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Reactivity of diiron(II) complexes with molecular oxygen

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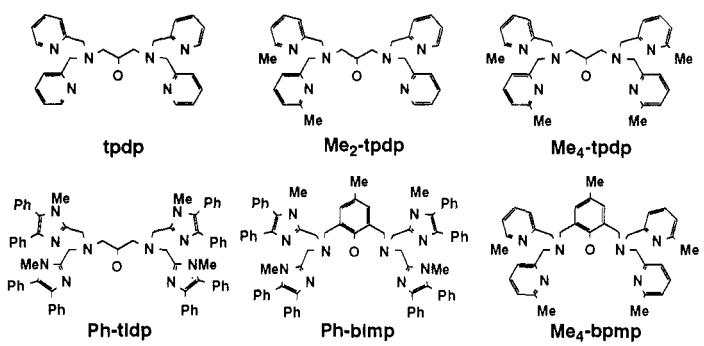
Abstract: A variety of dinucleating ligands (L) have been developed for preparation of diiron-dioxygen complexes, where L represents N_6O donor ligands with a phenolate or alkoxide bridging group. They form five-coordinate diiron(II,II) complexes with an exogenous bridging carboxylate, $[Fe_2(L)(RCOO)]^{2+}$, which react with O_2 to give μ-peroxo species. Their oxygen affinity and thermal stability of μ-peroxo species toward the irreversible oxidation have been found to be highly dependent on the electron donor ability of coordinating atoms, steric bulkiness and the stereochemistry of the bridging skeleton of the dinucleating ligands.

Introduction The chemistry of diiron-dioxygen complexes (ref. 1) is of particular importance to gain insight into the structures and functions of diiron centers of hemerythrin (Hr) (ref. 2), ribonucleotide reductase (RNR) (ref. 3), and methane monooxygenase (MMO) (ref. 4). The role of Hr is a dioxygen transport and it binds O_2 reversibly in a hydroperoxo fashion. The diiron center of RNR R2 activates O_2 to oxidize tyrosine to tyrosine radical for DNA biosynthesis. MMO also activates O_2 to hydroxylate methane to methanol. Recently, a "*peroxo intermediate*" has been found as an intermediate of dioxygen activation by diiron center in MMOH (ref. 5). Mechanism of dioxygen activation by MMOH has been proposed to involve a di(μ-oxo)diiron(IV,IV) species with a diamond core "*compound Q*"(ref. 6) , which is converted from a "*peroxo intermediate*".
The iron-dioxygen complexes have been shown to be highly susceptible to irreversible oxidation. Only a few iron(II) complexes that bind O_2 in a μ-peroxo fashion have been known (ref. 7-9). In order to suppress such irreversible oxidation of iron(II,II) ion, we have developed new dinucleating ligands with sterically hindered nitrogen bases (6-methylpyridyl or 4,5-diphenylimidazolyl group) as shown in Fig. 1. These sterically hindered ligands are effective to prevent the irreversible oxidation by dioxygen. In this study, we describe the controlling of the thermal stability of μ-peroxo complexes toward irreversible oxidation and the oxygen affinity of diiron(II,II) complexes.

Characterization of Diiron(II,II) Complexes In order to prepare the μ–peroxo complexes, it is essential to construct the reaction sites for dioxygen on the iron centers. The ligands, tpdp, Me_2-tpdp, Me_4-



$[Fe_2(Me_4\text{-tpdp})(C_6H_5CO_2)]^{2+}$	(1)
$[Fe_2(Me_4\text{-tpdp})(CF_3CO_2)]^{2+}$	(2)
$[Fe_2(Me_2\text{-tpdp})(CF_3CO_2)]^{2+}$	(3)
$[Fe_2(tpdp)(C_6H_5CO_2)]^{2+}$	(4)
$[Fe_2(Ph\text{-tidp})(C_6H_5CO_2)]^{2+}$	(5)
$[Fe_2(Ph\text{-}tidp)(C_6F_5CO_2)]^{2+}$	(6)
$[Fe_2(Ph\text{-tidp})(CF_3CO_2)]^{2+}$	(7)
$[Fe_2(Ph\text{-bimp})(C_6H_5CO_2)]^{2+}$	(8)
$[Co_2(tpdp)(CH_3CO_2)]^{2+}$	(9)

