A New Binucleating Ligand Based on Anthracene and Its Cofacial Dirhodium(I) and Diiridium(I) Complexes

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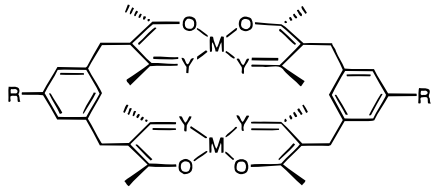
A new bis(β-keto enamine) ligand (**2a**, $ABIH_2$) containing a 1,8-anthracenediyl bridging group has been synthesized by a four-step procedure that relies on the Pd-catalyzed cross-coupling between (3,5-dimethylisoxazol-4-yl)-trialkyltin and 1,8-dibromoanthraquinone or -anthracene. The molecular structures of the 1,8-bis(3,5-dimethylisoxazol-4-yl)anthraquinone (**8**) and -anthracene (**10**) intermediates were determined by X-ray analysis. Crystal data for **8**: orthorhombic, space group *Pbca*; $a = 14.351$ (2), $b = 11.932$ (1), $c = 23.278$ (2) Å; $V = 3986$ (1) Å^3; $Z = 8$; $R = 0.057$ for 2615 reflections. Crystal data for **10**: orthorhombic, space group $P2_12_12_1$; $a = 7.104$ (1), $b = 12.805$ (1), $c = 22.280$ (2) Å; $V = 2026.7$ (6) Å^3; $Z = 4$; $R = 0.066$ for 3423 reflections. The rigid $ABIH_2$ ligand, whose chelating moieties are constrained to be cofacial, allows the preparation of a new family of cofacial bimetallic complexes $(ABI)[ML_2]_2$ with controllable environments around the metal centers. Two novel cofacial binuclear complexes **4** and **5**, with ML_2 = dicarbonylrhodium(I) and (η^4-1,5-cyclooctadiene)iridium(I), have been synthesized by reaction of $ABIH_2$ with $[(\mu\text{-Cl})Rh(CO)_2]_2$ and $[(\mu\text{-Cl})Ir(COD)]_2$, respectively. NMR data indicate the formation of meso and racemic atropisomers for **2a**, **4**, and **5**.

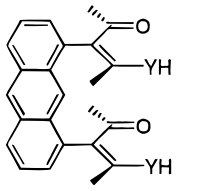
Introduction

We recently studied cofacial binuclear transition-metal complexes such as **1**[1,2] (see Chart 1) as potential catalysts for multielectron redox reactions. The cavities in these complexes (M···M 4.5−5.0 Å) may be appropriate for binding of small guest molecules. Previous work on the bis(β-keto enamine) complexes **1b**[2] demonstrated multielectron redox activity that is not observed in the analogous mononuclear systems, suggesting that the rigid structure improves the stability of the complexes when they are oxidized. However, the need for two bridging ligands, to enforce the desired cofacial geometry, limited the complexes to M(diketonato)$_2$ (**1a**) and M(imino ketonato)$_2$ (**1b**) coordination environments. More conformationally rigid ligands based on 1,8-disubstituted anthracenes (**2**), with their chelating moieties constrained to be cofacial, would eliminate the need for a second bridging group. Collman[3a] and Chang[3b] have demonstrated this principle in their studies of cofacial anthracene- and biphenylene-bridged diporphyrins; complexes of these ligands are electrocatalysts for reduction of O_2. Our goal was to use the ligands **2** as an entry to bimetallic complexes **3** with readily controllable environments around the metal centers. These complexes should provide for a variety of molecular and electronic structures by allowing the use of many different ancillary ligands along with the anthracenediyl-bridged ligands **2**. The more open structure of these complexes may also offer better access of substrate molecules to the intramolecular binding site. We now report the preparation of **2a**, $ABIH_2$, and two of its cofacial complexes **3a**, with ML_2 = dicarbonylrhodium(I) ($(ABI)[Rh(CO)_2]_2$, **4**) and (η^4-1,5-cyclooctadiene)iridium(I) ($(ABI)[Ir(COD)]_2$, **5**).

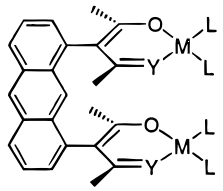
Chart 1



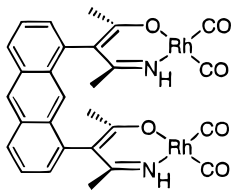
1a, R = H, Y = O, M = Cu
1b, R = *t*-Bu, Y = NH, M = Ni, Cu, Pd



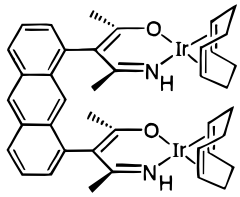
2a ($ABIH_2$), Y = NH
2b ($ABAH_2$), Y = O



3a ($(ABI)[ML_2]_2$), Y = NH
3b ($(ABA)[ML_2]_2$), Y = O



4 ($(ABI)[Rh(CO)_2]_2$)



5 ($(ABI)[Ir(COD)]_2$)

The S_N2 synthetic strategy normally used for alkylation of acetylacetonates cannot generally be used to prepare 3-arylacetylacetones such as **2b**. One method to activate aryl halides toward nucleophilic substitution is π-complexation to Fe; such

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(1) (a) Maverick, A. W.; Klavetter, F. E. *Inorg. Chem.* **1984**, *23*, 4129. (b) Maverick, A. W.; Martone, D. P.; Bradbury, J. R.; Nelson, J. E. *Polyhedron* **1989**, *8*, 1549.
(2) Bradbury, J. R.; Hampton, J. L.; Martone, D. P.; Maverick, A. W. *Inorg. Chem.* **1989**, *28*, 2392.
(3) (a) Collman, J. P.; Wagenknecht, P. S.; Hutchinson, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1537. (b) Liu, H. Y.; Abdalmuhdi, I.; Chang, C. K.; Anson, F. C. *J. Phys. Chem.* **1985**, *84*, 666 and references therein.

