroform/2-methoxyethanol mixtures under microwave conditions.

BLOCK **5** was prepared from BLOCK **1** by treatment with dimethyl acetylene dicarboxylate in the presence of [$RuH_2(CO)(PPh_3)_3$] according to the method of Mitsudo et al.[14,15] This reaction fails when applied to norbornanes containing uncomplexed 1,10-phenanthroline groups. The resultant cyclobutene-1,2-diester was subjected to low-temperature epoxidation as described above to produce complex BLOCK **5**.

The ability of ACE (alkene + cyclobutene epoxide) coupling[9] to accommodate cationic metal complexes was established here for the first time, by reaction of the ruthenium A-BLOCK **1** with the ruthenium B-BLOCK **5** to form the coupled diruthenium ligand-bridged complex **12**, which was isolated as the PF_6^- salt (Scheme 2). This compound was identical with the product formed from the appropriate di-bidentate bridging ligand[6] by treatment with [$Ru(bpy)_2(CF_3SO_3)_2$]. The coupling is presumed to involve thermal ring-opening of the cyclobutene epoxide to give a 1,3-dipolar species as the transient intermediate which is trapped by the norbornene dipolarophile.[9] This 1,3-dipolar cycloaddition process is highly stereoselective and leads exclusively to products in which the two metal centers are spatially separated by a rigid alicyclic framework.[9,10] The rigidity of the final product is assured since the ACE coupling process forms a 7-oxanorbornane ring at the junction of the two BLOCKs. Complex **15** was synthesized by the coupling of BLOCKs **3** and **4**.

---

* Author to whom correspondence should be sent. Fax: +61-7-47814600. E-mail: Richard.Keene@jcu.edu.au.

(1) Central Queensland University.

(2) James Cook University.

(3) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759; V. Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: Chichester, UK, 1991.

(4) Keene, F. R. *Coord. Chem. Rev.* **1997**, *166*, 121.

(5) Warrener, R. N.; Ferreira, A. B. B.; Schultz, A. C.; Butler, D. N.; Keene, F. R.; Kelso, L. S. *Angew. Chem.* **1996**, *108*, 2651; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2485.

(6) Warrener, R. N.; Schultz, A. C.; Houghton, M. A.; Butler, D. N. *Tetrahedron* **1997**, *53*, 3991.

(7) Armaroli, N.; Barigellitti, F.; Calogero, G.; Flamingi, L.; White, C. M.; Ward, M. D. *Chem. Commun.* **1997**, 2181.

(8) Connors, P. J.; Tzalis, D.; Dunnick, A. L.; Tor, Y. *Inorg. Chem.* **1998**, *37*, 1121.

(9) Warrener, R. N.; Schultz, A. C.; Butler, D. N.; Wang, S.; Mahadevan, I. B.; Russell, R. A. *Chem. Commun.* **1997**, 1023.

(10) Margetic, D.; Johnston, M. R.; Tiekink, E. R. T.; Warrener, R. N. *Tetrahedron Lett.* **1998**, 39, 5277.

(11) Warrener, R. N.; Houghton, M. A.; Schultz, A. C.; Keene, F. R.; Kelso, L. S.; Dash, R.; Butler, D. N. *Chem. Commun.* **1996**, 1151.

(12) Paquette, L. A.; Wyvratt, M. J. *J. Am. Chem. Soc.* **1974**, *96*, 4671.

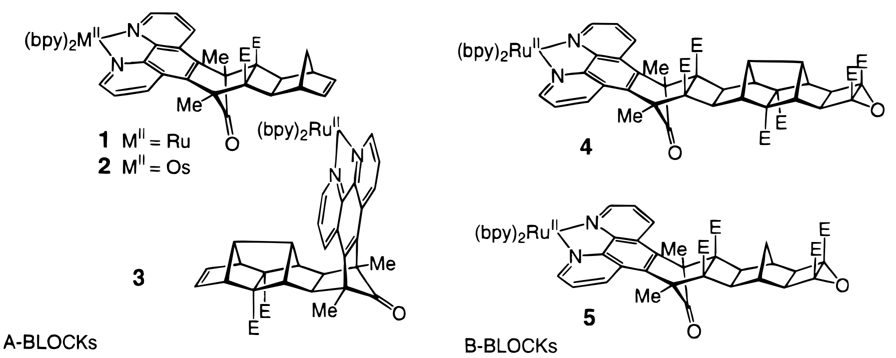
(13) Ridd, M. J.; Gakowski, D. J.; Sneddon, G. E.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1992**, 1949.

