

Aryl–Oxazoline Chelates of First-Row Transition Metals: Structures of { κ -C,N-(o- C_6H_4)CMe₂(COCH₂CMe₂N)}FeCl(py) and [(κ -C,N-(o- C_6H_4)CMe₂(COCH₂CMe₂N)}Cr(μ -Cl)]₂[‡]

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Aryl-oxazoline synthons have been explored for the preparation of strong-field first-row transition metal chelate species. With 4,4-dimethyl-2-phenyloxazoline (HPhOx), no CH bond activations afforded complexation, and aside from $Zn(\kappa - C, N-4, 4-Me_2-2-(o-C_6H_4) oxazoline)_2$ (Zn(PhOx)₂), aryl-coupling reactions were noted with 4,4-dimethyl-2-(2-lithiophenyl)oxazoline (LiPhOx) and MX₂; $[\kappa - N, N - \{4, 4 - Me_2 - (2 - o - C_6H_4) - 2 - oxazoline\}_2]CoCl_2 (1 - Co) was structurally characterized.$ Metalations with 4,4-dimethyl-2-benzyloxazoline (PhCH₂Ox) were prone to deprotonation, as exemplified by $(Me_2N)_3Ti(\eta - N - (4, 4 - dimethyl - (2 - CHPh) oxazoline))$ (2) and bis-N, N' - (4, 4 - dimethyl - (2 - CHPh) oxazoline))(2-pyridylmethylyl)oxazoline)Fe (3). Oxidative addition of 4,4-dimethyl-2-(2-bromophenylpropan-2-yl)oxazoline (**BrPhCMe₂Ox**) to Ni(COD)₂ provided $[\{\kappa - C, N - (o - C_6H_4)CMe_2(COCH_2CMe_2N)\}Ni]_2$ -(u-Br)₂(4₂). With 4,4-dimethyl-2-(2-lithiophenylpropan-2-yl)oxazoline (LiPhCMe₂Ox), salt (FeBr₂) metathesis proved uncompetitive with oxazoline ring-opening, as exhibited by $[{\kappa-N, O-C_6H_4CMe_2C} =$ NCMe₂CH₂(μ -O)-}BrFe{ κ -N,O-C₆H₄CMe₂C=NCMe₂CH₂(μ -O)-}FeBr]Li { κ -N,O-C₆H₄CMe₂-C= $NCMe_2CH_2(\mu-O)$ -{(DME) (5-Fe₂Li). Metatheses utilizing (PhCMe₂Ox)₂Zn, prepared from **LiPhCMe₂Ox** and ZnCl₂, gave structurally characterized dichromium, i.e., [$\{\kappa$ -C,N-(o-C₆H₄)CMe₂ $(COCH_2CMe_2N)$ Cr]₂(μ -Cl)₂(6_2), and iron, i.e., { κ -C,N-{(o-C₆H₄)CMe₂(COCH₂CMe₂N)}Fe(py)Cl (7) products. Bis-aryloxazoline metal complexes proved difficult to prepare, with $\{\kappa - C, N - (o - C_6 H_4) - v_6 - v_6 + v_6 - v_6 + v_6 - v_6 + v_6 - v_6 + v_6 +$ $CMe_2(COCH_2CMe_2N)$ M (M = Ni, 9) the only clear example, although NMR evidence exists for M = Fe(8).

Introduction

Recent investigations in these laboratories have focused on distinguishing electronic features that differentiate secondrow transition metal reactivity from that of the third row.¹⁻⁷ The greater density of states (DOS) in second-row species

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- (1) Hirsekorn, K. F.; Hulley, E. B.; Wolczanski, P. T.; Cundari, T. R. J. Am. Chem. Soc. **2008**, 130, 1183–1196.
- (2) Kuiper, D. S.; Douthwaite, R. E.; Mayol, A.-R.; Wolczanski, P. T.; Lobkovsky, E. B.; Cundari, T. R.; Lam, O. P.; Meyer, K. *Inorg. Chem.* **2008**, *47*, 7139–7153.
- (3) Kuiper, D. S.; Wolczanski, P. T.; Lobkovsky, E. B.; Cundari, T. R. J. Am. Chem. Soc. 2008, 130, 12931–12943.
- (4) Kuiper, D. S.; Wolczanski, P. T.; Lobkovsky, E. B.; Cundari, T. R. Inorg. Chem. 2008, 47, 10542–10553.
- (5) Rosenfeld, D. C.; Kuiper, D. S.; Lobkovsky, E. B.; Wolczanski,
 P. T. *Polyhedron* 2006, *25*, 251–258.
 (6) Rosenfeld, D. C.; Wolczanski, P. T.; Barakat, K. A.; Buda, C.;
- (6) Rosenfeld, D. C.; Wolczanski, P. T.; Barakat, K. A.; Buda, C.; Cundari, T. R.; Schroeder, F. C.; Lobkovsky, E. B. *Inorg. Chem.* **2007**, *46*, 9715–9735.
- (7) Veige, A. S.; Slaughter, L. M.; Lobkovsky, E. B.; Wolczanski, P. T.; Matsunaga, N.; Decker, S. A.; Cundari, T. R. *Inorg. Chem.* **2003**, *42*, 6204–6224.

facilitates chemical reactivity by enabling lower energy pathways from reactant to product.¹ In combination with somewhat lower bond energies,⁸ these factors explain the typically greater rates of second-row transition metal complexes relative to their third-row congeners and the widespread use of Pd, Rh, etc., catalysts in bond-making and -breaking processes requiring 2e⁻ changes.^{9–11}

Following similar logic, first-row transition metals should be even better suited for rapid chemical transformations because their DOS is even greater, as spectroscopic investigations have historically shown.¹² Furthermore, the application of first-row transition metals in stoichiometric and

⁽⁸⁾ Uddin, J.; Morales, C. M.; Maynard, J. H.; Landis, C. R. Organometallics 2006, 25, 5566–5581.

⁽⁹⁾ Hartwig, J. Organotransition Metal Chemistry: From Bonding to Catalysis; University Science Books: Sausilito, CA, 2009.

⁽¹⁰⁾ Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Sausilito, CA, 2009.

^{(11) (}a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA., 1987. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; John Wiley & Sons: New York, 2005.

⁽¹²⁾ Figgis, B. N.; Hitchman, M. A. Ligand Field Theory and Its Applications; Wiley-VCH: New York, 2000.



Figure 1. Angular overlap arguments show that both the interaction energy and orbital overlap favor C-based over N- and O-based ligands in terms of field strength.

catalytic transformations has two major advantages: (1) they are less expensive, assuming similar activity, and (2) depending on the metal, trace contamination (e.g., in drugs, food containers, etc.) is *usually* less of a health issue when the compounds are employed in the course of organic synthesis.^{13–16} Unfortunately, the field strengths of common coordination complexes are weak enough that 1e⁻ changes are more common, and these often prove detrimental to desired reactivity.^{17–19}

In principle, carbon-based ligands can impart strong fields to a first-row transition metal, as the illustration in Figure 1 reveals.^{20–24} Angular overlap arguments portray C-based orbitals as having very good interaction energies due to their relative proximity in energy to appropriate metal orbitals.^{12,25} In comparison, N- and O-based ligands are less well matched energetically due to their lower energy orbitals. Better orbital overlap ($S_C > S_N > S_O$) also contributes to the logic that carbon-based ligands are strong field in nature. Ligands based on main group elements of the second row (e.g., phosphines) and below may match corresponding metal orbitals better in energy, but this is compensated by overlaps that are significantly attenuated due to the relative diffusivity of their orbitals.

The concept of using carbon-based ligands to impart strong fields is as old as their applications in organometallic chemistry, where ligands such as cyclopentadienyl are known

(13) Ritter, S. K. Chem. Eng. News 2008, 86, 53-57.

- (15) (a) Sherry, B. D.; Furstner, A. Acc. Chem. Res. 2008, 11, 1500–1511.
 (b) Furstner, A.; Martin, R. Chem. Lett. 2005, 34, 624–629.
 (c) Furstner, A.; Leitner, A.; Mendez, M.; Krause, H. J. Am. Chem. Soc. 2002, 124, 13856–13863.
- (16) Buchwald, S. L.; Bolm, C. Angew. Chem., Int. Ed. 2009, 48, 0000.
- (17) (a) Klinker, E. J.; Shaik, S.; Hirao, H.; Que, L. Angew. Chem., Int. Ed. **2009**, 48, 1291–1295. (b) Dhuri, S. N.; Seo, M. S.; Lee, Y. M.; Hirao, H.; Wang, Y.; Nam, W.; Shaik, S. Angew. Chem., Int. Ed. **2008**, 47, 3356–
- 3359.
 (18) De Angelis, F.; Jin, N.; Car, R.; Groves, J. T. *Inorg. Chem.* 2006,
- 45, 4268–4276.
- (19) For elucidation of catalysis involving le⁻ changes, see: Poli, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 5058–5070.
- (20) Volpe, E. C.; Wolczanski, P. T.; Lobkovsky, E. B. Organometallics 2010, 29, 364–377.
- (21) Bower, B. K.; Tennent, H. G. J. Am. Chem. Soc. 1972, 94, 2512–2513.
- (22) Byrne, E. K.; Theopold, K. H. J. Am. Chem. Soc. 1989, 111, 3887–3896.
- (23) Dimitrov, V.; Linden, A. Angew. Chem., Int. Ed. 2003, 42, 2631– 1633.
- (24) Carnes, M.; Buccella, D.; Chen, J. Y. C.; Ramirez, A. P.; Turro,

to support low-spin systems for a number of first-row transition metals.^{9–11} If this concept is to work within the framework of classic coordination compounds, ancillary ligands containing metal-carbon bonds must ultimately be protected from reacting, yet judiciously positioned to impart their intrinsically greater fields. Herein are described initial synthetic efforts directed at the metalation of oxazolinebased ligands as sp², aryl, C-based chelates.^{26–41} The structural diversity of oxazolines⁴² and the presence of complementary heteroatom donors^{43–48} present an attractive target toward the eventual preparation of multidentate ligands that can be sterically or conformationally modified for ancillary applications.

