

these novel SiCAC reactions have high synthetic potential, further investigations on the mechanism, organometallic chemistry, and applications to organic syntheses are actively underway.

**Acknowledgment.** This research was supported by grants from the National Science Foundation and the National Institutes of Health. A generous support from Mitsubishi Kasei Corporation is gratefully acknowledged. The authors (R.J.D. and W.R.S.) thank Dr. Zhaoda Zhang for his helpful discussions as well as technical assistance.

**Supplementary Material Available:** Identification data for 7, 9, 10, 11, and 13, including 2D NMR spectra, i.e., COSY and HETCOR, for 10 and 11 (7 pages). Ordering information is given on any current masthead page.

(8) The intramolecular trapping of a  $\beta$ -silylethenyl-nickel species by an alkyne moiety in 1,7-octadiyne and related systems, giving the corresponding carbocyclization product, was reported by Tamao et al. See: Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 6478.

### (1,5-Cyclooctadiene)bis(3,6-di-*tert*-butylcatecholato)iridium(IV). An Organometallic Aryl Oxide Complex with a Charge-Transfer Transition at Unusually Low Energy

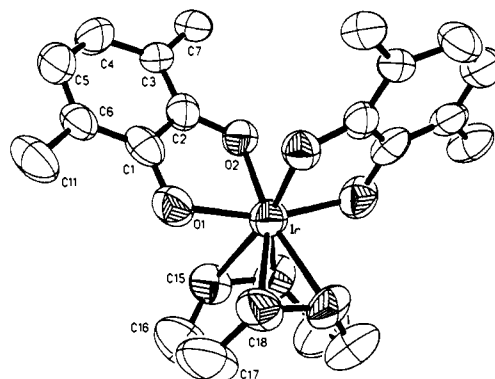
Christopher W. Lange and Cortlandt G. Pierpont\*

Department of Chemistry and Biochemistry  
University of Colorado, Boulder, Colorado 80309

Received February 19, 1992

Many of the interesting and important features of transition metal complexes containing catecholates and semiquinone ligands are related to the similarity in energy between quinone  $\pi^*$ -orbitals and the metal d-levels. In some cases this property is responsible for intense, low-energy charge-transfer transitions that sometimes extend well into the near-infrared NIR region.<sup>1</sup> Characterization on the "bending crystals" of  $\text{Rh}(\text{CO})_2(3,6\text{-di-}i\text{-tert-butylsemiquinone})$  has shown that a low-energy metal-ligand charge-transfer transition associated with stacked oligomers of complex units contributes to unique photomechanical properties in the solid state.<sup>2</sup> The higher d-orbital energy of iridium may result in charge-transfer transitions shifted further to lower energy, resulting in compounds with high optical sensitivity in the infrared. We now describe an unusual product obtained by the addition of cobaltocenium 3,6-di-*tert*-butylsemiquinone to  $[\text{Ir}(1,5\text{-COD})\text{Cl}]_2$ .

The anticipated product of the synthetic procedure was  $\text{Ir}(1,5\text{-COD})(3,6\text{-DBSQ})$ .<sup>3</sup> However, crystallographic characterization on the dark red complex obtained from this reaction showed that the product was actually  $\text{Ir}(1,5\text{-COD})(3,6\text{-DBCat})_2$  with the structure shown in Figure 1.<sup>4</sup> The Ir(IV) formulation



**Figure 1.** View showing the structure of  $\text{Ir}(1,5\text{-COD})(3,6\text{-DBCat})_2$ . A crystallographic 2-fold axis passes between the olefin groups and relates the two catecholates ligands. Selected bond lengths ( $\text{\AA}$ ): Ir-O1 2.014 (7), Ir-O2 2.014 (6), Ir-C15 2.207 (11), Ir-C18 2.192 (9), C1-O1 1.352 (13), C2-O2 1.318 (12), C15-C18' 1.413 (17).

