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Di-[1,10]-phenanthrolinyl Diazines: A New Family of Bis-tridentate Chelators

Darren Brown, Seema Muranjan, Youngchan Jang, and Randolph Thummel*

Department of Chemistry, University of Houston, Houston, Texas 77204-5003

thummel@uh.edu

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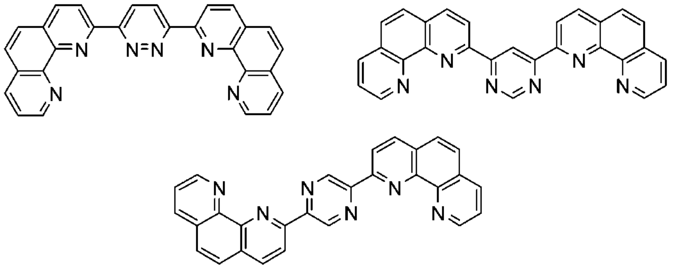
ABSTRACT



A series of three bis-tridentate bridging ligands has been prepared in which two 1,10-phenanthroline units have been symmetrically appended to a central pyridazine, pyrimidine, or pyrazine ring. These ligands have been treated with [Ru(tpy-*d*$_{11}$)Cl$_3$] to afford both mono- and bimetallic complexes that show very self-consistent NMR properties.

Recent interest in electron or energy transfer between two or more metal centers confined to a supramolecular assembly has prompted the preparation of a wide range of bridging ligands.[1] Many of these ligands have been bi- or tridentate chelators in which a pyridine ring is the coordinating unit. Thus, 2,2′-bipyridines (bpy) and 2,2′:6′,2″-terpyridines (tpy) have been connected by a variety of tethers and the influence of intermetallic distance or π-conjugation has been evaluated. More intimate bridging ligands will hold metals closer together and presumably improve communication. Such intimacy can be attained when a common aromatic ring is shared between the two chelating moieties. Thus, the family of di-2′-pyridyl diazines (**1**−**4**) has been extensively studied as bridging ligands and scaffolds for the formation of metallodendrimers.[2] These species may be viewed as two bpys that have been superimposed so as to create a common central ring and also provide a symmetrical bis-bidentate binding situation. Ligand **4** presents a steric problem upon dinuclear coordination due to an unfavorable interaction between the two pyridine H3′ atoms.

One could imagine an analogous situation for the superposition of two tpy units to form a bis-tridentate binding system. If the two tpys share a common central ring, one has the well-known tetra-(2′-pyridyl)-pyrazine (**5**).[3] If the tpys share a distal ring, bridging diazines analogous to **1**−**4** can be designed, and bis-2,2′-bipyrid-6-yl analogues of **2** and **3** have been reported.[4] We have devised synthetic approaches to three such bridging diazine ligands where the less flexible

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(1) (a) Jones, S. W.; Jordon, M. R.; Brewer, K. In *Multimetallic and Macromolecular Inorganic Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 1999; p 151. (b) Collin, J.-P.; Gaviña, P.; Heitz, V.; Sauvage, J.-P. *Eur. J. Inorg. Chem.* **1998**, 1. (c) Laye, R.; Couchman, S. M.; Ward, M. D. *Inorg. Chem.* **2001**, *40*, 4089.

(2) (a) Phillips, I. G.; Steel, P. J. *Aust. J. Chem.* **1998**, *51*, 371. (b) Kalyanasundaram, K.; Nazeeruddin, Md. K. *Inorg. Chem.* **1990**, *29*, 1888. (c) Ernst, S. D.; Kaim, W. *Inorg. Chem.* **1989**, *28*, 1520. (d) Kovbasyuk, L.; Hoppe, M.; Pritzkow, H.; Krämer, R. *Eur. J. Chem.* **2001**, 1353. (e) Klein, A.; Kasack, V.; Reinhardt, R.; Sixt, T.; Scheiring, T.; Zalis, S.; Fiedler, J.; Kaim, W. *J. Chem. Soc., Dalton Trans.* **1999**, 575. (f) Ruminski, R. R.; Johnson, J. O. *Inorg. Chem.* **1987**, *26*, 210. (g) Ernst, S.; Kasack, V.; Kaim, W. *Inorg. Chem.* **1988**, *27*, 1146. (h) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1987**, *26*, 68. (i) Chellamma, S.; Lieberman, M. *Inorg. Chem.* **2001**, *40*, 3177. (j) Neels, A.; Stoeckli-Evans, H. *Inorg. Chem.* **1999**, *38*, 6164. (k) Rasmussen, S. C.; Richter, M. M.; Yi, E.; Place, H.; Brewer, K. J. *Inorg. Chem.* **1990**, *29*, 3926. (l) Milkevitch, M.; Brauns, E.; Brewer, K. J. *Inorg. Chem.* **1996**, *35*, 1737. (m) Berger, S.; Klein, A.; Wanner, M.; Kaim, W.; Fiedler, J. *Inorg. Chem.* **2000**, *39*, 2516. (n) Youinou, M.-T.; Rahmouni, N.; Fischer, J.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 733.