Results

Oxazoline Ligands. Scheme 1 illustrates the set of ligands examined to varying degrees in this study and shows their syntheses, which are literature-derived or contain minor modifications from published procedures. In all cases the 4,4-dimethyl-2-oxazolyl fragment was used because of the convenient NMR handle presented by its methyl groups, and its steric features. The cadmium acetate assisted condensation of 2,2-dimethyl-2-aminoethanol to benzonitrile⁴⁹ proved significantly superior to the uncatalyzed process, and the product 4,4-dimethyl-2-phenyloxazoline (**HPhOx**, 80%) could

- (26) (a) Nishiyama, H.; Ito, J. Chem. Commun. 2010, 46, 203–212.
 (b) Nishiyama, H. Chem. Soc. Rev. 2007, 36, 1133–1141.
- (27) Denmark, S. E.; Stavenger, R. A.; Faucher, A.-M.; Edwards, J. P. J. Org. Chem. **1997**, *62*, 3375–3389.
- (28) Stark, M. A.; Jones, G.; Richards, C. J. Organometallics 2000, 19, 1282–1291.
- (29) Fossey, J. S.; Richards, C. J. J. Organomet. Chem. 2004, 689, 3056–3059.
- (30) Fossey, J. S.; Richards, C. J. *Organometallics* **2004**, *23*, 367–373. (31) Stol, M.; Snelders, D. J. M.; Godbole, M. D.; Havenith,
- R. W. A.; Haddleton, D.; Clarkson, G.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. Organometallics 2007, 26, 3985–3994.
- (32) Davies, D. L.; Al-Duaij, O.; Fawcett, J.; Giardiello, M.; Hilton, S. T.; Russell, D. R. *Dalton Trans.* **2003**, 4132–4138.
- (33) Davies, D. L.; Al-Duaij, O.; Fawcett, J.; Singh, K. Organometallics 2010, 29, 0000.
- (34) Wehman, E.; van Koten, G.; Jastrzebski, J. T. B. H.; Rotteveel,
 M. A.; Stam, C. H. Organometallics 1988, 7, 1477–1485.
- (35) Djukic, J.-P.; Michon, C.; Heiser, D.; Kyritsakas-Gruber, N.; De Cian, A.; Doetz, K. H.; Pfeffer, M. *Eur. J. Inorg. Chem.* **2004**, *10*, 2107–2122.
- (36) Bonnardel, P. A.; Parish, R. V.; Pritchard, R. G. J. Chem. Soc., Dalton Trans. 1996, 15, 3185–3193.
- (37) Giri, R.; Chen, X.; Yu, J.-Q. Angew. Chem., Int. Ed. 2005, 44, 2112–2115.
- (38) Chen, X.; Li, J.-J.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. J. Am. Chem. Soc. 2006, 128, 78–79.
- (39) Yuan, K.; Zhang, T. K.; Hou, X. L. J. Org. Chem. 2005, 70, 6085–6088.
- (40) Neal, S. R.; You, J.; Ellern, A.; Sadow, A. D. Polyhedron 2010, 29, 544–552.
- (41) Krumper, J. R.; Gerisch, M.; Suh, J. M.; Bergman, R. G.; Tilley, T. D. J. Org. Chem. 2003, 68, 9705–9710.
- (42) Gant, T. G.; Meyers, A. I. Tetrahedron Lett. 1994, 50, 2297-2360.
- (43) Inagaki, T.; Phong, L. T.; Furuta, A.; Ito, J.; Nishiyama, H. Chem.—Eur. J. 2010, 16, 3090–3096.
- (44) Tondreau, A. M.; Darmon, J. M.; Wile, B. M.; Floyd, S. K.; Lobkovsky, E.; Chirik, P. J. Organometallics **2009**, *28*, 3928–3940.
- (45) Zhang, M.; Gao, R.; Hao, X.; Sun, W.-H. J. Organomet. Chem. 2008, 693, 3867–3877.
- (46) Ferro, R.; Milione, S.; Bertolasi, V.; Capacchione, C.; Grassi, A. *Macromolecules* **2007**, *40*, 8544–8546.
- (47) Guillemot, G.; Neuburger, M.; Pfaltz, A. Chem.-Eur. J. 2007, 13, 8960-8970.
- (48) Godbole, M. D.; Puig, M. P.; Tanase, S.; Kooljman, H.; Spek, A. L.; Bouwman, E. *Inorg. Chim. Acta* **2007**, *360*, 1954–1960.
- (49) Kumar, S.; Kandasamy, K.; Singh, H. B.; Butcher, R. J. New J. Chem. 2004, 28, 640–645.

⁽¹⁴⁾ de Meijere, A. Chem. Rev. 2000, 100, 2739-2740.



Scheme 1



be directly lithiated to afford LiPhOx (80%).⁵⁰ The latter had only modest stability at room temperature and was routinely generated in situ when desired. Phenylacetic acid underwent condensation with 2,2-dimethyl-2-aminoethanol without the need for a catalyst to provide 4,4-dimethyl-2-benzyloxazoline (PhCH₂Ox).⁵¹ While 2-phenyl-2-methylpropionic acid could be purchased, synthesis of the o-Br derivative required sequential methylation of 2-o-bromophenylethanoic acid.⁵² Conversion to the acid chloride prior to condensation with 2,2-dimethyl-2-aminoethanol was done after several condensation attempts with 2-o-bromophenylethanoic acid failed. The acid chloride of the o-Br and parent compound were used to prepare the amide,53

which was then cyclized with the aid of base to generate the 4,4-dimethyl-2-(2-phenylpropan-2-yl)oxazoline (HPhCMe₂Ox) ligand precursor or its o-Br analogue (BrPhCMe₂Ox).⁵⁴ The latter could be lithiated at -78 °C to LiPhCMe₂Ox, but this species proved unstable upon warming (vide infra).

4,4-Dimethyl-2-phenyloxazoline. 1. Metalation Attempts. Previous efforts in utilizing heterolytic CH bond activation to generate an aryl-metal bond from 2-phenylpyridine were modestly successful,⁵⁵ but efforts to employ first-row transition metal halides and triflates in a similar vein with 4,4-dimethyl-2-phenyloxazoline (HPhOx) proved futile. Since direct lithiation to afford LiPhOx was successful, this reagent was utilized in metatheses with various first-row transition metal halides. Furthermore, LiPhOx was used to prepare two zinc reagents: the bis-phenyloxazoline derivative Zn(κ-C,N-4,4-Me₂-2-(o-C₆H₄)oxazoline)₂

⁽⁵⁰⁾ Astley, S. T.; Stephenson, G. R. Svnlett. 1992, 6, 507-509.

⁽⁵¹⁾ Marshall, L. J.; Roydhouse, M. D.; Slawin, A. M. Z.; Walton, J. C. J. Org. Chem. 2007, 72, 898-911.

⁽⁵²⁾ Beak, P.; Kerrick, S. T.; Gallagher, D. J. J. Am. Chem. Soc. 1993, 115, 10628-10636.

⁽⁵³⁾ Yuan, K.; Zhang, T. K.; Hou, X. L. J. Org. Chem. 2005, 70, 6085-6088.

⁽⁵⁴⁾ Evans, D. A.; Peterson, G. S.; Johnson, J. S.; Barnes, D. M.; Campos, K. R.; Woerpel, K. A. J. Org. Chem. **1998**, 63, 4541–4544. (55) Volpe, E. C.; Chadeayne, A. R.; Wolczanski, P. T.; Lobkovsky,

E. B. J. Organomet. Chem. 2007, 692, 4774-4783.

 $(Zn(PhOx)_2)^{50,56}$ and the oxazoline chloride species "ClZn-(κ -C,N-4,4-Me_2-2-(o-C₆H₄)oxazoline)" (ClZnPhOx), which, in THF, could be construed as dimeric or a THF adduct, as Scheme 2 illustrates.

First-row transition metal chlorides MCl_2 (M = Mn, Fe, Co) were chosen as an initial survey group to see whether the lithium or zinc reagents could be effective metalation agents. As Scheme 2 reveals, neither the lithium nor the zinc compounds proved to be useful in the set of reactions conducted. While paramagnetic products, some crystalline, were obtained, the material was isolated in low yields («50%), and the coupled dimer of 4,4-dimethyl-(2-o-C₆H₄)-2-oxazoline was identified in solution by ¹H NMR spectral comparisons.⁵⁷ A blue-green crystal from the cobalt reaction was subjected to single-crystal X-ray analysis, and, as suspected, the species was identified as the N,N-adduct of {4,4-Me₂-(2-o-C₆H₄)-2-oxazoline}₂, [κ -N,N-{4,4-Me₂-(2-o-C₆H₄)-2-oxazoline}₂]CoCl₂ (1-Co). Apparently, metalation and reductive elimination, or electron transfer and coupling, generated the organic dimer, which was then scavenged by remaining CoCl₂ in solution. Although the conditions were varied, direct metalation with these reagents (and other MX_2) seemed remote, and the approach was abandoned without further assay of the Mn and Fe materials.