for the complex in the solid state is consistent with the structural features of the quinone ligands. Ring C-C lengths reflect the expected aromatic structure of a catecholates ligand, and the C-O lengths are of values that are longer than semiquinone lengths.<sup>5</sup> In particular, the length to O1 is 1.35 (1)  $\text{\AA}$ , while the length to O2, trans to the COD olefin bond, is 1.32 (1)  $\text{\AA}$ . In toluene solution at room temperature, the  $S = 1/2$  complex molecule shows a broad EPR resonance centered about a  $g$ -value of 1.986 which is approximately 200 G in width. In frozen toluene at 77 K, the signal splits to give a slightly rhombic spectrum with components  $g_1 = 1.948$ ,  $g_2 = 1.952$ , and  $g_3 = 2.006$ . No hyperfine structure is observed for either the isotropic or anisotropic spectrum. Electrochemical characterization on  $\text{Ir}(1,5\text{-COD})(3,6\text{-DBCat})_2$  shows that the complex undergoes reversible one-electron oxidation and reduction reactions.<sup>6</sup> Couples are closely spaced at potentials of  $-0.092$  V and  $-0.636$  V (vs  $\text{Fc}^+/\text{Fc}$ ), respectively, and the complex may be chemically oxidized with  $\text{Ag}(\text{PF}_6)$  and reduced with cobaltocene.

Figure 2 shows the infrared spectrum obtained for the complex.<sup>7</sup> The sharp bands at lower energy are the usual ligand vibrations, but the broad, intense transition centered near  $4200\text{ cm}^{-1}$  is an electronic absorption. The band appears unsymmetrical in the figure due to moisture in the KBr matrix; in toluene solution at room temperature it appears as a single symmetrical transition at 2340 nm with a molar extinction coefficient of  $5100\text{ M}^{-1}\text{ cm}^{-1}$ . Assignment of this transition is not unambiguous. It may simply be a metal-catecholates charge-transfer transition,<sup>8</sup> but other possibilities exist. Intense, low-energy interligand charge-transfer transitions commonly occur for members of the  $\text{ML}_2(3,5\text{-DBCat})(3,6\text{-DBCat})$  series, with  $\text{M} = \text{Ru}$  and  $\text{Os}$  and  $\text{L}_2 = \text{bpy}$ ,  $2\text{PPh}_3$ , and  $2\text{CO}$ .<sup>9,10</sup> This requires significant mixing with an Ir(III) charge-localized form of the complex,  $\text{Ir}(1,5\text{-COD})(3,6\text{-DBSQ})(3,6\text{-DBCat})$ . The electrochemistry supports this in ap-

(5) (a) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 44. (b) Carugo, O.; Castellani, C. B.; Djinic, K.; Rizzi, M. *J. Chem. Soc., Dalton Trans.* **1992**, 837.

(6) Cyclic voltammograms were recorded in acetonitrile solution using tetrabutylammonium hexafluorophosphate as electrolyte. An  $\text{Ag}/\text{Ag}^+$  reference electrode was used, and the cobaltocenium/cobaltocene couple was used as an internal standard ( $-1.318$  V vs  $\text{Fc}^+/\text{Fc}$ ).

(7) IR (KBr)  $\nu$  (between 1000 and  $1600\text{ cm}^{-1}$ ): 1552 (s), 1480 (m), 1466 (m), 1402 (s), 1384 (m), 1353 (m), 1307 (s), 1284 (s), 1212 (m), 1151 (s)  $\text{cm}^{-1}$ . UV-vis-NIR (toluene): 292 ( $9200\text{ M}^{-1}\text{ cm}^{-1}$ ), 475 (2600), 513 (2600), 564 (1800), 854 (460), 975 (390), 1304 (480), 2340 (5100) nm.

(8) (a) Ernst, S.; Hanel, P.; Jordanov, J.; Kaim, W.; Kasack, V.; Roth, E. *J. Am. Chem. Soc.* **1989**, *111*, 1733. (b) Haga, M.; Isobe, K.; Boone, S. R.; Pierpont, C. G. *Inorg. Chem.* **1990**, *29*, 3795. (c) Dei, A.; Gatteschi, D.; Pardi, L.; Russo, U. *Inorg. Chem.* **1991**, *30*, 2589.

(9) Lever, A. B. P.; Auburn, P. R.; Dodsworth, E. S.; Haga, M.; Liu, W.; Melnik, M.; Nevin, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 8076.