(14) Mitsudo, T.; Kokuryo, K.; Shinsugi, T.; Nakagawa, Y.; Watanabe, Y.; Takegami, Y. *J. Org. Chem.* **1979**, *44*, 4492.

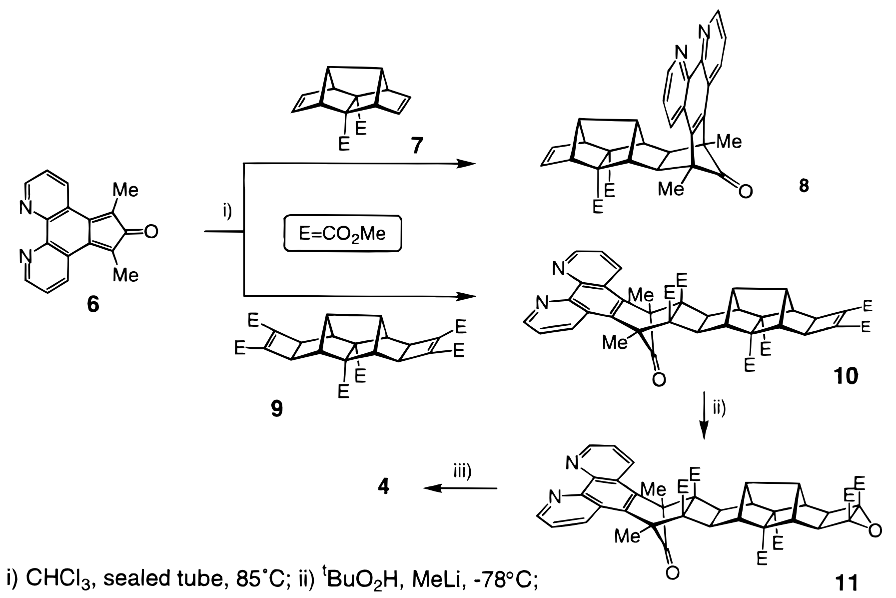
(15) Misudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580.

10.1021/ic9902370 CCC: $18.00

Chart 1



Scheme 1



i) $CHCl_3$, sealed tube, 85°C; ii) $^tBuO_2H$, MeLi, -78°C;
iii) microwave with $[M(bpy)_2(CF_3SO_3)_2]$

The mixed Ru–Os system **13** was prepared in a similar manner from the osmium-complexed A-BLOCK **2** and the ruthenium-complexed B-BLOCK **5**, while the related Ru–Os dinuclear ligand-bridged complex **14** by coupling **2** with **4**. No metal interchange or self-condensation products were observed. The products were formed in good yield (42–71%), a significant improvement on those obtained by sequential metalation of preassembled ditopic ligands.

The structures of the precursor and product complexes are supported by electrospray-mass spectrometry, and electronic and ^1H NMR spectral data (given as Supporting Information). Absorption spectra of the mononuclear building BLOCKs showed intense bands in the UV region attributed to $\pi-\pi^*$ transitions of the bipyridine and phenanthroline type ligands, and metal-to-ligand charge-transfer (MLCT) bands in the visible region.[16] The homodinuclear complexes **12** and **15** have similar MLCT absorptions to their mononuclear precursors (**1**, **3**, and **5**). The heteronuclear complexes **13** and **14** showed broad absorptions tailing out to >670 nm due to an overlapping of the Ru^{II} and Os^{II} MLCT transitions. The electronic spectra of all the dinuclear species prepared were essentially the sum of their mononuclear precursors.

Cyclic and differential pulse voltammetry confirmed the presence of two metal centers in each dinuclear product (Supporting Information). For each diruthenium complex, only one reversible two-electron redox couple was observed (ca. +0.990V; Pt working electrode vs Ag/Ag^+), indicating no electronic communication between the metal centers. The heterodinuclear complexes displayed two one-electron reversible couples corresponding to successive $Os^{III/II}$ (ca. +0.550V) and $Ru^{III/II}$ (ca. +0.990 V) oxidations, but neither redox couple was shifted relative to its monomeric precursor again indicating a lack of electronic coupling across the alicyclic frameworks.