2. Structure of $[\kappa - N, N - \{4, 4 - Me_2 - (2 - o - C_6H_4) - 2 - oxazoline\}_2]$ CoCl₂ (1-Co). Figure 2 illustrates one of the two [κ -N,N-(2-o-C₆H₄-4,4-Me₂-2-oxazolyl)₂]CoCl₂ (1-Co) molecules in the asymmetric unit, and Table 1 lists crystallographic and refinement parameters. Despite the modest data quality, the structure serves its purpose by revealing the oxidatively coupled κ -N,N-(2-o-C₆H₄-4,4-Me₂-2-oxazolyl)₂ group bound to the Co via the nitrogens of the oxazolines.⁵⁸ Average CoN and CoCl bond lengths of 2.044(6) and 2.241(16) Å, respectively, are within reason for a pseudotetrahedral Co(II) center. There are modest variations in the angles about the two independent molecules. While the NCoN and ClCoCl angles average 118.4(3)° and 114.6(6)°, respectively, the sets of NCoCl angles reveal deviations: N1Co1Cl1,2 = $103.13(12)^{\circ}$, $109.98(11)^{\circ}$, N2Co1Cl1,2 = $108.25(12)^{\circ}$, $102.35(12)^{\circ}$, $N3Co2Cl_{3,4} = 106.07(12)^{\circ}, 109.98(12)^{\circ}, N4Co2Cl_{3,4} =$ $108.01(12)^\circ$, $100.72(12)^\circ$. The differences merely reflect the ease of distortion in weak field, tetrahedral complexes and are of little consequence. The molecular C_2 symmetry of each unit derives from the twist of the κ -N,N-(2-o-C₆H₄-4,4-Me₂-2-oxazolyl)₂ group, which possesses oxazolyl-phenyl N-C-C-C and phenyl-phenyl C-C-C-C dihedral angles of roughly 60° and 116°, respectively.

4,4-Dimethyl-2-benzyloxazoline: Metalation Attempts. The preceding efforts suggested that the bite angle of the potential chelate κ -*C*,*N*-4,4-dimethyl-2-(*o*-phenyl)oxazoline (**PhOx**) may be too small, thereby promoting reductive elimination. Next, the 4,4-dimethyl-2-benzyloxazoline (**PhCH₂Ox**) ligand precursor was assayed for heterolytic CH bond activation with various metal halides and species containing ligands of greater basicity such as Fe{N(SiMe₃)₂}₂(THF) and Fe{N(SiMe₃)₂}₃.⁵⁹ While color changes to orange and yellow solutions, respectively, were evident, protolytic quenches of the material returned intact **PhOx**, and the protons of the benzyl unit were suspect.

(57) Nagano, T.; Hayashi, T. Org. Lett. 2005, 7, 491–493.



Figure 2. Molecular view of one of the two independent molecules of $[\kappa$ -N,N-{4,4-Me₂-(2-o-C₆H₄)-2-oxazoline}₂]CoCl₂ (1-Co; molecule containing Co2 is not shown). Pertinent interatomic distances (Å) and angles (deg) and similar parameters in the Co2 molecule: Co1N1,N2, 2.042(4), 2.045(4); Co2N3,N4, 2.037(4), 2.052(4); Co1Cl1,Cl2, 2.2380(16), 2.2569(16); Co2Cl3,Cl4, 2.2189(15), 2.2486(16); N1C3,Cl, 1.272(6), 1.495(6); N2C16,C18, 1.281(6), 1.505(6); N3C25,C23, 1.275(6), 1.490(6); N4C38,C40, 1.296(6), 1.503(6); N1Co1N2, 118.61(15); N3Co2N4, 118.12(16); Cl1Co1Cl2, 115.05(6); Cl3Co2Cl4, 114.23(6); N1Co1Cl1,Cl2, 103.13(12), 109.98(11); N2Co1Cl1,Cl2, 108.25(12), 102.35(12); N3Co2Cl3,Cl4, 106.07(12), 109.98(12); N4Co2Cl3,Cl4, 108.01(12), 100.72(12). Pertinent torsional angles (deg): N1C3C4C9, 60.3(7); N3C25C26C31, 63.9(7); C4C9C10C15, 119.2(7); C26C31C32C37, 113.6(7); N2C16C15C10, 59.9(2); N4C38C37C32, 59.3(7).

o-Metalation of the phenyl group to give traditional anionic equivalents of 4,4-dimethyl-2-(*o*-MC₆H₄CH₂)oxazoline, where M = Li, MgX, or ZnX/R, is prevented due to the acidity of these protons. Transition metal bases may react in a similar vein.

In order to test these suspicions with a starting material that would likely afford a diamagnetic product, $Ti(NMe_2)_4^{60}$ was treated with **PhCH₂Ox** according to eq 1. Intact phenyl resonances and a singlet corresponding to the lone vinylic H at δ 5.81 accompanied methyl singlets in a 12:6:6 H ratio in the ¹H NMR spectrum of the product, consistent with (Me₂N)₃Ti(η -N-(4,4-dimethyl-2-oxazoline)) (2). As a



check on the spectral assignments, the known⁶¹ 2-pyridyl equivalent of PhCH₂Ox, 2-pyCH₂Ox, was treated with half

⁽⁵⁶⁾ Berman, A. M.; Johnson, J. S. J. Org. Chem. 2006, 71, 219-224.

⁽⁵⁸⁾ For an interesting structural comparison, see: Kermagoret, A.; Braunstein, P. *Dalton Trans.* **2008**, 585–587.

⁽⁵⁹⁾ Olmstead, M. M.; Power, P. P.; Shoner, S. C. *Inorg. Chem.* **1991**, *30*, 2547–2551.

⁽⁶⁰⁾ Bradley, D. C.; Thomas, I. M. J. Chem. Soc. 1960, 3857-3861.

⁽⁶¹⁾ Fryzuk, M. D.; Jafarpour, L.; Rettig, S. J. *Tetrahedron: Asymmetry* **1998**, *9*, 3191–3202.

Table 1. Crystallographic Data for $[\kappa-N,N-(o-C_6H_4-4,4-Me_2-2-oxazolyl)_2]CoCl_2$ (1-Co), $[\{\kappa-N,O-C_6H_4CMe_2C=NCMe_2CH_2(\mu-O)-\}]$
$BrFe\{\kappa-N, O-C_{6}H_{4}CMe_{2}C = NCMe_{2}CH_{2}(\mu-O)-\}FeBr]Li\{\kappa-N, O-C_{6}H_{4}CMe_{2}C = NCMe_{2}CH_{2}(\mu-O)-\}(DME) (5-Fe_{2}Li), [\{\kappa-C, N-\{(o-C_{6}H_{4}CMe_{2}C = NCMe_{2}CH_{2}(\mu-O)-\}(DME) (5-Fe_{2}Li), [\{\kappa-C, N-\{(o-C_{6}H_{4}CMe_{2}CH_{2}(\mu-O)-1), [\{\kappa-C, N-\{(o-C_{6}H_{4}CMe_{2}CH_{2}(\mu-O)-1), [\{\kappa-C, N-\{(o-C_{6}H_{4}CMe_{2}CH_{2}(\mu-O)-1), [\{\kappa-C, N-\{(o-C_{6}H_{4}CMe_{2}CH_{2}(\mu-O)-1), [\{\kappa-$
$CMe_2(COCH_2C-Me_2N)$ Cr] ₂ (μ -Cl) ₂ (6 ₂), and { κ -C,N-{(ρ -C ₆ H ₄)CMe ₂ (COCH ₂ CMe ₂ N)} Fe(py)Cl (7)

	1- Co ^{<i>a</i>}	5-Fe ₂ Li	6 ₂ ^b	7^{c}
formula	C ₂₂ H ₂₄ N ₂ O ₂ Cl ₂ Co	C ₅₀ H ₇₂ N ₃ O ₇ Br ₂ Fe ₂ Li	C ₂₈ H ₃₆ N ₂ O ₂ Cl ₂ Cr ₂	C ₂₂ H ₂₆ N ₂ OClFe
fw	478.29	1105.59	607.49	425.75
space group	$P2_1/n$	$P\overline{1}$	$P2_{1}/c$	$P2_{1}/c$
Ż	8	2	2	4
a, Å	15.555(3)	13.7059(10)	6.9943(10)	15.8720(7)
b, Å	10.169(2)	14.3972(10)	26.459(4)	9.0323(4)
<i>c</i> , Å	28.108(6)	15.3609(11)	8.1697(11)	15.5493(8)
α, deg	90	68.213(3)	90	90
β , deg	90.88(3)	84.999(4)	104.974(5)	109.904(3)
γ , deg	90	75.078(4)	90	90
$V, Å^3$	4445.8(15)	2719.6(3)	1460.6(4)	2096.00(17)
$\rho_{\rm calc}, {\rm g} {\rm cm}^{-3}$	1.429	1.350	1.381	1.349
μ , mm ⁻¹	1.033	2.051	0.954	0.860
temp, K	173(2)	173(2)	203(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
R indices $[I > 2\sigma(I)]^{d,e}$	$R_1 = 0.0532$	$R_1 = 0.0639$	$R_1 = 0.0534$	$R_1 = 0.0530$
	$wR_2 = 0.1027$	$wR_2 = 0.1732$	$wR_2 = 0.1344$	$wR_2 = 0.1408$
<i>R</i> indices (all data) ^{<i>d</i>,<i>e</i>}	$R_1 = 0.1215$	$R_1 = 0.1196$	$R_1 = 0.0798$	$R_1 = 0.0774$
	$wR_2 = 0.1143$	$wR_2 = 0.2031$	$wR_2 = 0.1499$	$wR_2 = 0.1561$
GOF ^f	0.979	1.037	1.052	1.048

^{*a*} Two molecules in the asymmetric unit. ^{*b*} One-half of the dimer in the asymmetric unit. ^{*c*} Asymmetric unit contains 1/2 of a C₆H₆ molecule. ^{*d*} R₁ = $\sum ||F_o| - |F_c|| / \sum |F_o| - |F_c| / \sum |F_o| - |F_o| / \sum$

an equivalent of $Fe\{N(TMS)_2\}(THF)^{59}$ in the hope of making a related bis-chelate according to eq 2. A cherry red solution occurred immediately in benzene- d_6 , and the ¹H NMR spectrum revealed free HN(TMS)₂ and resonances of paramagnetic material tentatively assigned to bis-N,N'-(4,4-dimethyl-(2-pyridylmethylyl)oxazoline)Fe (3), including diastereotopic methyl and methylene signals. Forays with Ti and Fe into utilization of the oxazoline with the methylene backbone were convincing enough with respect to CH₂ deprotonation that **PhCH₂Ox** was abandoned as a prospective ligand.