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Scheme 1

6a, R = Me (59%)
6b, R = Bu (63%)

an approach has provided a route to 3-phenylacetylacetone.[4] We attempted to prepare ligands **2** by this method; although we succeeded in preparing a diiron complex from 1,8-dichloroanthracene,[5] we were unable to convert it to **2b**. As an alternative strategy for **2**, we chose the 3,5-dimethylisoxazol-4-yl (DMI) group as an acetylacetone synthon. Isoxazoles can be reductively cleaved to form β-keto enamines, which can usually be hydrolyzed to the corresponding β-diketones.[6] Our successful preparation of **2a** involved palladium-catalyzed cross-coupling between 4-(trialkylstannyl)-3,5-dimethylisoxazole and 1,8-dibromoanthraquinone or 1,8-dibromoanthracene. Direct complexation of $[(\mu\text{-Cl})\text{Rh}(\text{CO})_2]_2$ and $[(\mu\text{-Cl})\text{Ir}(\text{COD})]_2$ with **2a** in the presence of a base yielded the cofacial binuclear complexes **4** and **5**, respectively.

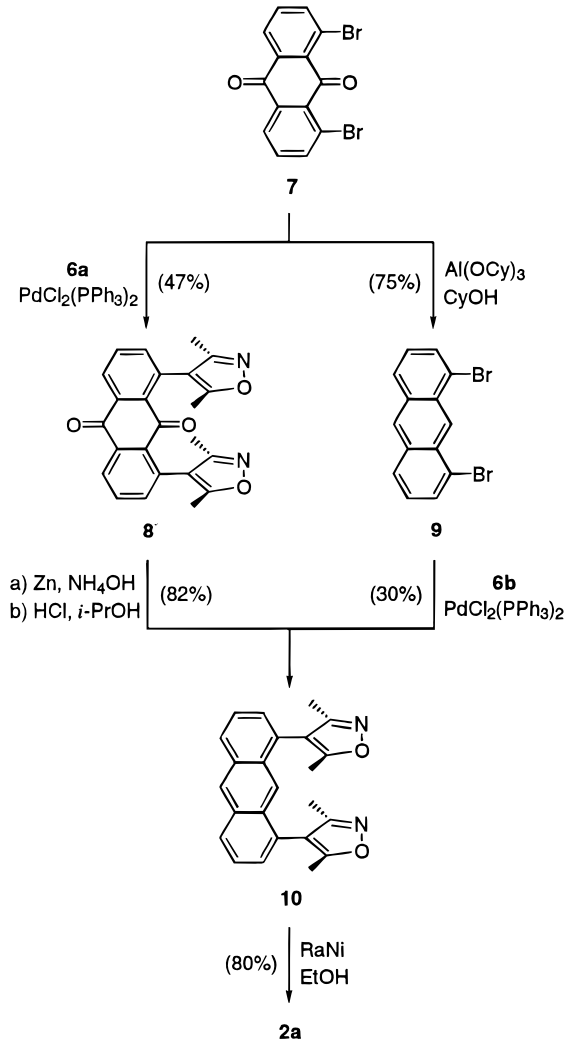
Results and Discussion

The Binucleating Ligand. We first attempted to cross-couple 1,8-disubstituted anthracene electrophiles (*e.g.*, 1,8-dichloroanthracene and 1,8-ditriflatoanthraquinone[7]) with Grignard[8] and organozinc[9] derivatives of DMI, but their high viscosity made them difficult to handle. Therefore, we searched for a more stable and manageable DMI organometallic compound. Treatment of the Grignard reagent of DMI with R_3-SnCl (R = Me, Bu) in THF afforded the trimethyl- (**6a**) and tributyltin (**6b**) reagents of DMI as air-stable, pale yellow liquids (Scheme 1). This method provides a good alternative to the literature procedure, in which **6a** and **6b** were obtained via DMI−organolithium reagents in 69%[10] and 51%[6b] yields, respectively.

On the basis of the method described for the 1,5-isomer,[11] we prepared 1,8-dibromoanthraquinone (**7**) (as a *ca.* 10:1 mixture with 1-bromo-8-chloroanthraquinone) by reaction of 1,8-dichloroanthraquinone with excess KBr.[12] Compound **7** couples with **6a** under Pd catalysis (Stille reaction) to produce 1,8-bis(3,5-dimethylisoxazol-4-yl)anthraquinone (**8**) (Scheme 2). Reduction of **8** with Zn in NH_3(aq)[13] afforded 1,8-bis(3,5-dimethyl-4-isoxazolyl)anthracene (**10**) in good yield. Lower overall yields of **10** were obtained by reaction of 1,8-dibromoanthracene (**9**)[14] with the tin reagent **6b**. In addition, the anthraquinone **8** is easier to purify by column chromatography than the anthracene derivative **10**, owing to its higher polarity in relation to the other reaction side products; **10** usually elutes as a mixture with the side product 3,5,3′,5′-tetramethyl-4,4′-biisoxazole.