Fig. 1 Dinucleating ligands and diiron(II,II) complexes

tpdp, and Ph-tidp, form mono-carboxylato complexes, although they sometimes contain additional coordinated water molecule(s), $[Fe_2(L)(RCOO)(H_2O)_n]^{2+}$, as shown in Fig. 2. The electronic spectra of those complexes in dichloromethane and acetonitrile revealed that the coordinated water molecule(s), however, dissociates to form five-coordinate iron centers, which have dioxygen binding sites. It should be noted that Ph-bimp and Me_4-bpmp tend to form bis-carboxylato complexes, $[Fe_2(L)(RCOO)_2]^+$, which have no coordination sites for a peroxo bridge. For Ph-bimp, however, only benzoate produced mono-benzoato complex, $[Fe_2(L)(RCOO)(H_2O)]^{2+}$, whereas for Me_4-bpmp, mono-carboxylate complex could not be obtained so far. It is difficult to control the coordination number around iron ions for Ph-bimp and Me_4-bpmp at the present stage.

The molecular structures of the dinuclear cation of **1**, **5** (ref. 10) and **8** (ref. 11) are shown in Fig. 2. The dinuclear complex cations of **1** and **8** consist of two distinct iron centers, one five- and one six-coordinate iron centers, which are doubly bridged by the alkoxide or phenolate oxygen of the dinucleating ligands and the benzoate oxygens. The six-coordinate centers contain an additional coordinated water molecule to form a distorted octahedral structure with an N_3O_3 donor set. Water molecule in **8** is directed toward the five-coordinate iron center, whereas that in **1** is toward the opposite side of the five-coordinate iron center. This is probably due to steric requirement of the dinucleating ligands. In contrast, both iron centers are five-coordinate in **5**. Introduction of methyl group into the 6-position of pyridyl group and phenyl groups into the 4,5-positions of imidazolyl group have significant influence on the Fe-N bond distances and stereochemistry. The average Fe-N bond distances in five- and six-coordinate iron centers in **1** and **8** are 2.19 and 2.27 Å, and 2.22 and 2.22 A, respectively. That of **5** is 2.19 Å. Those distances are substantially longer than those in the closely related complexes, which have no sterically bulky substituents. Elongation of the Fe-N bonds is partly due to unfavorable steric interaction between the hydrogen atoms of the methyl or phenyl groups and the coordinated atoms such as oxygens of the bridging benzoate in **1**. In addition of elongation of the Fe-N bonds, tilting of the pyridyl or imidazolyl plane with respect to the Fe-N bond vector is observed. This seems to be also attributable to the steric requirement mentioned above. Those two factors seems to weaken the electron donor ability of the nitrogen donors and to stabilize the iron(II) oxidation state, which facilitate reversible deoxygenation (vide infra).

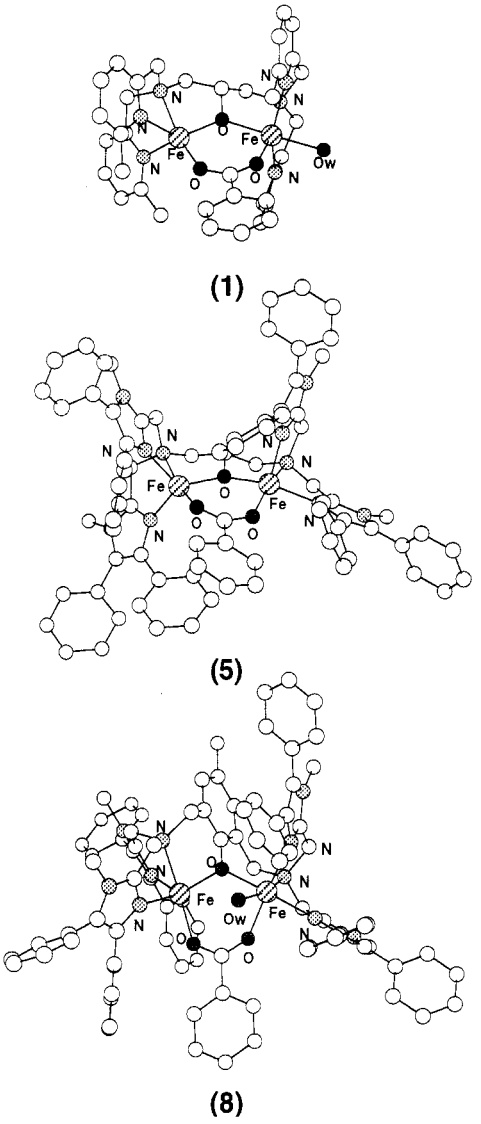


Fig. 2 Chem3D views of **1**, **5**, and **8**.