4,4-Dimethyl-2-(2-phenylpropan-2-yl)oxazoline. 1. Oxidative Addition Attempts with BrPhCMe₂Ox. Heterolytic ArH bond activation attempts with 4,4-dimethyl-2-(2-phenylpropan-2-yl)oxazoline (**HPhCMe₂Ox**) and various metal halides and triflates did not yield tractable products; often starting material was recovered. Oxidative addition of 4,4-dimethyl-2-(2-(2-Brphenyl)propan-2-yl)oxazoline (**BrPhCMe₂Ox**) to the prototypical metal reagent, Ni(COD)₂,⁶² in toluene afforded [{ κ -*C*, *N*-(*o*-C₆H₄)CMe₂(COCH₂CMe₂N)}Ni]₂(μ -Br)₂ (**4**₂) in 80% yield as a dark pink solid (eq 3). The compound was



sparingly soluble in toluene, THF, or CH₂Cl₂, but dissolved in acetonitrile to give yellow-orange solutions. It is likely that the purported dimer, **4**₂, is cleaved to give { κ -C,N-(o-C₆H₄)CMe₂(CO-CH₂CMe₂N)}NiBr(NCMe) (**4**-NCMe) and that the spectral characterization in acetonitrile- d_3 is of this diamagnetic derivative.

Attempts to induce oxidative addition of **BrPhCMe₂Ox** to FeX₂ (X = Cl, Br) through disproportionation of the iron species—a method that was used with modest success in these laboratories⁶³—failed in this instance. While material

tentatively formulated as simple nitrogen adducts, " $\{(o-C_6H_4)-CMe_2(COCH_2CMe_2N)\}_2FeX_2$ ", was isolated, subsequent reductions failed to elicit tractable products.

2. Metathesis Attempts with LiPhCMe₂Ox. While utilization of BrPhCMe₂Ox as a ligand precursor via oxidative addition is limited by choice of metal starting materials, especially if carbonyl complexes, etc., are to be avoided because of potential reactivity at the metal–carbon bond targeted, anion equivalents are typically more versatile. As delineated above, 4,4dimethyl-2-(2-(2-Li-phenyl)propan-2-yl)oxazoline (LiPhCMe₂Ox) was prepared upon lithiation of the corresponding bromide for use in metathesis reactions.

When LiPhCMe₂Ox was generated in THF at -78 °C, then warmed to 23 °C, the lithium reagent apparently rearranged to a benzocyclobutanimine via internal attack at the oxazoline C=N bond, followed by oxazoline C-O bond opening to ultimately produce the alkoxide, C₆H₄[CMe₂C=N]- $CMe_2CH_2OLi(THF)_n$. When cooled back to -78 °C and treated with FeBr₂, the alkoxide was trapped via metathesis and the product that crystallized from DME was identified as the mustard-yellow trinuclear complex [$\{\kappa - N, O - C_6 H_4 C M e_2 C =$ NCMe₂CH₂(μ -O)-}BrFe{ κ -N,O-C₆H₄CMe₂C=NCMe₂CH₂- $(\mu$ -O)-}FeBr]Li{ κ -N,O-C₆H₄CMe₂-C=NCMe₂CH₂(μ -O)-}-(DME) (5-Fe₂Li), as shown in Scheme 3. When held at -78 °C for 3 h, the lithiation reaction does produce LiPhCMe₂Ox, which was used in metathesis with ZnCl₂ to afford the zinc reagent (PhCMe₂Ox)₂Zn in 78% yield. Apparently reaction with $ZnCl_2$ occurs swiftly enough at -78 °C such that rearrangement of the lithium reagent does not interfere with chloride displacement. In order to avoid rearrangement complications, (PhCMe₂Ox)₂Zn was exploited as a metathesis reagent.

3. Structure of $5\text{-Fe}_2\text{Li}$. Information about the data collection and crystal refinement is given in Table 1, and a molecular view of $5\text{-Fe}_2\text{Li}$ is given in Figure 3 along with pertinent core distances and angles. The structure serves to confirm the intramolecular benzocyclobutanimine formation, as two such entities chelate the irons and a third chelates the lithium. The pseudotetrahedral iron centers possess distances expected for Fe(II), and the cores are distorted primarily

⁽⁶²⁾ Krysan, D. J.; Mackenzie, P. B. J. Org. Chem. 1990, 55, 4229–4230.

⁽⁶³⁾ Frazier, B. A.; Wolczanski, P. T.; Lobkovsky, E. B. Inorg. Chem. 2009, 131, 11576–11585.

Scheme 3





Figure 3. Structure of 5-Fe₂Li with solvent molecules removed. Only those atoms of the bound DME that were not severely disordered are shown. Distances (Å) and angles (deg) pertaining to the metal cores: Fe1Br1, 2.4085(7); Fe2Br2, 2.4469(7); Fe1O1, 1.909(3); Fe1O2, 2.009(2); Fe2O2, 1.924(3); Fe2O3, 1.929(3); Fe1N2, 2.125(3); Fe2N3, 2.122(3); Li1O1, 1.966(7); Li1O3, 1.915(7); Li1O4, 1.992(9); Li1N1, 2.112(7); O1Fe1O2, 111.89(11); O1Fe1N2, 116.35(12); O2Fe1N2, 80.74(11); O1Fe1Br1, 118.13(8); O2Fe1Br1, 110.08(8); N2Fe1Br1, 113.49(9); O2Fe2O3, 116.61(11); O2Fe2N3, 124.91(12); O3Fe2N3, 82.40(12); O2Fe2Br2, 108.84(8); O3Fe2Br2, 117.20(9); N3Fe2Br2, 105.05(8); O1Li1O3, 109.0(3); O3Li1O4, 111.6(3); O1Li1O4, 115.3(4); O3L11N1, 117.2(3); O1Li1N1, 85.6(2); O4Li1N1, 115.7(3); Fe1O1Li1, 121.5(2); Li1O3Fe2, 116.1(2); Fe1O2Fe2, 119.75(13).

via the chelate bite angles of the alkoxyimine ligand, which are 80.74° (11, Fe1) and 82.40° (12, Fe2).

4. Metathesis Attempts with (PhCMe₂Ox)₂Zn. Rearrangement issues that surfaced during the employment of LiPhC-Me₂Ox were obviated through utilization of the zinc reagent (PhCMe₂Ox)₂Zn, but a curious problem remained. Treatment of chromous chloride as its THF adduct⁶⁴ with any number of equivalents of (PhCMe₂Ox)₂Zn resulted in the transfer of only one aryl oxazoline to form the purple dimer $[\{\kappa - C, N - (o - C_6H_4)CMe_2(COCH_2CMe_2N)\}Cr]_2(\mu - Cl)_2(\mathbf{6}_2)$ in 40% yield upon crystallization from hot benzene. Solubility in nonpolar solvents hampered ¹H NMR spectral characterization of the dimer: hence its structure was determined by X-ray crystallography. The dimer readily dissolved in THF, but the observed paramagnetic spectral features are best construed as those of the turquoise THF adduct { κ -C,N-(o-C₆H₄)CMe₂(COCH₂CMe₂N){CrCl(THF) (6-THF). Squareplanar Cr(II) compounds are relatively common, and 6_2 and 6-THF are clear examples.^{65–69} Room-temperature Gouy balance measurement of the susceptibility of 6_2 afforded a $\mu_{\rm eff}$ of 5.0 $\mu_{\rm B}$ for the dimer. A $\mu_{\rm eff}$ of 6.9 would be expected for Cr(II) centers that were noninteracting, and a value of 8.9 would represent fully coupled Cr(II) cores; hence modest antiferromagnetic coupling is probable.^{65–68} The THF adduct 6-THF yielded a μ_{eff} of 4.9 in solution as measured by Evans' method, consistent with a normal high-spin S = 2configuration. All attempts to transfer an additional oxazoline unit to 6-THF with (PhCMe₂Ox)₂Zn failed, with recovery of starting material at low temperatures and evidence of reduction at higher temperatures. Other anion equivalents, e.g., LiPhCMe₂Ox, whose rearrangement is a probable interference, have also failed to yield tractable products thus far.

The addition of 1 equiv of (**PhCMe₂Ox**)₂**Zn** to FeCl₂(py)₄¹⁰ failed to transfer both oxazoline anion equivalents, but yielded, upon crystallization from benzene, yellow { κ -C,N-{(o-C₆H₄)-CMe₂(COCH₂CMe₂N)}Fe(py)Cl (7, 50%), which was structurally characterized by X-ray crystallography. ¹H NMR spectroscopic investigations of the product mixture revealed a diamagnetic byproduct, presumably [ZnCl(ArOx)]₂, and the paramagnetic product. An Evans' method measurement of **7** provided a μ_{eff} of 4.7 μ_{B} , consistent with an S = 2 center

⁽⁶⁴⁾ Kern, R. J. J. Inorg. Nucl. Chem. 1962, 24, 1105–1109.