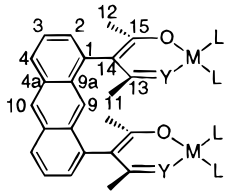
Methyl coupling also occurred during the conversion of **7** to **8**, forming 1-(3,5-dimethylisoxazol-4-yl)-8-methylanthraquinone in 12% yield. The generally faster rate of methyl transfer as well as the use of the more hindered anthraquinone **7** may explain the formation of some alkyl transfer product; in the anthracene system (**9** + **6b**), on the other hand, butyl coupling went undetected.

Scheme 2



(4) Sutherland, R. G.; Abd-El-Aziz, A. S.; Piórko, A.; Lee, C. C. *Synth. Commun.* **1987**, *17*, 393.
(5) Benites, M. R.; Fronczek, F. R.; Maverick, A. W. *J. Organomet. Chem.* **1996**, *516*, 17.
(6) (a) For a review, see: Grünanger, P.; Vita Finzi, P. *Isoxazoles*; The Chemistry of Heterocyclic Compounds, Vol. 49; Taylor, E. C., Weissberger, A., Eds.; John Wiley & Sons, Inc.: New York, 1991; Part 1, pp 273−281 and 391−416. (b) Sakamoto, T.; Kondo, Y.; Uchiyama, D.; Yamanaka, H. *Tetrahedron* **1991**, *47*, 5111. (c) Alberts, A. H.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3545.
(7) Benites, M. R.; Fronczek, F. R.; Maverick, A. W. Unpublished work.
(8) The Grignard reagent of 4-iodo-3,5-dimethylisoxazole (Kochetkov, N. K.; Sokolov, S. D.; Vagurtova, N. M. *J. Gen. Chem. USSR (Engl. Transl.)* **1961**, *31*, 2167) is obtained as a suspension when prepared in diethyl ether/THF (Kochetkov, N. K.; Sokolov, S. D. *J. Gen. Chem. USSR (Engl. Transl.)* **1963**, *33*, 1174) or pure THF or as a syrup in diethyl ether.
(9) The Grignard reagent could be converted to an organozinc reagent by treatment with anhydrous $ZnCl_2$ in Et_2O (see, for example: *Methoden der Organischen Chemie*; Müller, E., Bayer, O., Meerwein, H., Ziegler, K., Eds..; Thieme: Stuttgart, Germany, 1973; Vol. 13/ 2a, pp 650−651), but this material was also too viscous for use in cross-coupling reactions.
(10) Nesi, R.; Ricci, A.; Taddei, M.; Tedeschi, P. *J. Organomet. Chem.* **1980**, *195*, 275.
(11) (a)Hamanoue, K.; Kajiwara Y.; Miyake, T.; Nakayama, T.; Hirase, S.; Teranishi, H. *Chem. Phys. Lett.* **1983**, *94*, 276. (b) Brienne, M.-J.; Jacques, J. *Bull. Soc. Chim. Fr.* **1973**, 190.
(12) This procedure has since been modified to give pure compound **7** in 39% overall yield (Holden, T. M.; Isovitsch, R. A.; Maverick, A. W. Unpublished work, 1995): the mixture of **7** and 1-bromo-8-chloroanthraquinone produced in the first KBr treatment was crystallized from hot nitrobenzene before the second treatment with KBr.
(13) House, H. O.; Hrabie, J. A.; VanDerveer, D. *J. Org. Chem.* **1986**, *41*, 921.
(14) **9** was obtained as a *ca.* 10:1 mixture of 1,8-dibromo- and 1-bromo-8-chloroanthracenes, by starting from the corresponding 10:1 anthraquinone mixture and following the procedure reported by: Haenel, M. W.; Jakubik, D.; Kruger, C.; Betz, P. *Chem. Ber.* **1991**, *124*, 333.

Table 1. ^{1}H NMR Data[a]



compd	H-2	H-3	H-4	H-9	H-10	H-11	H-12	NH	L
8	8.41 (dd, 7.8, 1.2)	7.80 (t, 7.7)	7.48 (dd, 7.6, 1.3)			1.99	2.21		
						1.93*	2.15*		
10	8.10 (d, 8.6)	7.55 (dd, 8.5, 6.8)	7.32 (dd, 6.8, 0.9)	7.87	8.61	2.03	2.20		
						2.01*	2.18*		
2a[b]	7.34 (dd, 6.7, 1.2)	7.48 (dd, 8.5, 6.7)	8.00 (d, 8.5)	8.40	8.50	1.61	1.68	5.60, 10.72	
	7.33* (dd, 6.7, 1.2)	7.46* (dd?)[c]				1.55*	1.65*		
4[b]	7.32 (d, 6.7)	7.48 (dd, 8.5, 6.7)	7.98 (d, 8.5)	7.81	8.46	1.69	1.74	7.71	
				7.79*		1.65*	1.71*	7.55*	
5[d]	7.26 (d, 6.6)	7.43 (dd, 8.6,6.8)	7.97 (d, 8.5)	8.23	8.50	1.69	1.75	7.84	4.31 (1H), 4.18 (3H), 3.60 (1H),
						1.67*	1.74*	7.74*	3.44 (3H), 2.36 (8H), 1.88 (8H)

[a] 300 MHz, unless otherwise noted; in $CDCl_3$, δ/ppm (J/Hz in parentheses); assignments were made using NOE experiments; starred peaks correspond to the minor atropisomer. [b] 200 MHz. [c] Exact nature of pattern could not be determined due to overlap with 7.48 ppm resonance. [d] 250 MHz; all COD peaks appear as broad multiplets.