$E_{1/2}$ values of diiron(II,II) complexes are useful to compare the electron donor abilities of the dinucleating ligands. Those of **2** and **3** measured by cyclic voltammetry are 640 and 420 mV vs. SCE in acetonitrile. Thus introduction of methyl group into pyridyl group causes significant positive shift of $E_{1/2}$ value, suggesting that those substituents make the electron donor abilities of the ligands weaker. $E_{1/2}$ values of **1**, **5**, and **8** are 490, 345, and 600 mV vs. SCE, indicating that the order of the electron donor ability of those dinucleating ligands is Ph-tidp > Me_4-tpdp > Ph-bimp. The result indicates that the electron donor ability of imidazolyl group is stronger than that of pyridyl group, and 1,3-diamino-2-propanolate skeleton is a stronger electron donor than 2,6-diamino-4-methyl-phenolate one.

Reactivity of the complexes with dioxygen. Complexes **1** - **8** react with O_2 to give an oxy-complexes (μ-peroxo complexes) in acetone, acetonitrile, or dichloromethane with color change from almost color less to deep blue or deep blue green (ε = ~1000 - 3000 dm^3 mol^{-1} cm^{-1}), which is attributable to the

charge transfer transition from a coordinated peroxide to iron(III) ion. Formation of μ-peroxo species was confirmed by various spectroscopic techniques including resonance Raman spectroscopy, manometry, or X-ray crystallography. The thermal stabilities of these complexes toward the irreversible oxidation are highly dependent on the dinucleating ligands.

Reaction of **4** with O_2 in acetonitrile showed an instantaneous irreversible oxidation even at -40 °C. Que et al. also reported that oxy-**4** can not be formed in CH_2Cl_2 even at -80 °C, although they observed the formation of oxy-species in a CH_2Cl_2-DMSO solution. Complex **3** which has two 6-methylpyridyl side arms produced an oxy-species in acetone at -60 °C, which gradually decomposed within a few hours even at -60 °C. Introduction of two more methyl groups into pyridyl groups of Me_2-tpdp greatly stabilized the oxy-species. Complexes **1** and **2** react with O_2 to give oxy-species at below -30 °C, which are reasonably stable and deoxygenation can be achieved by bubbling of Ar gas into the solution. Thus they showed reversible oxygenation-deoxygenation at low temperature. At ambient temperature, however, the oxy-species are irreversibly oxidized to give brown species. Complexes **5**, **6**, and **7** also form oxy-species at low temperature (below -40 °C). In contrast to the Me_4-tpdp μ-peroxo complexes, deoxygenation occurs by warming upto room temperature without serious irreversible oxidation, which can be monitored by absorption spectra and NMR, indicating that the reactivity of the complexes with O_2 is very low at room temperature, although irreversible oxidation slowly proceeded for a few days under O_2 atmosphere at room temperature. The thermal stability of oxy-**5** is greater than that of oxy-**1** in dichloromethane .

Complex **8** react with O_2 in acetonitrile even at 20 °C to give an oxy-species, which is stable for several hours. The complex has an intense dark green color, its electronic spectrum in CH_3CN at 20 °C showing a broad absorption band at 800 – 500 nm (ε = ca. 1700 $dm^3\ mol^{-1}\ cm^{-1}$), as seen in Fig. 3 (spectrum a). Boiling the CH_3CN solution of **oxy-8** under N_2 resulted in decolorization of the solution (spectrum b). Bubbling of O_2 through the solution restored the original dark green color (spectrum c). The complex **oxy-8** is substantially thermally stable toward the irreversible oxidation compared to the μ-peroxo complexes reported so far.