⁽⁶⁵⁾ Sydora, O. L.; Wolczanski, P. T.; Lobkovsky, E. B.; Buda, C.; Cundari, T. R. *Inorg. Chem.* **2005**, *44*, 2606–2618.

 ⁽⁶⁶⁾ Sydora, O. L.; Kuiper, D. S.; Wolczanski, P. T.; Lobkovsky,
 E. B.; Dinescu, A.; Cundari, T. R. *Inorg. Chem.* 2006, 45, 2008–2021.

⁽⁶⁷⁾ Edema, J. J. H.; Gambarotta, S.; van Bolhuis, F.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1989**, *28*, 1407–1410.

⁽⁶⁸⁾ Edema, J. J. H.; Gambarotta, S.; van Bolhuis, F.; Spek, A. L. J. Am. Chem. Soc. 1989, 111, 2142–2147.

⁽⁶⁹⁾ Terry, K. W.; Gantzel, P. K.; Tilley, T. D. Inorg. Chem. 1993, 32, 5402–5404.

⁽⁷⁰⁾ Golding, R. M.; Mok, K. F.; Duncan, J. F. *Inorg. Chem.* **1966**, *5*, 774–778.



with little orbital contribution. Attempts to put two oxazolines on iron have met with some resistance. A new set of paramagnetic resonances arises when **7** is treated with **LiPhCMe₂Ox** that was generated *in situ*, and the same set is observed when FeBr₂(THF)₂⁷¹ is exposed to 2 equiv of **LiPhCMe₂Ox** (*in situ*). The ¹H NMR spectrum revealed four broad 3H singlets consistent with two sets of diastereotopic CMe₂ units. A quench of the material (C₆H₆/H₂O) derived from **7** afforded **HPhCMe₂Ox**, but no py; hence it is tentatively formulated as { κ -C,N-(o-C₆H₄)CMe₂(COCH₂CMe₂N)}₂Fe (**8**) based on ¹H NMR shifts comparable to **7**.

In one instance, 1 equiv of (PhCMe₂Ox)₂Zn has successfully been utilized to transfer both oxazolines. Treatment of $NiCl_2(DME)^{72}$ with (PhCMe₂Ox)₂Zn generated pale orange, diamagnetic { κ -C,N-(o-C₆H₄)CMe₂(COCH₂CMe₂N)}₂Ni (9) in modest yield (25%) upon crystallization from an ether/ THF mixture. Its NMR spectra indicated that both CMe₂ groups and the CH₂ on the oxazoline have diastereotopic substituents; hence the molecule is illustrated as having a rippled structure⁵⁵ that deviates from a simple square-planar arrangement. Attempts to observe coalescence of the diastereotopic protons were thwarted by decomposition at 80 °C, but since ready exchange was not seen, it is likely that a simple turnstile exchange of the two oxazolines is not evident, perhaps due to the steric interactions when an oxazoline CMe₂ group swings past the phenyl of the other ligand. In addition, a turnstile process would require the intermediacy of a pseudosquare-planar intermediate of significantly higher energy.

5. Structure of $[\{\kappa-C, N-(o-C_6H_4)CMe_2(COCH_2CMe_2N)\}$ -Cr]₂(μ -Cl)₂ (6₂). The molecular structure of $[\{\kappa-C, N-(o-C_6H_4)-CMe_2(COCH_2CMe_2N)\}Cr]_2(\mu$ -Cl)₂ (6₂) is illustrated in Figure 4, while pertinent details of the data collection are listed in Table 1. The chromiums are at 3.5369(9) Å from each other, which is a distance that can accommodate antiferromagnetic coupling interactions. The molecule possesses C_i symmetry, which is also observed crystallographically, such that both halves are equivalent. The remainder of the core is quite regular, with all angles within 5° of 90°, and the bond



Figure 4. Molecular view of $[\{\kappa-C, N-(o-C_6H_4)CMe_2(COCH_2-CMe_2N)\}Cr]_2(\mu-Cl)_2$ (62). Distances (Å) and angles (deg) of the core: Cr1Cr1A, 3.5369(9); Cr1N1, 2.071(3); Cr1C10, 2.091(4); Cr1Cl1, 2.4362(13); Cr1Cl1A, 2.3638(13); N1Cr1C10, 87.20(14); N1CrCl, 93.82(10); N1Cr1Cl1A, 173.58(11); C10CrCl1, 171.55(12); C10CrC1A, 94.82(11); C11CrCl1A, 85.08(4); Cr1Cl1Cr1A, 94.92(4).

distances listed in the caption of Figure 4 reveal no surprises for a standard Cr(II) square-planar system.^{65–69} Note that the sp³ center of the CMe₂ unit spanning the Ph and oxazoline portions of the ligand gives the bidentate chelate a "fold", such that one CMe₂ group is below the square plane and the C_r related CMe₂ unit on the adjacent half of the dimer is above it.

6. Structure of { κ -*C*,*N*-(o-C₆H₄)CMe₂(COCH₂CMe₂N)}-Fe(py)Cl (7). Figure 5 illustrates the molecular skeleton of { κ -*C*,*N*-(o-C₆H₄)CMe₂(COCH₂CMe₂N)}Fe(py)Cl (7), and the parameters affiliated with data collection and refinement are given in Table 1. While the bond distances of the core listed in the caption of Figure 5 are normal, the angles of the core reveal a significant distortion from tetrahedral geometry. The bite angle of the chelate is 95.73(13)°, significantly larger than the 87.20(14)° angle it exhibits in the structure of the chromium(II) dimer, **6**₂, but still less than the 109.5° expected for tetrahedral coordination. The Cl–Fe–C angle

⁽⁷¹⁾ Ittel, S. D.; English, A. D.; Tolman, C. A.; Jesson, J. P. Inorg. Chim. Acta 1979, 33, 101–106.

⁽⁷²⁾ Ward, L. G. Inorg. Synth. 1971, 13, 154-164.



Figure 5. Molecular view of { κ -*C*,*N*-(o-C₆H₄)CMe₂(COCH₂-CMe₂N)}Fe(py)Cl (7). Distances (Å) and angles (deg) of the core: Fe1C1, 1.984(4); Fe1N1, 2.053(3); Fe1N2, 2.090(3); Fe1C11, 2.2797(8); N1Fe1C11, 107.74(8); N1Fe1N2, 105.43(11); N1FeC1, 95.73(13); Cl1Fe1N2, 101.26(7); Cl1FeC1, 134.14(10); N2FeC1, 109.82(13).

is splayed to $134.14(10)^\circ$, while the Cl–Fe–N1 and –N2 angles of $107.74(8)^\circ$ and $101.26(7)^\circ$ are slightly less than the norm for a tetrahedron. The pyridine N2 is $105.43(11)^\circ$ from the N1 of the chelate and $109.82(13)^\circ$ from the C1 of the phenyl. So it appears that the CNNFe unit is roughly pyramidal, albeit with angles less than the tetrahedral norm, and the Cl is bent away from the phenyl and slightly toward the pyridine. The latter distortion does not correspond to an obvious steric interaction, but may alleviate some of the antibonding character of the d orbital that is highest in energy, which should be the one carrying the brunt of the Fe–C σ^* character.

7. Calculations on $\{\kappa - C, N - (o - C_6 H_4) CMe_2(COCH_2 - COCH_3)\}$ CMe_2N $_2Ni$ (9). Since suitable crystals for an X-ray analysis of $\{\kappa - C, N - (o - C_6H_4)CMe_2(COCH_2CMe_2N)\}_2Ni$ (9) were not obtained, a brief calculational study of the molecule was undertaken. As Figure 6 reveals, the optimized geometry of 9 is the expected distorted square-planar C_2 configuration: $d(\text{NiC}_{\text{ox}}) = 2.024 \text{ Å}, d(\text{NiC}_{\text{Ar}}) = 1.926 \text{ Å}, C_{\text{ox}}\text{NiC}_{\text{ox}} = 103.7^{\circ},$ $C_{Ar}NiC_{Ar} = 98.6^{\circ}$, bite angle $C_{ox}NiC_{Ar} = 94.1^{\circ}$. Despite the significant distortion from pseudo-square-planar geometry, the d orbital splitting diagram clearly reveals a "one over four", low-spin configuration that suggests the aryl-oxazoline is imparting a strong field, in accord with the premise of the project. While the $\Delta E = E(d_{x^2-y^2}) - E(d_{xz})$ gap of > 31 000 cm⁻ is probably an overestimation derived from the usual DFT problems in assessing the energies of virtual orbitals, the number is consistent with the diamagnetic nature of the complex and the strong field character of aryl ligands. The C_2 arrangement ensures that the two dimethyl fragments and the methylene group are diastereotopic, rendering four inequivalent methyls and inequivalent methylene protons. Attempts to locate the pseudo-square-planar intermediate that would allow the diastereotopic groups to become equivalent were not realized, but the square-planar species would not minimize; hence it is a plausible transition state for the rearrangement. It is also estimated to be > 30 kcal/mol above the ground-state structure, consistent with the NMR data.



Figure 6. Ligand field of $\{\kappa$ -*C*,*N*-(*o*-C₆H₄)CMe₂(COCH₂-CMe₂N) $\}_2$ Ni (9) generated via DFT calculations.

Discussion

The work described above illustrates many of the methods and accompanying pitfalls of utilizing the aryl-oxazoline ligands in complexing first-row transition metals. Heterolytic and other CH bond activations designed at complexation have thus far been unsuccessful, and potential fivemembered ring chelates suffered the fate of being oxidatively coupled by MX_2 starting materials, a common reaction. An increase in the ring size of the chelate demanded that the acidic CH₂ unit coupling the aryl with the oxazoline be exchanged for a CMe₂ group, since complexation accompanied by deprotonation was observed in test cases involving titanium and iron.