Table 2. ^{13}C NMR Data[a]

compd	C-1	C-2	C-3	C-4	C-4a	C-9	C-9a	C-10	C-11	C-12	C-13	C-14	C-15	L
8	133.5	138.9	127.7	133.1	134.4	164.4	131.2	183.3	10.6	11.5	158.8	115.9	164.3	
10	130.9	128.8	125.3	128.6	132.0	121.6	128.1	128.0	10.4	11.4	159.5	114.5	166.1	
											159.4*		166.0*	
2a[b]	132.6	129.3	125.6	127.6	138.1	122.0	132.2	127.4	21.6	28.5	161.0	106.4	196.8	
										28.4*	160.0*	106.1*	196.6*	
4[c]	132.6	128.6	125.8	127.5	139.1	121.9	132.3	126.9	25.9	28.1	167.1	108.0	179.0	187.2 (d, 70.8), 187.1 (d, 71.2),
		128.5*						126.8*		28.0*	166.8*		178.3*	186.1 (d, 64.2), 185.9 (d, 63.8)
5[d]	132.3	130.2	125.5	127.8	139.4	122.0	128.0	132.3	30.6	32.0	164.6	108.6	178.1	66.8, 66.2, 66.0, 53.4, 52.9, 52.7,
									30.5*					52.6, 28.3, 27.1

[a] 63 MHz, unless otherwise noted; in $CDCl_3$, δ/ppm; assignments for **2a** and **4** were made using DEPT, HMQC, and HMBC experiments; assignments for compounds **8**, **10**, and **5** were made by DEPT experiments and by comparison with the data from **2a** and **4**; starred peaks correspond to the minor atropisomer. [b] 50 MHz. [c] 75 MHz; J_{C-Rh}/Hz in parentheses. [d] 63 MHz.

We expected that the new dimethylisoxazole derivatives **8** and **10** would show atropisomerism, with racemic and meso atropisomers possible (meso shown in Scheme 2). Interconversion of the two atropisomers (*e.g.*, by rotation of one of the DMI moieties about the anthracene−DMI C−C bond) is likely to be extremely slow in both compounds for steric reasons. Indeed, the NMR spectra of both **8** and **10** show two sets of signals for the DMI methyl atoms (see Tables 1 and 2). Integration ratios, calculated from the two sets of methyl group protons (H-11 and H-12), suggest that both compounds are formed as roughly equal (*ca.* 0.9:1.0) mixtures of the two atropisomers, although we could not determine which is which.

Both **8** and **10** crystallize, and we determined their crystal structures. Crystallographic data are summarized in Table 3. Since it is usually possible to distinguish N and O atoms by X-ray methods, we were interested in whether the atropisomer distribution in either compound could be determined from the X-ray data. The molecules in both structures lie on general positions, so that there is no crystallographic symmetry imposed on either molecule. Still, we were unable to distinguish reliably between N and O in either structure. In **8** (see Figure 1), the atoms were modeled as half N and half O, and they are shown as "NO1", "NO2", etc. Attempts to refine them as separate N or O atoms led to displacement parameters that were always somewhat larger for O than for N; also, the refined C−heteroatom distances are not sufficiently different to make a distinction. In **10**, on the other hand, our model involves separate N and O atoms, and their arrangement in Figure 1 appears to favor the meso atropisomer. However, the refined displacement parameters for O are still slightly larger than those for N, and this makes assignment of a single predominant atropisomer difficult. Thus, the X-ray data for **8** and **10** do not help in determining the atropisomer distribution, but they do not conflict with the NMR data (which suggest that roughly equal quantities of meso and racemic atropisomers are present in both compounds).

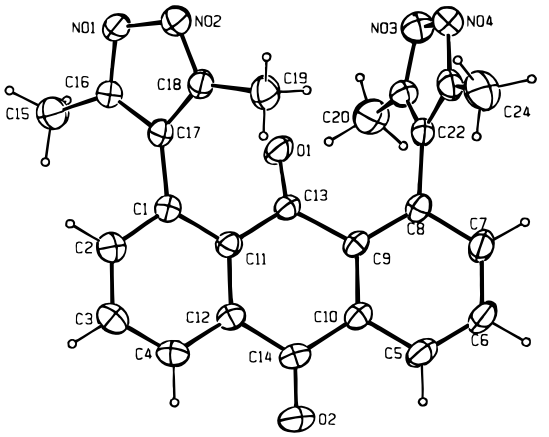
Table 3. Crystallographic Data for Compounds **8** and **10**

	8	**10**
formula	$C_{24}H_{18}N_2O_4$	$C_{24}H_{20}N_2O_2$
fw	398.4	368.4
space group	*Pbca*	$P2_12_12_1$
a, Å	14.351 (2)	7.104 (1)
b, Å	11.932 (1)	12.805 (1)
c, Å	23.278 (2)	22.280 (2)
V, Å^3	3986.2 (12)	2026.7 (6)
Z	8	4
T, °C	24	25
λ, Å	1.541 84	1.541 84
ρ_{calcd}, g cm^{-3}	1.328	1.207
μ, cm^{-1}	7.1	5.8
R^a	0.057	0.066
R_w[b]	0.065	0.061

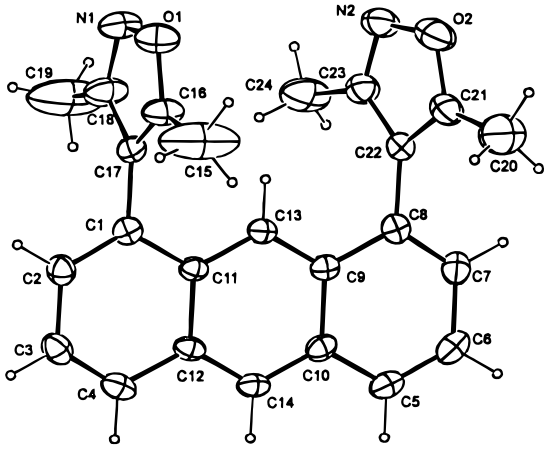
[a] $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Hydrogenolysis of **10** with Raney nickel gave the bis(β-keto enamine) **2a** ($ABIH_2$) in good yield. Attempts to selectively cleave the N−O bond in anthraquinone **8**, using RaNi or $Mo(CO)_6$[15] as the reducing agent, gave unidentified mixtures of

(15) Nitta, M.; Kobayashi, T. *J. Chem. Soc., Chem. Commun.* **1982**, 877.