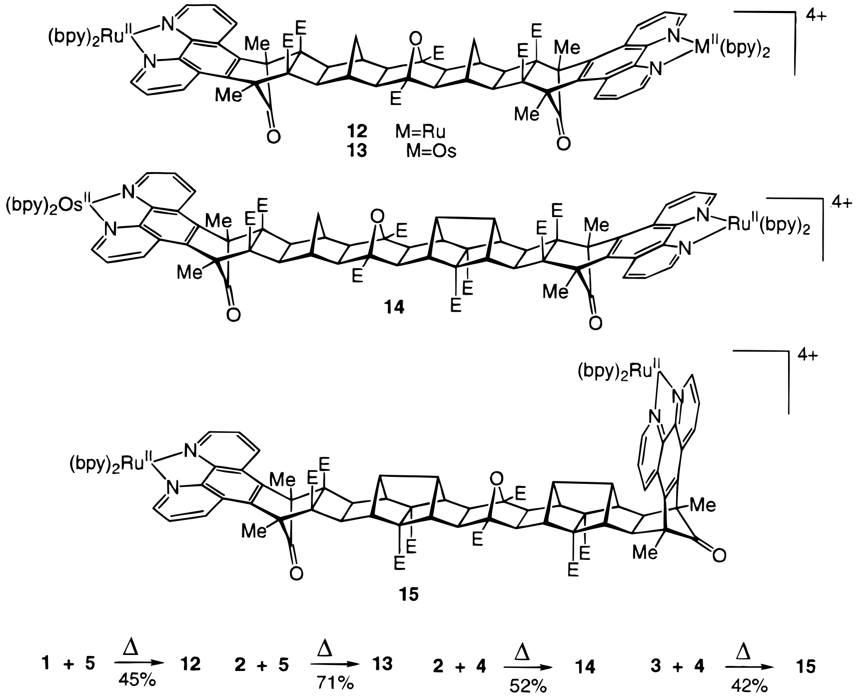
The uncoordinated ditopic ligands possess C_{2v} point group symmetry, which is lost on coordination within the tris(bidentate) complex. Anisotropic interactions with proximate pyridyl rings of peripheral bipyridine ligands render the two halves of the phenanthroline entity and the attached substituents of the ligands nonequivalent. ^1H NMR spectral studies of these complexes (Supporting Information) reveal that substituents with an axial orientation experience a greater differential ring current effect than equatorial substituents, the effect diminishing as the distance from the metal center is increased. For example, examination of the resonances for the norbornyl substituents attached to the phenanthroline group in the complex **5** reveals two C-methyl singlets at δ 2.01 and 2.03 and two methyl ester resonances at δ 3.00 and 3.27, which contrast with the two ester groups at the terminus of the ligand which are almost superimposed (δ 3.71 and 3.72).

We have previously undertaken extensive studies of other dinuclear systems bridged by various small rigid conjugated

---

(16) Juris, A.; Barigelletti, S.; Campagna, S.; Balzani, V.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85 and references therein.

Scheme 2



heterocyclic ligands. Because of the close proximity of the metal centers there were appreciable differences in the ^{1}H NMR spectra of the diastereoisomers (ΔΔ/ΛΛ and ΔΛ/ΛΔ) arising primarily from different anisotropic interactions.[4,17−20] The smallest dinuclear complex in this study (**12**) has a significantly greater metal−metal displacement (calculated at ca. 24.1 Å using semiempirical PM3(tm) geometry optimizations[21,22]), and accordingly we see no differences in the ^{1}H NMR due to the presence of both diastereoisomers. No attempt was made to separate or prepare stereoisomerically pure complexes.