Thus the thermal stabilities of the complexes are highly dependent on the dinucleating ligands; Ph-bimp > Ph-tidp > Me_4-tpdp > Me_2-tpdp > tpdp. This order is almost correlated with the relative degree of steric bulkiness and the electron donor ability of the dinucleating ligands. The thermal stability is also dependent on the electron donor ability of the bridging carboxylates; the relative order is CF_3COO^- > $C_6F_5COO^-$ > $C_6H_5COO^-$. Thus the weaker electron donors tend to stabilize oxy-species.

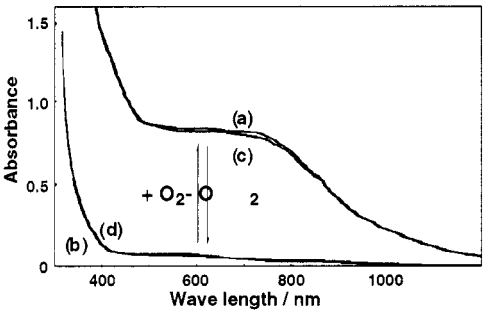


Fig. 3 Absorption spectral changes for $[Fe_2(Ph\text{-}bimp)(C_6H_5COO)(O_2)]^{2+}$ (**oxy-8**) in acetonitrile at 20 °C demonstrating the reversible oxygenation-deoxygenation cycles.

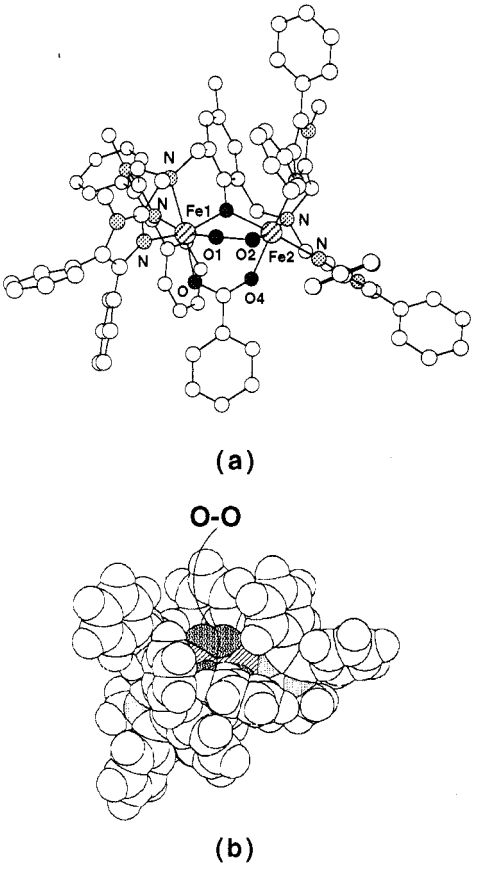


Fig. 4 Chem3D view (a) and space-filling view (b) of **oxy-8**.

Characterization of oxy-8 The molecular structure of the dinuclear cation of **oxy-8** is shown in Fig. 4a. The complex has a triply bridged structure with cis-1,2-μ-peroxide, μ-phenolate of Ph-bimp, and μ-benzoate, which is quite similar to that of a μ-peroxo dicobalt complex, $[Co_2(bpmp)(C_6H_5COO)(O_2)](BF_4)_2{\cdot}H_2O$ (**10**) (ref. 12). Such a cis-μ-1,2-peroxo coordination mode has been also found for