(3) (a) Thummel, R. P.; Chirayil, S. *Inorg. Chim. Acta* **1988**, *154*, 77. (b) Vogler, L. M.; Brewer, K. J. *Inorg. Chem.* **1996**, *35*, 818. (c) Arana, C. R.; Abruña, H. D. *Inorg. Chem.* **1993**, *32*, 194. (d) Vogler, L. M.; Scott, B.; Brewer, K. J. *Inorg. Chem.* **1993**, *32*, 898. (e) Vogler, L. M.; Jones, S. W.; Jensen, G. E.; Brewer, R. G.; Brewer, K. J. *Inorg. Chim. Acta* **1996**, *250*, 155.

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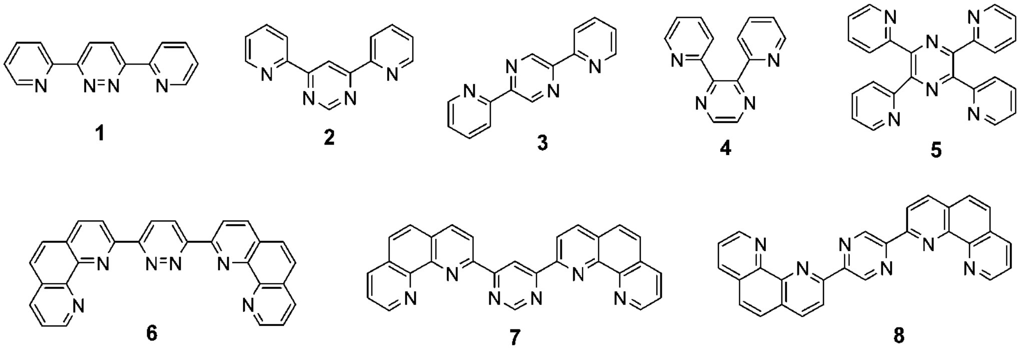
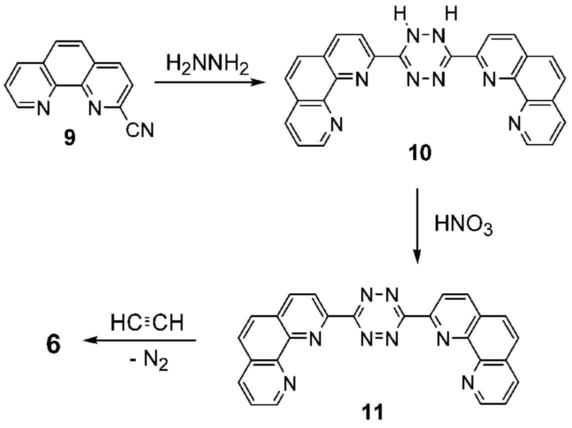
Scheme 1



1,10-phenanthroline (phen) moiety has been incorporated in place of the pendent bpy subunits.

The synthesis of 3,6-diphen-pyridazine (**6**) is analogous to the route employed for the preparation of **1**[5] (Scheme 2).

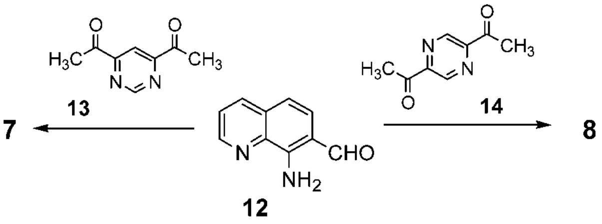
Scheme 2



The reaction of 2-cyanophen with hydrazine in refluxing ethanol provided a 73% yield of the dihydrotetrazine **10**, which was subsequently oxidized with nitric acid in acetic acid. The bright red-colored tetrazine **11** was obtained in 40% yield. Cycloaddition of acetylene to **11** in refluxing DMF followed by the extrusion of dinitrogen provided a 47% yield of the desired pyridazine **6**.