8

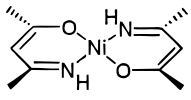


10

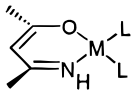
Figure 1. ORTEP diagrams of compounds **8** and **10**.

products, possibly owing to partial reduction of the anthraquinone moiety under the reaction conditions. NMR spectra for **2a** (Tables 1 and 2) show several doubled ^{1}H and ^{13}C resonances, which are consistent with the presence of two atropisomers in *ca.* 2.3:1 ratio (calculated from the integration of the two sets of methyl group protons, H-11 and H-12). Surprisingly, **2a** did not convert to the corresponding β-diketone (**2b**, $ABAH_2$) when treated with acid (aqueous HCl or H_2SO_4)[6a] at room temperature or in refluxing EtOH. This unusual resistance to hydrolysis may be caused by the bulky anthracene substituent.

Metal Complexes. Although the chemistry of symmetrical (β-keto enamine) complexes (such as **11**) is well-known, there have been few reports on the synthesis of the less symmetric



11



12

(β-imino ketonato)ML_2 systems **12**.[16,17] Rh(I) and Ir(I) dicarbonyl complexes of Schiff base[17] and other asymmetric *N,O*-bidentate ligands[18] have been synthesized by treatment of the corresponding $[(\mu\text{-Cl})M(CO)_2]_2$ with the chelating ligand in the presence of $BaCO_3$. Kumar *et al*. have reported the formation of dirhodium(I) and diiridium(I) complexes containing the binucleating Schiff base α,α′-bis(salicylideneamino)-*m*-xylene ($SIXH_2$)[19] by reaction of the corresponding $[(\mu\text{-Cl})M(COD)]_2$ and $SIXH_2$ with NaOH(aq). On the basis of this method, we have successfully converted the new binucleating ligand **2a** to its cofacial dicarbonylrhodium (**4**) and (η^4-1,5-cyclooctadiene)-iridium (**5**) binuclear complexes, by reaction with $[(\mu\text{-Cl})Rh(CO)_2]_2$ and $[(\mu\text{-Cl})Ir(COD)]_2$, respectively, in the presence of K_2CO_3(aq) (Scheme 3). Treatment of **2a** with $[(\mu\text{-Cl})Rh(CO)_2]_2$ and $BaCO_3$(s), following the procedure of Rubailo *et al*.,[17] also afforded **4**; however, no reaction took place when K_2CO_3(s) was used as base under the same reaction conditions. Conversion of the free ligand into its binuclear complexes was followed by ^{1}H NMR.

Both complexes were isolated as yellow, air-stable solids, and they are soluble in organic solvents. Complex **5** decomposes in aerated solutions over a few hours, unlike **4**, which remains stable in solution for weeks.

^{1}H and ^{13}C NMR data, Tables 1 and 2, are consistent with the proposed structures of **4** and **5**. In general appearance, the aromatic regions of the spectra of both bimetallic complexes are similar to that of the free ligand **2a**, with the exception of the H-9 protons (located inside the cavity), which show upfield shifts. A larger shielding effect is observed for H-9 in the dirhodium complex. Complexation of **2a** causes a general downfield shift of the proton and carbon atoms of the β-keto enamine moiety. On the other hand, the COD olefinic (3.4−4.4 ppm) and aliphatic (1.8−2.4 ppm) protons are shifted upfield in **5** compared to those of free COD (5.6 and 2.4 ppm, respectively).

The spectral data support the formation of both meso and racemic atropisomers for complex **4**, as shown by the two sets of resonances for H-9 and the amino and methyl (H-11 and H-12) group protons, as well as for the carbons at the 2-, 10-, 12-, 13-, and 15-positions. Furthermore, the four doublets shown by the carbonyl ligands in **4** (δ 187.2, 187.1 ppm ($J_{C-Rh} \approx 71$ Hz, *trans* to O)[20] and 186.1, 185.9 ppm ($J_{C-Rh} \approx 64$ Hz, *trans* to N)) are consistent with the presence of the two geometries for the rhodium complex. NMR data for **5** do not exhibit the same degree of splitting for the proton and carbon resonances for the two isomeric forms as those for complex **4**. However, the presence of two sets of amino and methyl (H-11 and H-12) protons and methyl carbon C-11 resonances indicates the formation of both atropisomers for the diiridium complex **5** in *ca.* 2.3:1 ratio (calculated from the integration of the imino group protons), as observed for the free ligand **2a**. The proximity of other signals to the amino and methyl group proton resonances of **4** prevents an accurate measurement of the ratio of its atropisomers.