Conclusions

The paper describes a significant advance in synthetic methodology for the preparation of homometallic and heterometallic ligand-bridged dinuclear complexes. The stereoselectivity of the coupling protocols ensures the formation of compounds in which the geometry is predetermined by that possessed by the precursor mononuclear BLOCKs. The spatial relationship of the metal centers may be controlled by the rational design of the bridge framework: the approach has provided the heterodinuclear species required for an investigation of the effects of spatial separation on intercomponent energy transfer processes, the results of which will be described elsewhere.[22]

Experimental Section

Physical Measurements. Instrumentation used for spectral (electronic, 300 MHz ^{1}H NMR) and electrochemical measurements has been described previously.[20] Electrochemical measurements were made in acetonitrile/0.1 M $[(n\text{-}C_4H_9)_4]ClO_4$ solution at a platinum disk working electrode using a Ag/Ag^+ (0.01 M) reference electrode. Cylic voltammetry scan rates were 100 mV/s, and for differential pulse voltammetry measurements the conditions used were scan rate 4 mV/s, pulse amplitude 50 mV, pulse width 60 ms and pulse period 1 s. Microwave reactions were conducted in a modified 600W Sharp Carousel R-2V55 microwave oven. High-resolution mass spectra were obtained on a Micromass Autospec magnetic sector instrument with an electrospray source; accurate mass determinations used poly(ethylene glycol) intrinsic standards.

Syntheses. Ligands in BLOCKs **1**, **2**, and **5** were synthesized using methods reported previously,[6,9] as were the complex precursors $[Ru(bpy)_2(CF_3SO_3)_2]$ and $[Os(bpy)_2CO_3]$.[13,23]

Ligands 8 and 10. These were prepared by heating excess DAPC (**6**) dissolved in $CHCl_3$ (ca. 3 cm^3) with either bis-alkene (**7**; 50 mg, 0.184 mmol) or bis-cyclobutene-diester (**9**; 500 mg, 0.370 mmol) overnight in a sealed tube at 90 °C. Data for **8**: yield, 17 mg (17%); mp >350 °C; accurate mass, observed *m/z* 532.1994, $C_{33}H_{28}N_2O_5$ requires 532.1998. Data for **10**: yield, 280 mg (38%); mp 311 °C (decomp); accurate mass, observed *m/z* 816.2543, $C_{45}H_{40}N_2O_{13}$ requires 816.2530.

Ligand 11. A tetrahydrofuran/dichloromethane solution of monoadduct **10** (250 mg, 0.306 mmol) was cooled to −78 °C. An aliquot of *tert*-butyl hydroperoxide (0.410 mol) was added, followed by methyllithium (0.460 mmol). Purification of the crude product was analogous to that previously reported for the epoxide ligand in BLOCK **5**.[9] Data for **11**: yield, 154 mg (60%); mp 283 °C (decomp); accurate mass, observed *m/z* 832.2478, $C_{45}H_{40}N_2O_{14}$ requires 832.2480.

$[Os(bpy)_2(CF_3SO_3)_2]$. $[Os(bpy)_2CO_3]$ (400 mg, 0.675 mmol) was suspended in nitrogen-purged 1,2-dimethoxyethane (20 cm^3), and trifluoromethanesulfonic acid (1.0 cm^3) was added slowly with stirring. The mixture was heated to 100 °C for 2 h and then cooled to 0 °C overnight. The dark precipitate was filtered, washed with diethyl ether, and dried. Yield: 459 mg (85%).

Complex Building BLOCKs 1−5. In a typical reaction, the appropriate ligand (ca. 50 mg, 0.10 mmol) was dissolved in chloroform (8 cm^3), and 2-methoxyethanol (5 cm^3) was added followed by an equimolar quantity of $[Ru(bpy)_2(CF_3SO_3)_2]$ (72 mg) or $[Os(bpy)_2(CF_3SO_3)_2]$ (80 mg). The maroon suspension was heated under microwave conditions (4 min at med/high setting, followed by an additional 4 min

---

(17) Rutherford, T. J.; Van Gijte, O.; Kirsch − De Mesmaeker, A.; Keene, F. R. *Inorg. Chem.* **1997**, *36*, 4465.

(18) Patterson, B. T.; Keene, F. R. *Inorg. Chem.* **1998**, *37*, 645.

(19) Keene, F. R. *Chem. Soc. Rev.* **1998**, *27*, 185.

(20) Kelso, L. S.; Reitsma, D. A.; Keene, F. R. *Inorg. Chem.* **1996**, *35*, 5144.

(21) *SPARTAN*, v 5.0; Wavefunction, Inc.: Irvine, CA, 1997.

