Inorg. Chem. 1993, 32, 783–784

Spectroelectrochemical Characterization of $Ir_2(dimen)_4^+$ and $Ir_2(dimen)_4^0$ (dimen = 1,8-Diisocyanomenthane)

Michael G. Hill,† Andrew G. Sykes,‡ and Kent R. Mann*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received September 4, 1992

The electrochemical and photophysical properties of d^8–d^8 binuclear complexes have been extensively investigated during the past 15 years.[1] Early reports focused on photoinduced electron-transfer reactions,[2-5] while more recent studies have delineated excited-state atom transfer as an important reactivity mode for these compounds.[1a-c] Additionally, d^8–d^8 species have been shown to activate small molecules via electrocatalytic cycles.[6]

Many of these reactions are proposed to involve oxidized or reduced d^8–d^8 complexes as intermediates. While d^7–d^8 and d^7–d^7 oxidized species have recently been isolated and characterized,[7,8] the reactive nature of analogous reduced species has made their characterization more difficult. To date, the only spectroscopic evidence of a reduced d^8–d^8 complex comes from pulse radiolysis experiments with $Rh_2(TM4)_4^{2+}$ and $Pt_2(pop)_4^{4-}$ (where TM4 = 2,5-diisocyano-2,5-dimethylhexane, and pop^{2-} = pyrophosphate) in which the metastable $Rh_2(TM4)_4^+$ and $Pt_2(pop)^{5-}$ ions were transiently formed.[9] Efforts to generate these compounds electrochemically have been unsuccessful due to secondary reactions which lead to irreversible cathodic responses.[10,11] Herein, we report the reversible 1e^- electrochemical reductions of $Ir_2(dimen)_4^{2+}$ in 0.1 M $TBA^+PF_6^-/CH_3CN$ (TBA^+ = n-tetrabutylammonium; dimen = 1,8-diisocyano-*p*-menthane).[12] The stabilities of $Ir_2(dimen)_4^+$ and $Ir_2(dimen)_4^0$ have enabled us to characterize these species with UV–vis and IR spectroelectrochemical methods.

Figure 1 shows the UV–vis spectroelectrochemistry of $Ir_2(dimen)_4^{2+}$ in 0.1 M $TBA^+PF_6^-/CH_3CN$ ($TBA^+PF_6^-$ = tetrabutylammonium hexafluorophosphate). As evidenced by the CV recorded in the spectroelectrochemical cell[13] (inset, Figure 1), $Ir_2(dimen)_4^{2+}$ undergoes two chemically reversible, 1e^- reductions ($E_{2+/+}{}^{\circ\prime} = -1.34$ V; $E_{+/0}{}^{\circ\prime} = -1.53$ V vs AgCl/Ag in 1.0 M KCl). As the potential is swept through the first process, the initial bands at 327 nm (ϵ = 36 600 $M^{-1}\,cm^{-1}$), 375 nm (ϵ = 18 000 $M^{-1}\,cm^{-1}$), and 575 nm (ϵ = 7300 $M^{-1}\,cm^{-1}$) disappear, and are replaced by three prominent bands at 320 nm (ϵ = 20 900 $M^{-1}\,cm^{-1}$), 595 nm (ϵ = 12 300 $M^{-1}\,cm^{-1}$), and 800 nm (ϵ = 3700 $M^{-1}\,cm^{-1}$). Further reduction of this monocation to the neutral $Ir_2(dimen)_4^0$ complex is characterized by the appearance of absorption peaks at 300 nm (ϵ = 25 100 $M^{-1}\,cm^{-1}$) and 432 nm (ϵ = 14 400 $M^{-1}\,cm^{-1}$). Reversing the sweep direction affects the opposite spectral changes.

Analogous IR data are shown in Figure 2. Upon the first 1e^- reduction, the ν(CN) stretch of $Ir_2(dimen)_4^{2+}$ (2156 cm^{-1}) gives way to a broad band at 2090 cm^{-1} that we assign to $Ir_2(dimen)_4^+$. Reduction of $Ir_2(dimen)_4^+$ to $Ir_2(dimen)_4^0$ yields an IR spectrum with two ν(CN) stretches (2058 and 1869 cm^{-1}). The isosbestic points indicate clean, reversible electrochemical conversions between the dication, monocation, and neutral oxidation states of $Ir_2(dimen)_4^{n+}$ (Scheme I).