Both the diphen-pyrimidine **7** and the diphen-pyrazine **8** were synthesized by a double Friedländer condensation using an appropriate diacetyl diazine precursor and 2 equiv of 8-amino-7-quinolinecarbaldehyde (**12**)[6] (Scheme 3). The 4,6-diacetylpyrimidine (**13**) was prepared by first coupling (1-ethoxyethenyl)tri-*n*-butylstannane[7] with 4,6-dichloropyrimidine followed by acid hydrolysis of the ethoxyvinyl groups.[8] The condensation with **12** proceeded smoothly to provide a 50% yield of **7**. The diacetylpyrazine **14** was prepared in 28% yield by the free radical acetylation of pyrazine using acetaldehyde and *t*-butylhydroperoxide in the presence of ferric sulfate.[9] Condensation with quinoline aminoaldehyde **12** gave the expected **8** in 41% yield.

Scheme 3



All three bridging ligands were readily characterized by ^{1}H NMR. The 2-phen moieties gave very similar and characteristic patterns in the aromatic region. The central ring was distinguished by either one singlet (δ 9.36 for **6** and 10.25 for **8**) or two singlets (δ 9.51 and 10.61 for **7**). The deshielding of these protons was consistent with their proximities to nitrogen.

Treating the ligands **6**−**8** with 1 equiv of [Ru(tpy-d_{11})-Cl$_3$] led to the incorporation of a single Ru(tpy-d_{11}) subunit at one of the two equivalent tridentate sites and consequent formation of the red mononuclear complex (Schemes 4 and 5).

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(4) (a) Schubert, U. S.; Eshbaumer, C. *Org. Lett.* **1999**, *1*, 1027. (b) Benaglia, M.; Ponzini, F.; Woods, C. R.; Siegal, J. S. *Org. Lett.* **2001**, *3*, 967. (c) Jones, P. D.; Glass, T. E. *Tetrahedron Lett.* **2001**, *42*, 2265. (d) Hanan, G. S.; Arana, C. R.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1996**, *2*, 1292. (e) Hanan, G. S.; Arana, C. R.; Lehn, J.-M.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1122. (f) Bassani, D. M.; Lehn, J.-M.; Fromm, K.; Fenske, D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2364. (g) Funeriu, D. P.; Lehn, J.-M.; Fromm, K. M.; Fenske, D. *Chem. Eur. J.* **2000**, *6*, 2103. (h) Breuning, E.; Ziener, U.; Lehn, J.-M.; Wegelius, E.; Rissanen, K. *Eur. J. Inorg. Chem.* **2001**, 1515. (i) Bark, T.; Düggeli, M.; Stoeckli-Evans, H.; von Zelewsky, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2848. (j) Heirtzler, F.; Weyhermüller, T. *J. Chem. Soc., Dalton Trans.* **1997**, 3653.

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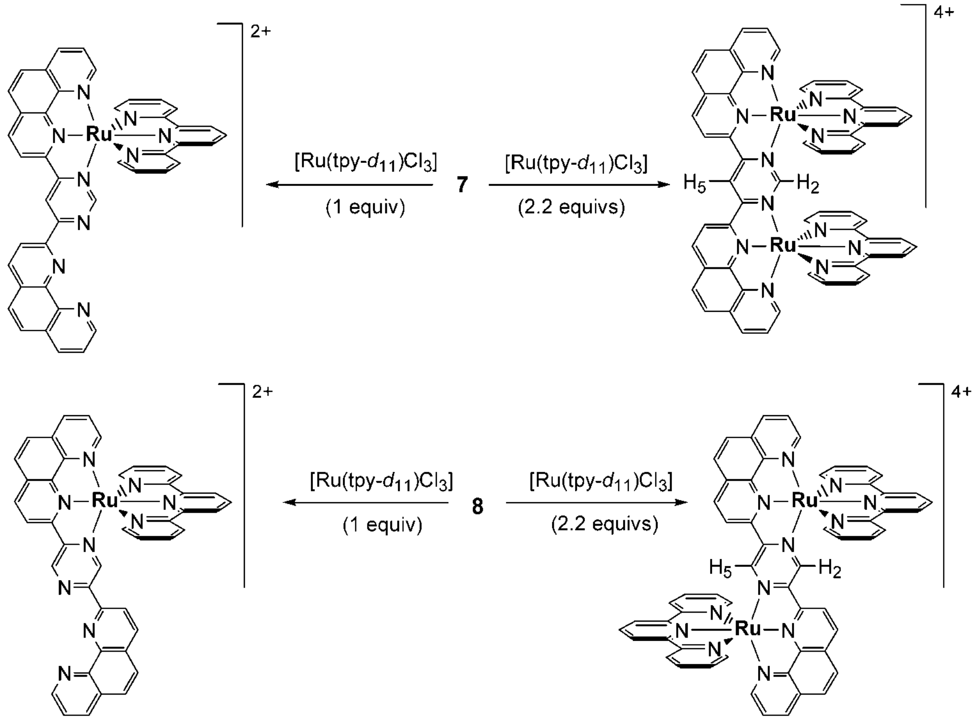
(7) Gadwood, R. C.; Rubino, M. R.; Nagarajan, S. C.; Michel, S. T. *J. Org. Chem.* **1985**, *50*, 3255.