HRMS and FAB mass spectroscopies confirm the structures of **4** and **5**, respectively. The FAB mass spectrum of **5** (Figure 2) shows the parent ion at *m/z* 968−973; isotope peak intensities are as expected. Infrared data for complex **4** show two strong absorptions at 2073 and 2005 cm^{-1} for the CO ligands. The carbonyl stretching for the β-keto enamine moiety shifts to lower values on coordination of the **2a** ligand (ν_{CO} 1608 cm^{-1}), with **5** (ν_{CO} 1559 cm^{-1}) showing a red shift that is 13 cm^{-1} greater than that for **4** (ν_{CO} 1572 cm^{-1}).

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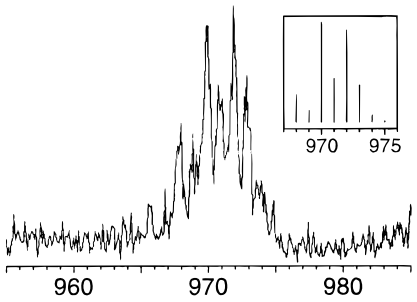
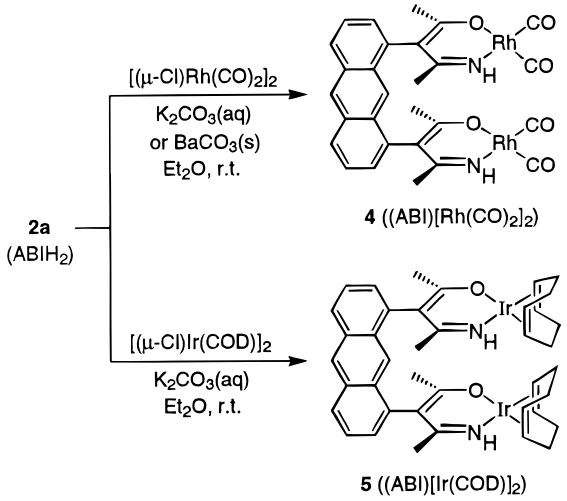


Figure 2. Molecular ion portion of FAB-MS recorded for (ABI)[Ir(COD)]$_2$ (**5**). The inset shows ion distribution calculated for ^{12,13}C and ^{191,193}Ir isotopes.

Scheme 3



Summary

We have prepared the new binucleating ligand **2a**, via bis(3,5-dimethylisoxazol-4-yl) intermediates, and its cofacial bis(dicarbonylrhodium) (**4**) and bis((η^4-1,5-cyclooctadiene)iridium) (**5**) complexes. These compounds represent the first members of a new family of cofacial bimetallic complexes. We expect that these complexes will be available with a variety of metal coordination environments and provide access for intramolecular binding of small substrate molecules between the metal centers.

Experimental Section

3,5-Dimethyl-4-iodoisoxazole[9] and $PdCl_2(PPh_3)_2$[21] were prepared by following the literature procedures. Anhydrous THF and diethyl ether were purchased from Aldrich Chemical Co. Other chemicals and solvents were reagent grade and were used as received. Flash chromatography was performed on silica gel 60 (230−400 mesh). NMR spectra were recorded by using Bruker AC200, AC250, and ARX300 NMR spectrometers. Infrared spectra were obtained with a Perkin-Elmer 1760X instrument. An HP 5971 instrument was used for GC-MS. FAB and high-resolution mass spectra were acquired with Finnigan TSQ-70 triple-quadrupole and Finnigan MAT-900 double-focusing mass spectrometers, respectively, using 3-nitrobenzyl alcohol as the matrix.

Trialkyl(3,5-dimethylisoxazol-4-yl)tins 6a and 6b. According to the method described by Kochetkov and Sokolov,[8] a mixture of 3,5-dimethyl-4-iodoisoxazole (3.64 g, 16.3 mmol) and Mg turnings (1.3 g, 52 mmol) in refluxing THF (60 mL) was treated with a solution of $BrCH_2CH_2Br$ (2.81 mL, 32.6 mmol) in THF (10 mL) under N_2, and the mixture was refluxed for an additional 2.5 h. The orange-brown suspension was allowed to cool to room temperature, and after dropwise addition of Me_3SnCl for **6a** (1 M in THF, 16.4 mL, 16.4 mmol) or Bu_3SnCl for **6b** (3.85 mL, 13.6 mmol), the resulting yellow suspension was stirred at room temperature overnight. The final reaction mixture was quenched with H_2O (100 mL) and the product extracted with diethyl ether (3 × 20 mL). The organic phase was then dried over $MgSO_4$, filtered, and concentrated to give a brown crude oil. Purification by flash chromatography and distillation under reduced pressure gave **6a** and **6b**, respectively, as light yellow liquids. ^{1}H NMR spectra of both compounds agree with those reported in the literature.[6b,10]

6a: R_f 0.52 (hexane−EtOAc, 4:1); yield 2.48 g (59%); EI-MS *m/z* (%) 261 (2, M^+ for ^{120}Sn), 246 (100, $M^+ - CH_3$), 216 (52, $M^+ - 3CH_3$), 165 (31, $Sn(CH_3)_3$), 135 (44, $SnCH_3$), 120 (25), 80 (29, C_5H_6N), 43 (27).

6b: bp 135−141 °C/0.6 mmHg (lit.[6b] 140−150 °C/0.6 mmHg); yield 4.0 g (63%); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 164.7 (CN), 173.5 (CO), 105.7, 29.0, 27.2 (CH_2), 13.6, 13.3, 13.2 (CH_3), 9.6 (CH_2); EI-MS *m/z* (%): 386 (18, $[M - H]^+$ for ^{120}Sn), 330 (13, $M^+ - Bu$), 274 (78, $M^+ - 2Bu + H$), 218 (94, $M^+ - 3Bu + 2H$), 216 (100, $M^+ - 3Bu$), 121 (36), 80 (54, C_5H_6N), 43 (33), 41 (40).