(22) Kelso, L. S.; Smith, T. A.; Schultz, A. C.; Junk, P. C.; Warrener, R. N.; Ghiggino, K. P.; Keene, F. R. *J. Phys. Chem. A*, in press.

(23) Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587.

on high) resulting in an intense orange/red solution. The solvent was removed under vacuum, the residue dissolved in acetone/water and cation sorbed onto a column of SP Sephadex C-25. On elution with 0.25M NaCl in 25% acetone/water, a single orange band was collected and the desired complex precipitated by addition of a saturated KPF_6 solution (2 cm^3). The precipitate was filtered after settling overnight, washed with diethyl ether and air-dried. Data for **1**: yield, 98.3 mg (82%): mass spectrum, observed *m*/*z* 1053.1968 (most abundant isotope peak within cluster); $[C_{50}H_{42}N_6O_5Ru](PF_6)^+$ requires 1053.1948. Data for **2**: yield, 113.4 mg (88%); mass spectrum, observed *m*/*z* 1143.2512 (most abundant isotope peak within cluster); $[C_{50}H_{42}N_6O_5Os](PF_6)^+$ requires 1143.2510. Data for **3**: yield, 75.4 mg (61%); mass spectrum, observed *m*/*z* 1091.2068 (most abundant isotope peak within cluster); $[C_{53}H_{44}N_6O_5Ru](PF_6)^+$ requires 1091.2073. Data for **4**: yield, 90.6 mg (59%); mass spectrum, observed *m*/*z* 1391.2549 (most abundant isotope peak within cluster); $[C_{65}H_{56}N_6O_{14}Ru](PF_6)^+$ requires 1391.2559. Data for **5**: yield, 86.8 mg (64%); mass spectrum, observed *m*/*z* 1211.2138 (most abundant isotope peak within cluster); $[C_{56}H_{48}N_6O_{10}Ru](PF_6)^+$ requires 1211.2133.

Dinuclear Complex 13. Complexes **2** (38 mg, 0.030 mmol) and **5** (40 mg, 0.029 mmol) were heated in a sealed tube at 140 °C for 30 h with a minimum of acetonitrile (3 drops). On cooling, the solution was diluted with acetone/water and the product purified by cation exchange chromatography (SP Sephadex C-25). Elution with 0.25 M NaCl solution removed a minor band of mononuclear material; at an eluent concentration of 0.5 M NaCl, the major olive green band was collected and the complex (**13**) was isolated as the PF_6^- salt: yield, 55.4 mg (71%); mass spectrum, observed *m*/*z* 1177.2277 (most abundant isotope peak within cluster), $[C_{106}H_{90}N_{12}O_{15}OsRu](PF_6)_2^{2+}$ requires 1177.2309.

Homodinuclear complexes **12** and **15** and heterodinuclear complex **14** were prepared in an identical fashion via coupling of the appropriate mononuclear building BLOCKs (**1** with **5**, **2** with **4**, **3** with **4**). Data for **12**: yield, 45%; mass spectrum, observed *m*/*z* 1132.2065 (most abundant isotope peak within cluster), $[C_{106}H_{90}N_{12}O_{15}Ru_2](PF_6)_2^{2+}$ requires 1132.2030. Data for **14:** yield, 52%; mass spectrum, observed *m*/*z* 1267.2550 (most abundant isotope peak within cluster), $[C_{115}H_{98}N_{12}O_{19}OsRu](PF_6)_2^{2+}$ requires 1267.2520. Data for **15**: yield, 42%; mass spectrum, observed *m*/*z* 1241.2309 (most abundant isotope peak within cluster), $[C_{118}H_{100}N_{12}O_{19}Ru_2](PF_6)_2^{2+}$ requires 1241.2325.

Acknowledgment. This work was funded by the Australian Research Council (ARC Senior Research Fellowship to R.N.W. (1992−1996); Large Grants (to R.N.W. and F.R.K.); and Central Queensland University. A.C.S. acknowledges the award of a CQU postgraduate scholarship and funding from the CMA. Mr. Tom Frey is thanked for the HR-ESMS analyses.

Supporting Information Available: Listings of physical data (^1H NMR and UV−visible spectra, electrochemical redox potentials) for complexes **1**−**5**, **12**−**15**, and ligands **8**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9902370