(8) (a) Bessani, D. M.; Lehn, J. M. *Bull. Soc. Chim. Fr.* **1997**, *134*, 897. (b) Majeed, A. J.; Antonses, Ø.; Benneche, T.; Undheim, K. *Tetrahedron* **1989**, *45*, 993.

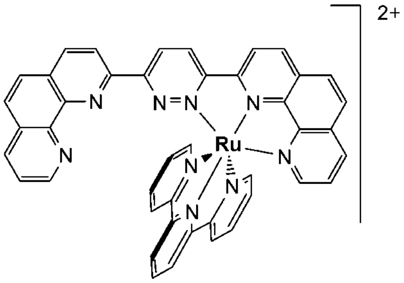
(9) Caronna, T.; Fronza, G.; Minisci, F.; Porta, O. *J. Chem. Soc. Perkin Trans. 2* **1972**, 2035.

Scheme 4



Use of the deuterated reagent allowed us to observe NMR signals only from the bridging ligand, which greatly facilitated analysis, particularly for the mononuclear complexes where all the protons on the bridging ligand were nonequivalent.[10] For the mononuclear complex of **6**, the incorporated Ru(tpy-d_{11}) subunit effectively blocks the other tridentate binding site so that a second Ru(tpy-d_{11}) moiety cannot be introduced in an N6 binding mode. Nevertheless, the pendant uncomplexed phen can rotate away from the Ru(II) center and a second metal might be introduced at this bidentate site.

Scheme 5



When **7** and **8** were treated directly with 2.2 equiv of [Ru(tpy-d_{11})Cl$_3$], the bimetallic complexes were obtained as their green hexafluorophosphate salts in 41 and 34% yields, respectively. The complex of **7** is similar to ones prepared by the Lehn[4d] and Siegal[4b] groups using analogous ligands involving a bis-bpy pyrimidine-type bridge. The metals are oriented in a syn fashion so that a pincer-type array results (Scheme 4). The structure drawing may be somewhat deceptive in that it depicts the molecule such that the two tpy ligands appear to lie in parallel planes. However, tridentate coordination by the phen-pyrimidine moiety will cause a pinching that may force the tpys closer together than they appear. A molecular mechanics calculation[11] bears out this hypothesis, and a more detailed structural analysis awaits the growth of an appropriate crystal.

The bimetallic complex of **8** positions the Ru(tpy-d_{11}) subunits in an anti orientation, and one additional C−C bond intervenes between the two metal centers. Even with the pinching effect, the tpys are expected to lie in parallel planes.

Both complexes have high symmetry and are achiral. The NMR spectrum of each complex exhibits the typical pattern for a 2-substituted phen, while the central ring of **7** shows two singlets for the pyrimidine protons. Since the bridging ligand is approximately planar, H5 now lies in a more deshielding region and is shifted downfield by 0.23 ppm, appearing at δ 9.74. On the other hand, H2 is held between the two tpy ligands where it is heavily shielded and, thus, shifted upfield by 4.11 ppm to δ 6.50. The bimetallic complex of **8** shows only a single two-proton resonance for the pyrazine protons H2 and H5. This proton should feel one-half of the shielding and deshielding effects felt by H2 and H5 of the corresponding complex of **7**. Thus, one can

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[10] Chirayil, S. C.; Hegde, V.; Jahng, Y.; Thummel, R. P. *Inorg. Chem.* **1991**, *30*, 2821.

[11] Molecular mechanics calculations performed with PC MODEL from Serena Software, Bloomington, IN.

calculate an expected upfield shift of +1.94 ppm. The observed singlet at δ 8.49 agrees fairly well with this prediction, showing an upfield shift of 1.76 ppm.

Further studies on this interesting family of ligands are underway and will include a careful assessment of photophysical and electrochemical properties, variation of the appended phen moiety, heterodinuclear complexes, and the self-assembly of ligand-bridged supramolecular structures.

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Supporting Information Available: Experimental procedures and characterization relating to the syntheses of **6**−**8**, **10**, **11**, and the Ru(II) complexes of **6**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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