1,8-Dibromoanthraquinone (7). According to the procedure reported for the 1,5- isomer,[11] 1,8-dichloroanthraquinone (2.0 g, 7.0 mmol) was treated with KBr (4.0 g, 33.6 mmol), $CuCl_2$ (0.1 g, 0.7 mmol), and 85% H_3PO_4 (4 mL) in nitrobenzene (15 mL). Water was distilled from the reaction mixture until the temperature reached 200 °C, and then the mixture was refluxed for 24 h. The crude product was precipitated from the cooled mixture with methanol, collected, taken up in CH_2Cl_2, and isolated by evaporation of the solvent. Purification by column chromatography (CH_2Cl_2) yielded 2.0 g of a 6:1 mixture (as estimated by ^{1}H NMR) of **5** and 1-bromo-8-chloroanthraquinone. The same procedure was repeated using this product as starting material to give 1.3 g of a 10:1 mixture of **7** (yield ∼45%)[12] and 1-bromo-8-chloroanthraquinone. Spectral data for **7** agree with those reported in the literature.[22]

7: ^{13}C NMR ($CDCl_3$, 50 MHz) δ 181.7, 181.4, 141.1, 137.7, 135.0, 133.4, 126.7, 122.0.

1-Bromo-8-chloroanthraquinone: EI-MS *m/z* (%) 324 (20), 322 (78), 320 (59, M^+ for ^{79}Br and ^{35}Cl), 296 (5), 294 (22), 292 (18, $M^+ - CO$), 268 (7), 266 (30), 264 (23, $M^+ - 2CO$), 243 (6), 241 (17, $M^+ - Br$), 215 (6), 213 (16, $M^+ - Br - CO$), 185 (43), 150 (100), 75 (98), 74 (51).

1,8-Bis(3,5-dimethylisoxazol-4-yl)anthraquinone (8). To a solution of **7** (0.68 g, 1.9 mmol) and **6a** (1.7 g, 6.6 mmol) in toluene (45 mL) was added $PdCl_2(PPh_3)_2$ (0.03 g, 0.04 mmol), and the reaction mixture was brought to reflux under N_2. After 72 h, the resulting brown mixture was allowed to cool to room temperature, diluted with diethyl ether (30 mL), and extracted with H_2O (2% 15 mL). The organic phase was then dried over $MgSO_4$ and concentrated to give a crude orange solid. Purification by flash chromatography afforded **8** and the major side product 1-(3,5-dimethylisoxazol-4-yl)-8-methylanthraquinone as yellow-orange solids. Crystals of **8** were obtained from hot *i*-PrOH.

8: R_f 0.23 (hexane−EtOAc, 1:1); yield 0.35 g (47%); EI-MS *m/z* (%) 398 (47, M^+), 357 (86, $M^+ - C_2H_3N$), 338 (14, $M^+ - 4CH_3$), 324 (36), 296 (41), 286 (40), 272 (53), 214 (40), 200 (26), 189 (100), 174 (36), 75 (24).

1-(3,5-Dimethylisoxazol-4-yl)-8-methylanthraquinone: R_f 0.51 (hexane−EtOAc, 2:1); yield 0.07 g (12%); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.37 (dd, J = 7.8, 1.6, 1H), 8.20 (dd, J = 7.8, 1.3, 1H), 7.77 (t, J = 7.6, 1H), 7.66−7.55 (m, 2H), 7.49 (dd, J = 7.6, 1.6, 1H), 2.68 (s, 3H), 2.28 (s, 3H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 185.8, 183.7, 164.2 (CO), 159.0 (CN), 141.3, 138.4, 138.2, 134.5, 134.3, 134.1, 132.8 (higher intensity of this resonance suggests coincidental overlap of two CH signals), 132.7, 130.9, 127.5, 125.6, 116.6, 22.7, 11.4, 10.6; EI-MS *m/z* (%) 317 (9, M^+), 276 (100, $M^+ - C_2H_3N$), 261 (62, $M^+ - C_2H_3N - CH_3$), 205 (23), 176 (46), 151 (18), 88 (9), 75 (7), 63 (8).

1,8-Bis(3,5-dimethylisoxazol-4-yl)anthracene (10). (a) Via Cross-Coupling. To a solution of **9** (0.36 g, 1.1 mmol)[14] and **6b** (1.8 g, 4.7 mmol) in toluene (25 mL) was added $PdCl_2(PPh_3)_2$ (0.03 g, 0.04 mmol), and the resulting orange solution was heated to reflux for 62 h under N_2. The final dark brown solution was allowed to cool to room temperature, diluted with diethyl ether (30 mL), and extracted with

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H_2O (3% 15 mL) and saturated aqueous KF solution (4% 15 mL). The organic phase was filtered, dried over $MgSO_4$, filtered, and concentrated to give a yellow solid. The crude product was purified by flash chromatography (hexane−AcOEt (3:1), $R_f = 0.39$), to give **10** as a pale yellow solid, and crystallized by slow evaporation from the eluting solution as pale yellow needles: yield 0.12 g (31%); EI-MS *m/z* (%) 368 (100, M^+), 311 (12, $M^+ - C_2H_3NO$), 284 (25, $M^+ - C_4H_6NO$), 283 (25), 268 (23), 242 (38), 241 (50), 240 (35), 213 (43), 202 (20). Small amounts of the monocoupled compounds 1-bromo- and 1-chloro-8-(3,5-dimethylisoxazol-4-yl)anthracenes (M^+ *m/z* 351−353 and 307−309, respectively), were also formed, most likely because the reaction was incomplete and because some 1-bromo-8-chloroanthracene was present in the starting material. However, because of their similar R_f values, no attempt was made to separate them.