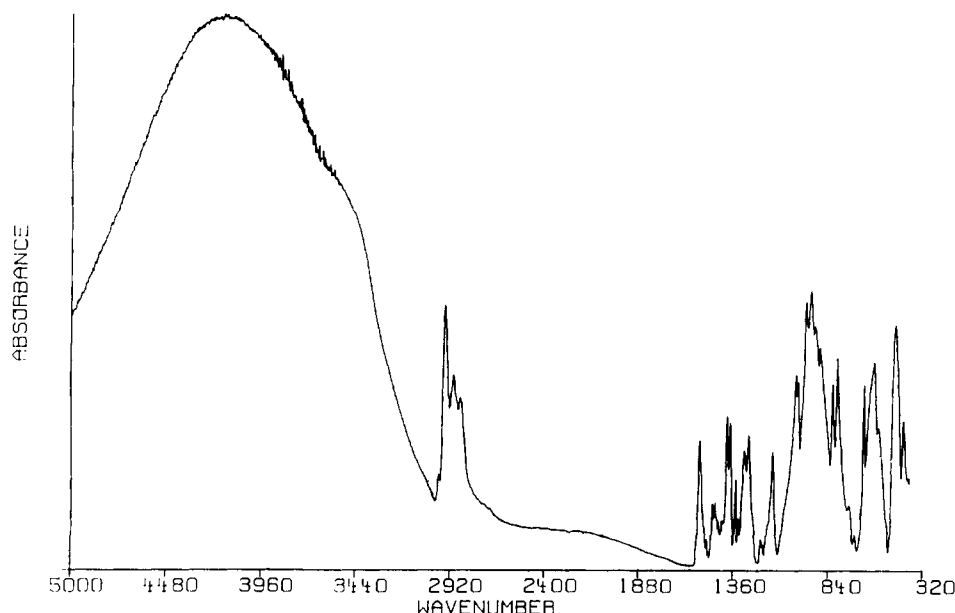
(10) (a) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 35. (b) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1991**, *30*, 2906. (c) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.*, submitted for publication.

(1) Haga, M.; Dodsworth, E. S.; Lever, A. B. P.; Boone, S. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1986**, *108*, 7413.

(2) Lange, C. W.; Foldeaki, M.; Nevodchikov, V. I.; Cherkasov, V. K.; Abakumov, G. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1992**, *114*, 4220.

(3) Synthesis of  $\text{Ir}(1,5\text{-COD})(3,6\text{-DBCat})_2$ :  $[\text{Ir}(1,5\text{-COD})\text{Cl}]_2$  (0.153 g, 0.23 mmol) dissolved in 5 mL of  $\text{CH}_2\text{Cl}_2$  was added to a solution of  $[\text{Co}(\text{Cp})_2](3,6\text{-DBSQ})$  prepared by combining cobaltocene (0.091 g, 0.48 mmol) and 3,6-di-*tert*-butyl-1,2-benzoquinone (0.10 g, 0.47 mmol) in 10 mL of  $\text{CH}_2\text{Cl}_2$ . The mixture became dark red, and a brown precipitate separated from the solution. The precipitate was collected by filtration, and the red filtrate was slowly evaporated under a flow of  $\text{N}_2$ . Dark red crystals of  $\text{Ir}(1,5\text{-COD})(3,6\text{-DBCat})_2$  were obtained from the evaporated filtrate in yields that have varied from 30% to 50%. The brown precipitate has not yet been identified. Details of the reaction and products will be published separately.

(4) X-ray analysis of  $\text{Ir}(1,5\text{-COD})(3,6\text{-DBCat})_2$ : tetragonal, space group  $P4_32_12$ ;  $a = 15.007$  (2)  $\text{\AA}$ ,  $c = 15.234$  (4)  $\text{\AA}$ ,  $V = 3431$  (1)  $\text{\AA}^3$ ,  $Z = 4$ ;  $R = 0.040$  for 2261 unique observed reflections. Details of the structure determination are given in the supplementary material.



**Figure 2.** Infrared spectrum of Ir(1,5-COD)(3,6-DBCat)<sub>2</sub> recorded as a KBr pellet showing the normal ligand vibrational bands at low energy and an electronic transition centered at 4200 cm<sup>-1</sup>. Band asymmetry is due to moisture in the KBr; a single symmetrical transition is observed for the complex in solution.

peering as two quinone ligand-based redox couples that most closely resemble the couples of Fe(bpy)(3,6-DBSQ)(3,6-DBCat).<sup>11</sup> Structural features of the molecule, with the anisotropy and absence of ligand proton hyperfine coupling of the EPR spectrum, show that the electronic description is not purely that of the Ir(III) form,<sup>2</sup> however.