$[Fe_2(N\text{-}Et\text{-}hptb)(Ph_3PO)_2(O_2)]^{3+}$ (**11**) (ref. 13), and $[Fe_2(O_2)(O_2CCH_2Ph)_2\{HB(pz')_3\}_2]$ (**12**) (ref. 14). Each iron center has a distorted octahedral geometry with a facial-N_3O_3 donor set, but the two iron centers are not equivalent. The O1-O2 bond distance is 1.426(6) Å, which is slightly longer than those of **11** (1.416 Å), and **12** (1.409 Å), and shorter than those in $[Fe_6(O_2)(O_2)_2(C_6H_5COO)_{12}(H_2O)_2]$ (1.480(12) Å) (ref. 15) and $[Fe_6(O)_2(O_2)_3(OAc)_6]^-$ (1.472(9) Å) (ref. 16), and in the range observed for the μ-peroxo transition metal complexes (ref. 17). The Fe–O(peroxide) bonds are asymmetric (Fe1–O1 = 1.944(4) and Fe2–O2 = 1.864(4) Å) and significantly shorter than the average Fe–O(phenolate and benzoate) distance (2.030(5) Å). The Mössbauer spectrum of a powdered sample of **oxy-8** at 77 K exhibited two sets of quadrupole doublets (δ_1 = 0.58 mm s^{-1} and ΔE_{Q1} = 0.74 mm s^{-1}, and δ_2 = 0.65 mm s^{-1} and ΔE_{Q2} = 1.70 mm s^{-1}, ratio of areas = 1.1 : 1), which can be assigned to two distinct high-spin iron(III) centers. Thus the O–O bond distance and Mössbauer data suggest the Fe^{3+}-O_2^{2-}–Fe^{3+} formulation (ref. 18). The average Fe–N(imidazole) bond distance (2.156(5) Å) and the Fe-N one including Fe-N(tertiary amine nitrogens) (2.200 Å) of **oxy-8** are slightly shorter than those of **8** (2.184 Å and 2.227 Å, respectively), reflecting the oxidation state change. They are, however, substantially longer than those of iron(III) site (2.097(2) Å) and iron(II) site (2.124(3) Å) in a mixed valence complex $[Fe_2(bimp)(C_6H_5COO)_2]^{2+}$ which has no sterically bulky substituent on imidazolyl groups (ref. 19). Such a significant elongation of the Fe–N bonds due to introduction of phenyl groups is also attributable to unfavorable steric interaction between the hydrogen atoms of the 4-phenyl group of the coordinated imidazole groups and the oxygen atoms of the bridging peroxide (O2) and benzoate (O4) as found for diiron(II,II) complexes **1**, **5**, and **8**. Phenyl groups at the 4-position of the imidazole groups coordinated to Fe2 form a hydrophobic pocket in which the peroxide resides (Fig. 4b).

Oxygen affinity of diiron(II,II) complexes It is interesting to investigate the factors which affect the oxygen affinity of diiron(II) complexes with various dinucleating ligands. The equilibrium constants, K of eq. (1) for the oxygenation reaction in dichloromethane were determined by spectrophotometric titration (ref. 20) where $P(O_2)_{1/2} = 1 / K$ and $P(O_2)_{1/2}$ value represents partial oxygen pressure at which half amount of complex is oxygenated.

$$[Fe_2] + O_2 \overset{K}{\rightleftharpoons} [Fe_2(O_2)] \quad (1)$$

Oxygen affinities of **5**, **6**, and **7** which have the same dinucleating ligand (Ph-tidp) vary with the bridging carboxylate: the order is $C_6H_5COO^- > C_6F_5COO^- > CF_3COO^-$, which is well correlated with the electron donor abilities of carboxylates. It should be noted, however, that those of the Me_4-tpdp and Ph-bimp complexes are greater than those of the corresponding Ph-tidp complexes, although the electron donor abilities of Me_4-tpdp and Ph-bimp are weaker than that of Ph-tidp. The oxygen affinity of **8** is exceptionally high compared with those of the Me_4-tpdp and Ph-tidp complexes, which is more than 2 x 10^3 - 3 x 10^4 times greater than those of the Me_4-tpdp and Ph-tidp complexes.

Discussion Introduction of 6-methyl group into coordinated pyridyl group has substantial influence on the thermal stability of μ-peroxo diiron complexes. The relative order of thermal stability of **oxy-1**, **-3**, and **-4** depends on the numbers of 6-methyl groups in the dinucleating ligands (Me_4-tpdp > Me_2-tpdp > tpdp), which is also correlated with the electron donor ability of the dinucleating ligands. Thermal stabilities of the Ph-tidp and Ph-bimp complexes are greater than those of the above complexes. The results suggest that the introduction of sterically bulky substituent into the pyridyl or imidazolyl group suppresses some deleterious, irreversible decay reactions of μ-peroxo species. If the decay reaction proceeds via a higher valent species such as Fe(IV), the electron donor ability of the ligands seems to be important because the weaker electron donor would suppress the formation of an Fe(IV) species and facilitate the reformation of diferrous species from μ-peroxo diferric species. If the decay reaction is bimolecular, the steric properties of the ligand seem to be also important because the sterically bulkier ligand which can form a hydrophobic pocket surrounding the O_2-binding site would provide unfavorable interactions in the transition state of the decay reaction. In either case, a sterically bulky substituent would suppress the