(b) Via Reduction of 8. A mixture of **8** (0.27 g, 0.67 mmol) and Zn dust (2.0 g) in 28% aqueous NH_3 (30 mL) was heated at 50−55 °C for 7 h. The resulting red mixture was allowed to cool and was filtered; the residue and filtrate were each extracted with CH_2Cl_2 and EtOAc. The combined organic extracts were evaporated to dryness. The pale yellow residue was then dissolved in a hot mixture of *i*-PrOH (35−40 mL) and 12 M HCl (1−2 mL) and the solution refluxed for 4 h. The final yellow solution was concentrated to give **10** as a yellow solid: yield 0.20 g (82%).

3,3′-(1,8-Anthracenediyl)bis(4-amino-3-penten-2-one) (2a, $ABIH_2$). A mixture of **10** (0.20 g, 0.54 mmol) and RaNi (0.1−0.2 g) in EtOH (150 mL) was heated at reflux for 8 h. The final reaction mixture was allowed to cool and was filtered through Celite, and the residue washed with EtOAc. The combined filtrates were evaporated to dryness to give **2a** as an orange-brown solid: yield 0.16 g (80%); IR (KBr, cm^{-1}) 3381 (vs br, NH), 2929 (w, CH), 1265 (m, CN), 1608 (vs, CO); HRMS (*m*/*z*) calcd for $C_{24}H_{25}N_2O_2$ $[M + H]^+$ 373.1916, found 373.1917.

3,3′-(1,8-Anthracenediyl)bis(4-imino-2-pentanonato-*N*,*O*)bis(dicarbonylrhodium) (4, (ABI)[Rh(CO)$_2$]$_2$). (a) Using K_2CO_3(aq) as Base. To a solution containing $[(\mu\text{-Cl})Rh(CO)_2]_2$ (12 mg, 0.03 mmol) and **2a** (10.0 mg, 0.03 mmol) in dry diethyl ether (10 mL) was added dropwise aqueous K_2CO_3 solution (0.6 mL, 0.2 M) under N_2; the mixture was stirred vigorously at room temperature. After 0.5 h, ^1H NMR of the reaction mixture showed complete conversion of the free ligand **2a** to complex **4**. The resulting reaction mixture was then evaporated to dryness under a stream of N_2. The dark crude solid was taken up in $CHCl_3$ and the solution filtered and concentrated to afford pure **4** as a yellow solid: IR (KBr, cm^{-1}) 3451 (br, NH), 2071 (vs, CO), 1996 (vs, CO), 1571 (m, CO), 1415 (m); IR ($CHCl_3$, cm^{-1}) 2073 (vs), 2005 (vs), 1572 (m, CO); HRMS (*m*/*z*) calcd for $C_{28}H_{23}N_2Rh_2O_6$ $[M + H]^+$ 688.9666, found 688.9615.

(b) Using $BaCO_3$(s) as Base. To a solution containing $[(\mu\text{-Cl})Rh(CO)_2]_2$ (12 mg, 0.03 mmol) and **2a** (10.0 mg, 0.03 mmol) in benzene (10 mL) was added $BaCO_3$(s) (8−10 mg, 0.04−0.05 mmol) under N_2, and the mixture was stirred vigorously at room temperature. After 15 min, ^1H NMR of the reaction mixture showed complete conversion of the free ligand **2a** to complex **4**. The resulting mixture was worked up as described above to give **4** as a yellow solid.

3,3′-(1,8-Anthracenediyl)bis(4-imino-2-pentanonato-*N*,*O*)bis((η^4-1,5-cyclooctadiene)iridium) (5, (ABI)[Ir(COD)]$_2$). To a solution containing $[(\mu\text{-Cl})Ir(COD)]_2$ (30 mg, 0.042 mmol) and **2a** (15.0 mg, 0.042 mmol) in dry diethyl ether (15 mL) was added dropwise aqueous K_2CO_3 solution (1.5 mL, 0.33 M) under N_2; the mixture was stirred vigorously at room temperature. After 0.5 h, ^1H NMR showed complete conversion of the free ligand **2a** to complex **5**. The reaction mixture was then evaporated to dryness under a stream of N_2. The greenish yellow crude solid was washed with hexane and then dissolved in $CHCl_3$ or CH_2Cl_2; the solution was filtered and concentrated to afford **5** as a yellow solid: IR (KBr, cm^{-1}) 3421 (w, NH), 2934 (w, CH), 2873 (w, CH), 2828 (w, CH), 1614 (sh), 1559 (s, CO), 1472 (m), 1386 (m); FAB-MS *m/z* 968.0−972.1 (M^+; see Figure 2).

X-ray Analyses. Diffraction data for **8** and **10** were collected on an Enraf-Nonius CAD4 diffractometer fitted with a Cu Kα source and a graphite monochromator, using the $\theta-2\theta$ scan method. Final unit cell constants were determined from the orientations of 25 centered high-angle reflections. The intensities were corrected for absorption using ψ-scan data for five reflections. The MolEN[23] set of programs was used for structure solution and refinement. Full details of the crystal structure analyses of **8** and **10** are available in CIF format via the Internet.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for complexes **4** and **5** (2 pages). X-ray crystallographic files, in CIF format, for compounds **8** and **10** are available on the Internet only. Ordering and access information is given on any current masthead page.

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