The { κ -C,N-(o-C₆H₄)CMe₂(COCH₂CMe₂N)} chelate was successfully utilized in the synthesis of several compounds containing Cr, Fe, and Ni. Aside from two diamagnetic examples involving nickel, the remaining compounds were not low spin. While this fact may seem discouraging in light of the proposed utilization of carbon-based ligands as progenitors of strong fields, the low coordination number compounds realized in this study present difficulties in assessing the project. For example, the d orbital splittings of $\{\kappa$ -C, $N-(o-C_6H_4)CMe_2(COCH_2CMe_2N)$ Fe(py)Cl (7) are intrinsically small because of pseudotetrahedral coordination and the presence of only one Fe-Ar bond. The fold of the ligand that is intrinsic to the sp³ nature of the CMe₂ linkage between phenyl and oxazoline units has consequences with regard to the orientation of the Ar and N donation; hence the chelate can vary its bite angle. This can be advantageous in adapting the best configuration for a particular metal, but the CMe₂ group may present a subtle steric problem for the addition of other { κ -C,N-{(o-C₆H₄)CMe₂(COCH₂CMe₂N)} units or other ligands. It was encouraging that the calculation of $\{\kappa$ -C,N-(o- C_6H_4)CMe₂(COCH₂CMe₂N) $\}_2$ Ni (9) revealed a ligand field splitting diagram consistent with that of a square-planar species, despite the severe C_2 distortion of the complex. Clearly the presence of two M–Ar bonds has a profound influence on the field about the metal, just as proposed. Efforts to introduce related oxazoline-based chelates into octahedral settings are ongoing.

Experimental Section

General Considerations. For metal complexes, manipulations were performed using either glovebox or high-vacuum techniques. Ligand syntheses were performed under argon using Schlenk techniques. Hydrocarbon and ethereal solvents were dried over and vacuum transferred from sodium benzophenone ketyl (with 3-4 mL of tetraglyme/L added to hydrocarbons). Methylene chloride was distilled from and stored over CaH₂. Benzene-d₆ and toluene- d_8 were sequentially dried over sodium and stored over sodium. THF- d_8 was dried over sodium benzophenone keyl. Acetonitrile- d_3 was dried over CaH₂ and stored over 4 A molecular sieves. The compounds 4,4-dimethyl-(2-benzyl)-oxazoline (**PhCH₂Ox**),⁵¹ Ti(NMe₂)₄,⁶⁰ Fe{N(TMS)₂}₂(THF),⁵⁹ Ni(COD)₂,⁶² FeBr₂(THF)₂,⁷¹ CrCl₂(THF),⁶⁴ FeCl₂(py)₄,⁷⁰ and NiCl₂(DME)⁷² were prepared according to literature procedures. SOCl₂ (Aldrich) was used immediately or distilled prior to use; NEt₃ (Aldrich) was dried and stored over 4 A molecular sieves; ZnCl₂ was dried according to a literature procedure;⁷³ all other reagents were purchased and used as received. All glassware was oven-dried.

¹H and ¹³C $\{^{1}H\}$ NMR spectra were obtained using Mercury-300, Inova-400, and Inova-500 spectrometers, and chemical shifts are reported relative to benzene- d_6 (¹H δ 7.16; ¹³C{¹H} δ 128.39), THF- d_8 (¹H δ 3.58; ¹³C{¹H} δ 67.57), acetonitrile- d_3 (¹H δ 1.94; $^{13}C{^{1}H} \delta 1.79$, and toluene- d_8 ($^{1}H \delta 2.09$; $^{13}C{^{1}H} \delta 20.40$). Solution magnetic measurements were conducted via Evans' method⁷⁴ in benzene- d_6 or toluene- d_8 . Solid-state magnetic measurements were performed using a Johnson Matthey magnetic susceptibility balance calibrated with HgCo(SCN)₄. Combustion analyses were performed by Robertson Microlit Laboratories, Madison, NJ, and by services at the University of Erlangen-Nuremberg, Germany. Difficulties in obtaining satisfactory and consistent values for the organometallic compounds were noted; those reported were obtained for the purest samples as determined from spectroscopic (principally NMR) methods.

Syntheses. 1. 4,4-Dimethyl-(2-pyridylmethyl)-2-oxazoline (2-pyCH₂Ox). To a solution of 2-pyridylacetonitrile⁷⁵ (440 mg, 3.72 mmol) and 2-amino-2-methylpropanol (663 mg, 7.45 mmol) in 10 mL of toluene was added 50 mg (0.186 mmol) of Cd(OAc)₂. 2H₂O. The mixture was allowed to reflux under argon for 10 h. After washing with H₂O, the crude mixture was extracted with CH₂Cl₂, dried over MgSO₄, filtered, and concentrated to a light brown oil. The crude oil was distilled under reduced pressure to yield a yellow oil (70%). ¹H NMR (400 MHz, benzene-*d*₆): δ 8.43 (d, 1H, *J* = 4), 7.12 (d, 1H, *J* = 8), 7.02 (t, 1H, *J* = 8), 6.56 (t, 1H, *J* = 6), 3.84 (s, 2H), 3.53 (s, 2H), 1.09 (s, 6H).

2. 4,4-Dimethyl-2-(2-arylpropan-2-yl)-2-oxazoline (aryl = Ph, HPhCMe₂Ox; 2-BrPh, BrPhCMe₂Ox). HPhCMe₂Ox has been synthesized previously.³⁸ Herein both HPhCMe₂Ox and BrPhCMe₂Ox were both synthesized via the following modified procedure. A 50 mL three-neck round-bottom flask fitted with a reflux condenser and external oil bubbler was flushed with argon and charged with 15 mL of SOCl₂. A 13 mmol amount of α , α -dimethylarylacetic acid (aryl = Ph, **a**; 2-BrPh, **b**) was added, and the solution heated to reflux for 3 h. The cooled mixture was then concentrated and triturated with CH₂Cl₂ (2 × 5 mL). The oily product was dissolved in 15 mL of CH₂Cl₂. A solution of 2-amino-2-methyl-1-propanol (1.39 g, 15.6 mmol) and NEt₃ (2.72 mL, 19.5 mmol) in 20 mL of CH₂Cl₂ was cooled to 0 °C. The acid chloride solution was added dropwise under argon. The reaction was allowed to warm slowly to 23 °C over 4 h and stirred for an addition 10 h. The mixture was washed first with H₂O (20 mL) then with brine (20 mL), and the organics were dried over MgSO₄, filtered, and concentrated. The crude product was recrystallized from 6:1 hexanes/ethyl acetate to yield a white, crystalline solid (90% after 3 crops).

A 10 mmol amount of the above amide, 4-(dimethylamino)pyridine (110 mg, 0.9 mmol), and NEt₃ (3.1 mL, 22 mmol) were dissolved in 30 mL of CH₂Cl₂. A solution of *p*-toluenesulfonyl chloride in 20 mL of CH₂Cl₂ was added via syringe under argon. After stirring at 23 °C for 2 days, the reaction mixture was diluted with CH₂Cl₂ and extracted with saturated NH₄Cl followed by aqueous NaHCO₃. The organic layer was dried over MgSO₄, treated with decolorizing carbon, filtered, and concentrated. The crude product was purified by flash chromatography (6:1 hexanes/ethyl acetate) to give a clear oil (65%). ¹H NMR (400 MHz, benzene-*d*₆): δ 7.45 (d, *J* = 8, 1H), 7.18 (d, *J* = 8.0, 1H), 6.93 (t, *J* = 8, 1H), 6.66 (t, *J* = 8, 1H), 3.63 (s, 2H), 1.72 (s, 6H), 1.19 (s, 6H). ¹³C NMR (400 MHz, benzene-*d*₆): δ 170.24, 144.75, 135.31, 128.59, 128.22, 127.81, 124.84, 79.82, 67.73, 42.86, 28.58, 27.94.

3. Zn(κ -C,N-4,4-Me₂-(o-C₆H₄)-2-oxazoline)₂ (Zn(PhOx)₂). LiPhOx (1.99 g, 10.98 mmol) and ZnCl₂ (0.75 g, 5.50 mmol) were added to a 100 mL round-bottom flask to which 50 mL of toluene was vacuum transferred at -78 °C. The mixture was stirred at -78 °C for \sim 4 h and allowed to warm to 23 °C over 10 h. After subsequent filtration and washing of the salt cake with toluene, the solvent was removed. The product was triturated (2 × 5 mL of pentane) and filtered in pentane, leaving a white solid (1.82 g, 80%). ¹H NMR (400 MHz, benzene- d_6): δ 8.07 (d, J = 7.2, 1H), 8.03 (d, J = 8.0, 1H), 7.44 (t, J = 7.2, 1H), 7.22 (t, J = 7.6, 1H), 3.73 (s, 2H), 0.86 (s, 6H). ¹³C NMR (500 MHz, benzene- d_6): δ 173.64, 168.30, 139.61, 135.29, 131.70, 128.68, 125.87, 125.45, 82.43, 65.13, 28.52. Anal. Calcd for C₂₂H₂₄-N₂O₂Zn: C, 63.95; H, 5.85; N, 6.77. Found: C, 63.60; H, 5.59; N, 6.75.