TABLE 1. Thermodynamic Data for Oxygenation Reaction in Dichloromethane[a]

comp	$P_{1/2}$/Torr[b]	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
5	8560	-55 ± 3	-263 ± 14
6	32100	-55 ± 3	-274 ± 12
7	76800	-52 ± 2	-271 ± 7
2	5770	-46 ± 3	-229 ± 16
1[c]	2.4		
8[d]	2		
9	203000	-76 ± 4	-361 ± 361

[a] Standard state is 1 Torr at 20 °C. [b] $P_{1/2}$ values are normalized at 20 °C except for **1** and **8**. [c] measured at -40.1 °C. [d] measured at 20.0 °C in acetonitrile.

irreversible oxidation and facilitate the reversible oxygenation. Molecular structure of **8** revealed that μ-peroxo group is deeply buried in a hydrophobic cavity formed by phenyl groups. Thus weaker electron donor and sterically bulkier ligand play an important role for thermal stability of μ-peroxo diiron species.

It has been shown that the oxygen affinity correlates with the electron donor ability of the ligand for many cobalt(II) complexes : the stronger the electron donor ability of the ligand, the greater the electron density on metal center, the easier the electron drift from metal to dioxygen, and the higher the oxygen affinity. This is the case within a series of complexes **5**, **6**, and **7**. In contrast, although the electron donor ability of Me_4-tpdp is weaker than that of Ph-tidp, oxygen affinity of **2** is greater than that of **7**. Thus this is not the case. The observed high oxygen affinity of **2** compared to **7** is mainly attributable to "*entropy effect*". Importance of "*entropy effect*" in oxygen affinity is observed for a closely related dicobalt complex, $[Co_2(tpdp)(CH_3COO)]^{2+}$. The oxygen affinity of **9** is lower than those of the diiron complexes. Enthalpy change of **9** is -76 kJ mol^{-1}, which is significantly larger than those of diiron complexes. Such large enthalpy change appears to be mainly due to the ligand field stabilization effect, which is absent in the high spin iron(III) complexes. The observed low oxygen affinity of this complex is clearly due to the unfavorable "*entropy effect*". Thus the "*entropy effect*" plays an important role for the oxygen affinity of the present type of complexes.

As mentioned above, the oxygen affinity of **8** is exceptionally high, which is more than 2 x 10^3 - 3 x 10^4 times greater than those of the Me_4-tpdp and Ph-tidp complexes. The former has a 2,6-bis(aminomethyl)phenolate bridging skeleton, whereas the latters have 1,3-diamino-2-propanolate bridging skeleton. Such increased oxygen affinity was also observed for the corresponding cobalt complex **10** ($P_{1/2}$ = ca.0.1 Torr at 20 °C in acetonitrile) compared to **9** (ref. 21). Thus the oxygen affinity of the present type of complexes is highly dependent on the stereochemistry of the bridging skeleton; 2,6-bis(aminomethyl)phenolate bridging skeleton appears to be suitable for the formation of an additional μ-peroxo bridge compared to 1,3-diamino-2-propanolate bridging skeleton. Comparison of the molecular structures of deoxy- and oxy forms (**8** and **oxy-8**) provides some interesting informations for the oxygen affinity. The structures around two iron atoms in both forms are almost superimposed, indicating that deoxy-form has a suitable O_2 binding sites on the two iron centers in μ-peroxo fashion. This stereochemistry provided by 2,6-bis(aminomethyl)phenolate bridging skeleton seems to be responsible for the observed high oxygen affinity.

Those μ-peroxo complexes are interesting as models for a "*peroxo intermediate*" found in MMOH. Although **oxy-8** is thermally stable, it has some activity for oxidation of triphenylphosphine and thioanisole to the corresponding oxide (ref. 22). Further studies are in progress.

Summary. In order to prepare μ-peroxo diiron complexes, we developed various dinucleating ligands. Sterically bulky substituents of the present type of dinucleating ligands which weaken the electron donor ability and form a hydrophobic pocket for a O_2 binding site would suppress the irreversible oxidation and facilitate the reversible oxygenation. In addition, the oxygen affinity is highly dependent on the stereochemistry of the bridging skeleton of the dinucleating ligands.

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