Scheme I

$$Ir_2(dimen)_4^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Ir_2(dimen)_4^{+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Ir_2(dimen)_4^{0}$$

According to the MO scheme developed for d^8–d^8 complexes,[14,15] reduction of $Ir_2(dimen)_4^{2+}$ by one electron should result in the population of a low-lying $p_z\,\sigma$ orbital, yielding a $^2A_{1g}$ ground state $(d_{z^2}\sigma)^2(d_{z^2}\sigma^*)^2(p_z\sigma)^1$ electronic configuration) with a formal metal–metal bond order of $^1/_2$. Qualitatively, this enhanced metal–metal interaction is expected to shift the $d_{z^2}\sigma^* \rightarrow p_z\sigma$ transition of $Ir_2(dimen)_4^+$ to lower energy than the corresponding band of $Ir_2(dimen)_4^{2+}$. Our data support these predictions. Following the work of Che, Gray, and co-workers,[9] we assign the intense 595-nm absorbance in the UV–vis spectrum of $Ir_2(dimen)_4^+$ (Figure 1) to the Laporte-allowed $^2A_{1g} \rightarrow {}^2A_{2u}$ $(d_{z^2}\sigma^* \rightarrow p_z\sigma)$ transition. Both the shape[16] and bathochromic shift of this band are consistent with a stronger metal–metal interaction in the monocation relative to the dicationic d^8–d^8 parent. From the single ν(CN) stretch observed in the IR spectrum of $Ir_2(dimen)_4^+$ we conclude that the basic square planar geometry of $Ir_2(dimen)_4^{2+}$

---

* To whom correspondence should be addressed.

† Present address: California Institute of Technology, Pasadena, CA 91125.

‡ Present address: Northern Arizona University, Flagstaff, AZ 86011.

(1) For recent reviews, see: (a) Roundhill, M. D.; Gray, H. B.; Che, C.-M. *Acc. Chem. Res.* **1989**, *22*, 55. (b) Smith, D. C.; Gray, H. B. *Coord. Chem. Rev.* **1990**, *100*, 169. (c) Sweeney, R. J.; Harvey, E. L.; Gray, H. B. *Coord. Chem. Rev.* **1990**, *105*, 23.

(2) Mann, K. R.; Lewis, N. S.; Miskowski, V. M.; Erwin, D. K.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 5525.

(3) Milder, S. J.; Goldbeck, R. A.; Kliger, D. S.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 6761.

(4) (a) Che, C. M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796. (b) Fordyce, W. A.; Brummer, J. G.; Grosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7061. (c) Che, C.-M.; Cho, K.-C. *J. Chem. Soc., Chem. Commun.* **1987**, 133. (d) Hurst, J. K.; Thompson, D. H. P.; Connolly, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 507. (e) Heuer, W. E.; Totten, M. D.; Rodman, G. S.; Hebert, E. J.; Tracy, H. J.; Nagle, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 1163. (f) Peterson, J. R.; Kalyanasundaram, J. *Phys. Chem.* **1985**, *89*, 2486.

(5) (a) Marshall, J. L.; Stobart, S. R.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 3027. (b) Fox, L. S.; Kozik, M.; Winkler, J. R.; Gray, H. B. *Science* **1990**, *247*, 4946. (c) Caspar, J. V.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 3029.

(6) Smith, D. C.; Gray, H. B. *Catal. Lett.* **1990**, *6*, 195. (b) Hill, M. G.; Mann, K. R. *Catal. Lett.* **1991**, *11*, 341.

(7) (a) Connelly, N. G.; Garcia, N. G. *J. Chem. Soc., Chem. Commun.* **1987**, 246. (b) Boyd, D. C.; Matsch, P. A.; Mixa, M. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 331. (c) Boyd, D. C.; Szalapski, R.; Mann, K. R. *Organometallics* **1989**, *8*, 790. (d) Hill, M. G.; Lamanna, W.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 4687. (e) DeGray, J. A.; Rieger, P. H.; Connelly, N. G. *J. Magn. Reson.* **1990**, *88*, 376.