4. [κ - $N_{\gamma}N$ -{4,4-Me₂-(2-o-C₆H₄)-2-oxazoline}₂]CoCl₂ (1-Co). A 500 mg portion of LiPhOx (2.74 mmol) and 178 mg of CoCl₂ (1.37 mmol) were added to a 50 mL round-bottom flask to which ether (25 mL) was vacuum transferred at -78 °C. The reaction mixture was allowed to stir at -78 °C for 2 h, then warmed slowly to 23 °C over 10 h. The mixture was filtered in ether, stripped, triturated with hexanes (2 × 5 mL), and filtered to yield a blue-green solid (395 mg, 60%). X-ray diffraction quality crystals were grown from THF/hexanes. ¹H NMR (400 MHz, benzene- d_6): δ 7.61 (d, J = 8, 1H), 7.12 (m, 1H), 7.01 (t, J = 8, 1H), 6.81 (d, J = 8, 1H), 3.78 (s, 1H), 3.75 (s, 1H), 1.56 (s, 3H), 0.65 (s, 3H).

5. (NMe₂)₃Ti{ η -N-(4,4-Me₂-2-(CHPh)oxazolidine)} (2). A mixture of Ti(NMe₂)₄ (500 mg, 2.23 mmol) and PhCH₂Ox (423 mg, 2.23 mmol) in 20 mL of benzene was heated at 100 °C in a bomb reaction vessel for 7 days. The solvent was removed to obtain a redorange oil. Addition of diethyl ether (20 mL) led to precipitation of an orange solid, which was filtered and washed with ether (3 × 10 mL) to afford 240 mg (29%). ¹H NMR (400 MHz, benzene- d_6): δ 7.32 (t, 2H, J = 7), 7.21 (d, 2H, J = 7), 7.05 (t, 1H, J = 7), 5.81 (s, 1H), 4.13 (s, 2H), 3.14 (s, 12H), 2.55 (s, 6H), 1.30 (s, 6H). ¹³C{¹H} NMR (500 MHz, benzene- d_6): δ 158.85, 141.84. 128.92, 128.53, 123.66, 102.14, 85.82, 66.47, 46.35, 42.44, 26.84.

6. Bis{*N*,*N*-(4,4-dimethyl-(2-pyridylmethylyl)oxazoline)}Fe (3). A benzene-*d*₆ solution of Fe{N(TMS)₂}₂(THF) (20 mg, 0.045 mmol)

⁽⁷³⁾ Pray, A. R. Inorg. Synth. 1990, 28, 321-322.

 ^{(74) (}a) Evans, D. F. J. Chem. Soc. 1959, 2003–2005. (b) Schubert,
 E. M. J. Chem. Ed. 1992, 69, 62.

⁽⁷⁵⁾ Klapars, A.; Waldman, J. H.; Campos, K. R.; Jensen, M. S.; McLaughlin, M.; Chung, J. Y. L.; Cvetovich, R. J.; Chen, C. Y. J. Org. Chem. **2005**, 70, 10186–10189.

was added to **2-pyCH₂Ox** (17 mg, 0.089 mmol) in an NMR tube. Upon addition, the solution turned cherry red. ¹H NMR (400 MHz, benzene- d_6): δ 189.64 (s, 1H), 53.89 (s, 1H), 51.07 (s, 1H), 23.75 (s, 1H), 10.29 (s, 1H), -12.09 (s, 1H), -21.72 (s, 1H), -37.67 (s, 3H), -47.90 (s, 3H).

7. $[{\kappa - C, N - (o - C_6H_4)CMe_2(COCH_2CMe_2N)}Ni]_2(\mu - Br)_2$ (42). A solution of BrPhCMe₂Ox (108 mg, 0.365 mmol) in 5 mL of toluene was added to Ni(COD)₂ (100 mg, 0.365 mmol) at -78 °C. Warming slowly to room temperature led to the formation of a pink precipitate. After stirring at 23 °C for ~4 h, the resulting dark pink solid was isolated by filtration and washing several times with toluene (49 mg, 80%). The compound is only sparingly soluble in toluene, THF, or dichloromethane, but dissolves in acetonitrile to give an orange-yellow solution, which is presumably $\{\kappa$ -C,N-(o-C₆H₄)CMe₂(COCH₂CMe₂N) $\}$ NiBr-(NCMe) (4-NCMe). ¹H NMR (500 MHz, acetonitrile- d_3): δ 7.17 (br s, 1H), 6.89 (d, J = 5.5, 1H), 6.83 (t, J = 7.2, 1H), 6.72 (t, J =6.3, 1H), 4.01 (s, 2H), 2.43 (s, 6H), 1.38 (s, 6H). ¹³C NMR (500 MHz, acetonitrile-d₃): δ 179.13, 149.04, 143.95, 138.62, 124.76, 124.45, 123.10, 82.60, 68.62, 44.59, 28.94, 27.70 (see Supporting Information). Anal. Calcd for C₂₈H₃₆N₂O₂Ni: C, 47.38; H, 5.11; N, 3.95. Found: C, 46.92; H, 4.92, N, 3.70.

8. [{ κ -N,O-C₆H₄-CMe₂C=NCMe₂CH₂-(μ -O)}BrFe{ κ -N,O-C₆H₄-CMe₂C=NCMe₂CH₂(μ -O)}FeBr]Li{ κ -N,O-C₆H₄-CMe₂C=NCMe₂CH₂-(μ -O)}(DME) (5-Fe₂Li). ^{*n*}BuLi (0.21 mL, 1.6 M in hexanes) was added to a solution of BrPhCMe₂Ox (100 mg, 0.338 mmol) in 20 mL of THF at -78 °C under argon. This was allowed to warm over 4 h and was stirred for an additional hour at 23 °C. The solution was cooled to -78 °C, and FeBr₂(THF)₂ (61 mg, 0.169 mmol) added via addition finger. The reaction was kept at -78 °C for 4 h and then allowed to warm slowly to 23 °C. The reaction was filtered, stripped, triturated with pentane (2 × 5 mL), and filtered to give 67 mg of mustard-yellow solid (43%). Red, X-ray diffraction quality crystals were grown from a cold solution of DME.

9. (**PhCMe₂Ox**)₂**Zn.** ^{*n*}BuLi (0.42 mL, 1.6 M in hexanes) was added to a solution of **BrPhMe₂Ox** (200 mg, 0.676 mmol) in 40 mL of THF at -78 °C under argon. After 3 h at -78 °C, ZnCl₂ (46 g, 0.338 mmol) was added via addition finger. The reaction was kept at -78 °C for at least 4 h and warmed to 23 °C over 4 h. The reaction mixture was stripped, triturated with benzene, and filtered, and the salt cake washed several times (4 × 30 mL). The mixture was stripped and triturated with pentane, yielding 131 mg (78%) of white solid, which was collected by filtration. ¹H NMR (500 MHz, benzene-*d*₆): δ 8.09 (dd, *J* = 6.5, 2.0, 1H), 7.49 (d, *J* = 7.0, 1H), 7.38–7.25 (m, 2H), 3.31 (s, 2H), 1.85 (s, 6H), 0.89 (s, 6H). ¹³C NMR (500 MHz, benzene-*d*₆): δ 177.88, 162.09, 151.94, 140.46, 125.79, 125.28, 123.59, 78.79, 68.34, 43.80, 31.00, 28.01. Anal. Calcd for C₂₈H₃₆N₂O₂Zn: C, 67.53; H, 7.29; N, 5.63. Found: C, 67.26; H, 7.50; N, 5.38.

10. $[\{\kappa-C,N-(o-C_6H_4)CMe_2(COCH_2CMe_2N)\}Cr]_2(\mu-Cl)_2(6_2)$. To a mixture of $[CrCl_2(THF)]_2$ (98 mg, 0.251 mmol) and **Zn**-(**PhCMe_2Ox**)_2 (250 mg, 0.502 mmol) was distilled 15 mL of THF at -78 °C. The suspension was stirred at -78 °C for 5 h and warmed to 23 °C over 4 h. The resulting blue solution was filtered through Celite and stripped. Trituration with benzene (2 × 5 mL) resulted in formation of a purple solid (61 mg, 40%). X-ray diffraction quality crystals were grown by hot filtration and recrystallization from benzene. ¹H NMR (400 MHz, benzene d_6): δ 17.17, 16.13, 14.00, 1.60, -2.86, -11.80, -77.80. Anal. Calcd for C₂₈H₃₆N₂O₂Cl₂Cr₂: C, 55.36; H, 5.97; N, 4.61. Found: C, 55.73; H, 5.79; N, 4.06. $\mu_{eff} = 5.0$ at 295 K (Gouy balance). **11.** { κ -C,N-(o-C₆H₄)CMe₂(COCH₂CMe₂N)}CrCl(THF)

11. { κ -*C*,*N*-(*o*-C₆H₄)CMe₂(COCH₂CMe₂N)}CrCl(THF) (6-THF). Purple 6₂ dissolves in THF to give a blue solution. Evaporation of solvent gives a dark blue solid, presumably the monomeric THF adduct. If dissolved in THF-*d*₈, the NMR spectrum shows a set of broad, paramagnetic peaks. ¹H NMR (400 MHz, THF-*d*₈): δ 20.64, 17.86, 10.00, -2.00, -2.83, -16.55, -79.06. μ_{eff} = 4.9 (Evans' method in THF-*d*₈).