Interligand charge transfer between catecholate donor and olefin acceptor orbitals exists as a third possibility for the low-energy transition.<sup>12</sup> Two features of the complex may be indirectly related to this assignment. Synergistic interligand  $\pi$  donor-acceptor bonding would remove charge from the catecholate C-O antibonding orbital. This may contribute to the shorter C-O length for oxygen atoms bonded trans to Ir-olefin bonds and the relatively long C-C bonds for the coordinated olefin groups. Second, it was of interest to investigate the counterligand dependence of the low-energy transition. Attempts to replace the 1,5-COD ligand with CO, DIPHOS, and 2,2'-bipyridine have all failed.<sup>13</sup> The 1,5-COD ligand is tightly bound to the high oxidation state metal, although the Ir-C lengths to the olefin carbon atoms are not unusually short<sup>14</sup> and the trans Ir-O length is identical to the length at the positions cis to the olefin bonds. This is in contradistinction to the catecholate-nitrosyl bonding in Ir-(NO)(PPh<sub>3</sub>)(Br<sub>4</sub>Cat) where cooperative trans donor-acceptor coordination resulted in shortening of both trans Ir-N and Ir-O bonds.<sup>15</sup> Whether or not it is responsible for the low-energy electronic transition, interligand bonding between the catecholate and olefin ligands of Ir(1,5-COD)(3,6-DBCat)<sub>2</sub> may be an important ligand stabilization effect.

Further studies on coligand bonding effects within the IrL<sub>2</sub>-(Cat)<sub>2</sub> series will provide more detailed information on the origin

of this unusual transition.

**Acknowledgment.** Support for the research carried out at the University of Colorado was provided by the National Science Foundation through Grant CHE 90-23636. We wish to thank Professor G. A. Abakumov for providing the sample of 3,6-di-*tert*-butyl-1,2-benzoquinone used in this investigation. Iridium salts were provided by Johnson-Matthey, Inc., through their Metal Loan Program.

**Supplementary Material Available:** Tables giving crystal data and details of the structure determination, atomic coordinates, anisotropic thermal parameters, hydrogen atom locations, and bond lengths and angles for Ir(1,5-COD)(3,6-DBCat)<sub>2</sub> (9 pages); tables of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

### A Solid-State <sup>2</sup>H NMR Relaxation Study of a 12 Base Pair RNA Duplex

Andy C. Wang,<sup>†</sup> Michael A. Kennedy,<sup>‡§</sup> Brian R. Reid,<sup>†,‡</sup> and Gary P. Drobny<sup>‡,§</sup>

Department of Biochemistry  
University of Washington  
Seattle, Washington 98195  
Department of Chemistry  
University of Washington  
Seattle, Washington 98195  
Battelle Pacific Northwest Laboratories  
Richland, Washington 99352

Received September 9, 1991

In a recent attempt to determine the solution-state structure of a 12 base pair DNA-RNA-DNA chimera ([d(CGCG)r(AAU)d(CGCG)]<sub>2</sub>), Wang et al.<sup>1</sup> found that the nonselective <sup>1</sup>H T<sub>1</sub> relaxation times of the RNA were significantly longer than

(11) Fe(bpy)(3,6-DBSQ)(3,6-DBCat) undergoes oxidation at -0.319 V and reduction at -0.831 V (vs Fe<sup>+/0</sup>/Fe). Both are reversible one-electron processes that will be described in a separate publication.

(12) Benedix, R.; Hennig, H.; Kunkely, H.; Vogler, A. *Chem. Phys. Lett.* **1991**, *175*, 483.

(13) In typical experiments, Ir(1,5-COD)(3,6-DBCat)<sub>2</sub> (0.05 g) was refluxed in toluene for the period of 1 day in the presence of an excess of either 2,2'-bipyridine or 1,2-bis(diphenylphosphino)ethane (DIPHOS) or with CO bubbled through the solution. Electronic spectra obtained on these solutions at the conclusion of the experiment indicated the presence of unreacted Ir(1,5-COD)(3,6-DBCat)<sub>2</sub>.

(14) See, for examples: (a) Basson, S. S.; Leipoldt, J. G.; Purcell, W.; Schoeman, J. B. *Acta Crystallogr.* **1989**, *C45*, 2000. (b) Bright, T. A.; Jones, R. A.; Koschmieder, S. U.; Nunn, C. M. *Inorg. Chem.* **1988**, *27*, 3819.

(15) Shorthill, W. B.; Buchanan, R. M.; Pierpont, C. G.; Ghedini, M.; Dolcetti, G. *Inorg. Chem.* **1980**, *19*, 1803.

<sup>†</sup> Department of Biochemistry, University of Washington Seattle, WA 98195.

<sup>‡</sup> Department of Chemistry, University of Washington Seattle, WA 98195.

<sup>§</sup> Battelle Pacific Northwest Laboratories Richland, WA 99352.