12. { κ -C,N-(o-C₆H₄) $CMe_2(COCH_2CMe_2N)$ }Fe(py)Cl (7). a. To a mixture of FeCl₂(py)₄ (223 g, 0.502 mmol) and Zn(PhCMe₂Ox)₂ (250 g, 0.502 mmol) was distilled 15 mL of THF at -78 °C. The suspension was stirred at -78 °C for 5 h, allowed to warm to 23 °C, and stirred an additional 36 h. The golden brown solution was filtered and washed (2×10 mL). The filtrate was concentrated, cooled, and filtered cold to yield 100 mg of yellow solid (52%). X-ray diffraction quality crystals were grown by hot filtration and recrystallization from benzene. b. BrPhCMe₂Ox (250 mg, 0.844 mmol) in 5 mL of THF was added to a solution of "BuLi (0.58 mL, 1.6 M in hexanes) in 10 mL of THF at -78 °C under argon. After 2 h at -78 °C, FeCl₂(py)₄ (374 mg, 0.844 mmol) was added via addition finger. The reaction was kept at -78 °C for 5 h and then allowed to warm to 23 °C over 10 h. The yellow-brown reaction mixture was stripped, triturated with benzene (2 \times 5 mL), filtered, and washed several times (2 \times 15 mL). Concentration of the solvent yielded a crystalline yellow material, which was collected by filtration (190 mg, 58%). ¹H NMR (400 MHz, benzene- d_6): δ 266.41 (1H), 246.08 (1H), 162.10 (2H), 137.15(1H), 130.91(1H), 80.85(1H), 77.15(1H), 42.38(3H), 19.15 (2H), 15.36 (3H), -15.94 (2H), -32.35 (1H), -35.33 (3H). Anal. Calcd for $C_{19}H_{23}N_2OCIFe$: C, 59.01; H, 6.00; N, 7.24. Found: C, 59.01; H, 5.91; N, 5.73. $\mu_{eff} = 4.7 \,\mu_{B}$ (Evans' method in C_6D_6).

13. $\{\kappa$ -C,N-(o-C₆H₄)CMe₂(COCH₂CMe₂N) $\}_{2}$ Fe (8). a. BrPhC-Me₂Ox (46 mg, 0.155 mmol) in 2 mL of THF was added to a solution of "BuLi (0.11 mL, 1.6 M in hexanes) in 5 mL of THF at -78 °C. After 2 h at -78 °C, 7 (60 mg, 0.155 mmol) was added via an addition finger. The reaction was allowed to warm to 23 °C over 10 h. The light brown mixture was stripped of solvent, triturated (2 \times 5 mL) with Et₂O, dissolved in 20 mL of Et₂O, and filtered through Celite. Yellow microcrystalline material was obtained from a concentrated Et₂O solution. b. BrPhCMe₂Ox (170 mg, 0.556 mmol) in 2 mL of THF was added to a solution of "BuLi (0.38 mL, 1.6 M in hexanes) in 10 mL of THF at -78 °C. After 2 h at -78 °C, FeBr₂(THF)₂ (100 mg, 0.278 mmol) was added via an addition finger. The reaction was allowed to warm to 23 °C over 10 h. The mixture was stripped of all volatiles, triturated with Et₂O $(2 \times 5 \text{ mL})$, and filtered through Celite. Evaporation of the solvent led to a tan solid with spectral features similar to the yellow material above, but neither method affords pure material. ¹H NMR (400 MHz, benzene- d_6): δ 212.17 (1H), 139.71 (1H), 70.12 (1H), 19.70 (3H), 16.64 (1H), 13.29 (1H), -14.32 (3H), -29.03 (3H), -29.57 (1H), -38.16 (3H).

14. $\{\kappa - C_{0}N - (o - C_{6}H_{4})CMe_{2}(COCH_{2}CMe_{2}N)\}_{2}Ni$ (9). To a mixture of NiCl₂(DME) (88 mg, 0.282 mmol) and Zn(PhCMe₂Ox)₂ (200 mg, 0.282 mmol) was distilled 25 mL of THF at -78 °C. The yellow suspension was stirred at -78 °C for 5 h and slowly warmed to room temperature. The resulting orange solution was stripped, triturated with ether, and filtered to give a peach-colored solid. The solid was recrystallized from an ether/THF mixture to give a pale orange crystalline solid (34 mg, 25%). ¹H NMR (500 MHz, benzene- d_6): δ 7.23 (δ , J = 7.2, 1H), 7.13 (d, J = 7.7, 1H), 6.98 (t, J = 7.3, 1H), 6.85 (t, J = 7.1, 1H), 3.66 (s, 3H), 3.36 (d, J = 8.1, 1H), 3.12 (d, J = 8.1, 1H), 1.81 (s, 3H), 0.94 (s, 3H), 0.69(s, 3H). ¹³C NMR (500 MHz, benzene-d₆): δ 177.82, 171.46, 148.36, 143.17, 124.28, 121.62, 121.20, 79.35, 68.97, 45.03, 35.51, 27.91, 25.47, 23.19 (see Supporting Information). Anal. Calcd for C₂₈H₃₆N₂O₂Ni: C, 68.45; H, 7.39; N, 5.70. Found: C, 68.36; H, 7.30; N, 5.62.

Single-Crystal X-ray Diffraction Studies. Upon isolation, the crystals were covered in polyisobutenes and placed under a 173 K N₂ stream on the goniometer head of a Siemens P4 SMART CCD area detector (graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS). All non-hydrogen atoms were treated as idealized contributions (Riding model).

15. $[\kappa$ -*N*,*N*-{**4,4-Me**₂-(**2**-*o*-**C**₆**H**₄)-**2**-**o**xazoline}₂]CoCl₂ (1-Co). A blue-green prism (0.20 × 0.15 × 0.10 mm) was obtained from THF. A total of 31 094 reflections were collected with 6389 being symmetry independent ($R_{int} = 0.1368$), and 3233 were greater

than $2\sigma(I)$. A semiempirical absorption correction from equivalents was applied, and the refinement utilized $w^{-1} = \sigma^2(F_0{}^2) + (0.0350p)^2 + 0.0p$, where $p = (F_0{}^2 + 2F_c{}^2)/3$. **16.** [{ κ -N,O-C_6H_4-CMe_2C=NCMe_2CH_2-(\mu-O)}BrFe{ κ -N,O-C_6H_4-CMe_2C=NCMe_2CH_2-(\mu-O)]

16. $[\{\kappa\text{-}N,O\text{-}C_6\text{H}_4\text{-}C\text{Me}_2\text{C}=\text{NCMe}_2\text{CH}_2\text{-}(\mu\text{-}O)\}\text{BrFe}\{\kappa\text{-}N,O\text{-}C_6\text{H}_4\text{-}C\text{Me}_2\text{C}=\text{NCMe}_2\text{CH}_2\text{-}(\mu\text{-}O)\}\text{FeBr}]\text{Li}\{\kappa\text{-}N,O\text{-}C_6\text{H}_4\text{-}C\text{Me}_2\text{C}=\text{NCMe}_2\text{CH}_2\text{-}(\mu\text{-}O)\}(\text{DME})$ (5). A red block (0.10 × 0.10 × 0.03 mm) was obtained from DME. A total of 57 092 reflections were collected, with 13 571 being symmetry independent ($R_{\text{int}} = 0.0764$), and 8050 were greater than $2\sigma(I)$. A semiempirical absorption correction from equivalents was applied, and the refinement utilized $w^{-1} = \sigma^2(F_o^2) + (0.1000p)^2 + 3.0822p$, where $p = (F_o^2 + 2F_c^2)/3$. 17. $[\{\kappa\text{-}C,N\text{-}(4,4\text{-Dimethyl-2-}(2\text{-phenylpropan-2-yl)oxazoline})\}$ -

17. [{ κ -C,N-(4,4-Dimethyl-2-(2-phenylpropan-2-yl)oxazoline)}-Cr]₂(μ -Cl)₂ (6₂). A purple block (0.30 × 0.15 × 0.05 mm) was obtained from benzene. A total of 9496 reflections were collected, with 2092 being symmetry independent ($R_{int} = 0.0463$), and 1516 were greater than $2\sigma(I)$. A semiempirical absorption correction from equivalents was applied, and the refinement utilized $w^{-1} = \sigma^2(F_o^2) + (0.0727p)^2 + 2.5196p$, where $p = (F_o^2 + 2F_c^2)/3$.

18. { κ -*C*,*N*-(4,4-Dimethyl-2-(2-phenylpropan-2-yl)oxazoline)}-Fe(η -*N*-pyridyl)Cl (7). A yellow block (0.40 × 0.15 × 0.05 mm) was obtained from benzene. A total of 20 134 reflections were collected, with 3968 being symmetry independent ($R_{int} = 0.0814$), and 2930 were greater than $2\sigma(I)$. A semiempirical absorption correction from equivalents was applied, and the refinement utilized $w^{-1} = \sigma^2 (F_o^2) + (0.0858p)^2 + 0.827p$, where $p = (F_o^2 + 2F_c^2)/3$.

Computational Details. The geometry of compound [bisoxazoline] was optimized and the electronic structure was calculated using the Orca⁷⁶ software package. The hybrid functional B3LYP was used with the GTO basis sets published by the Ahlrichs group.^{77–79} The triple- ζ basis set def2-TZVP(-f) was used for nickel, and the remaining atoms were treated with the double- ζ split-valence basis set def2-SV(P). The RIJCOSX approximation⁸⁰ was used to speed up calculations using an auxiliary basis set that matched the orbital basis.

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Supporting Information Available: CIF files of 1-Co, 5-Fe₂Li, 6_2 , and 7. This material is available free of charge via the Internet at http://pubs.acs.org.

⁽⁷⁶⁾ Neese, F. *Orca*, an ab initio, DFT and Semiempirical Electronic Structure Package, Version 2.7, Revision 0; Institut für Physikalische und Theoretische Chemie, Universität Bonn: Bonn, Germany, August 2009.

⁽⁷⁷⁾ Schäfer, A.; Horn, H.; Ahlrichs, R. J. Chem. Phys. **1992**, 97, 2571.

⁽⁷⁸⁾ Schäfer, A.; Huber, C.; Ahlrichs, R. J. Chem. Phys. **1994**, 100, 5829.

⁽⁷⁹⁾ Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* 2005, 7, 3297.
(80) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. *Chem. Phys.* 2009, 356, 98.