(8) (a) Mann, K. R.; Bell, R. A.; Gray, H. B. *Inorg. Chem.* **1979**, *18*, 2671. (b) Maverick, A. W.; Smith, T. P.; Maverick, E. F.; Gray, H. B. *Inorg. Chem.* **1987**, *26*, 4336. (c) Bohling, D. A.; Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1981**, *20*, 194. (d) Smith, D. C.; Marsh, R. E.; Schaefer, W. P.; Loehr, T. M.; Gray, H. B. *Inorg. Chem.* **1990**, *29*, 534. (e) Olmstead, M. M.; Balch, A. L. *J. Organomet. Chem.* **1978**, *148*, C15.

(9) Che, C.-M.; Atherton, S. J.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5143.

(10) Najdzionek, J. S. Ph.D. Dissertation. California Institute of Technology, 1982.

(11) Kim, J.; Fan, F. F.; Bard, A. J.; Che, C.-M.; Gray, H. B. *Chem. Phys. Lett.* **1985**, *121*, 543.

(12) Other quasi-reversible electrochemical reductions of binuclear Ir(I) complexes have recently been reported: Rodman, G. S.; Bard, A. J. *Inorg. Chem.* **1990**, *29*, 4699.

(13) Bullock, J. P.; Mann, K. R. *Inorg. Chem.* **1989**, *28*, 4006.

(14) Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3553.

(15) Smith, D. C.; Miskowski, V. M.; Mason, W. R.; Gray, H. B. *J. Am. Chem. Soc.* **1990**, *112*, 3759.

(16) Extrom, C. E.; Hill, M. G.; Mann, K. R. Work in progress.

(17) The stability of the $Ir_2(dimen)_4^+$ radical allowed us to obtain its EPR spectrum. In frozen 0.1 M $TBA^+PF_6^-/CH_3CN$ solutions (77 K), $Ir_2(dimen)_4^+$ shows three signals, with $g_1 = 2.064$, $g_2 = 2.060$, and $g_3 = 2.01$. We considered the possibility that $Ir_2(dimen)_4^+$ may best be described as a d^8–d^9 dimer, however, the g-values of the nearly axial signal ($g_\perp > g_\parallel$) are not consistent with those expected for a d^9 transition metal complex with an unpaired electron in a $d_{x^2-y^2}$ orbital.[18]

0020-1669/93/1332-0783$04.00/0

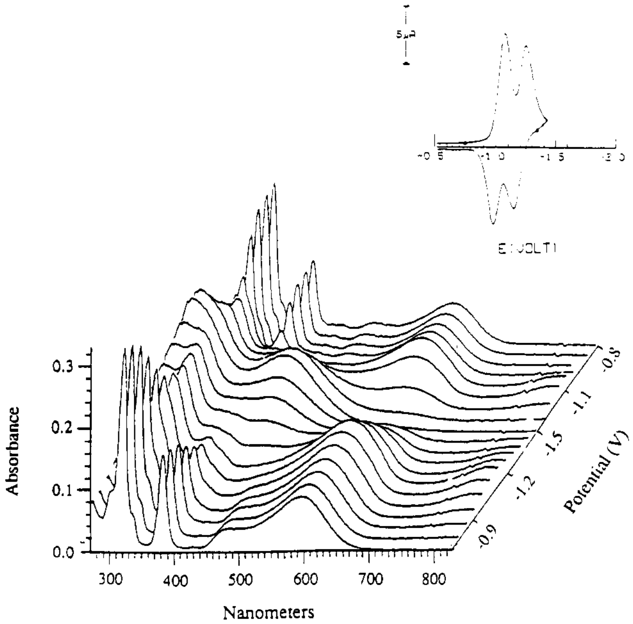

Figure 1. UV-vis spectroelectrochemical reduction of $Ir_2(dimen)_4^{2+}$ in 0.1 M $TBA^+PF_6^-/CH_3CN$. Absorbance spectra are plotted as a function of applied potential (vs Pt pseudoreference electrode). Data were collected at a sweep rate of 5 mV/s.

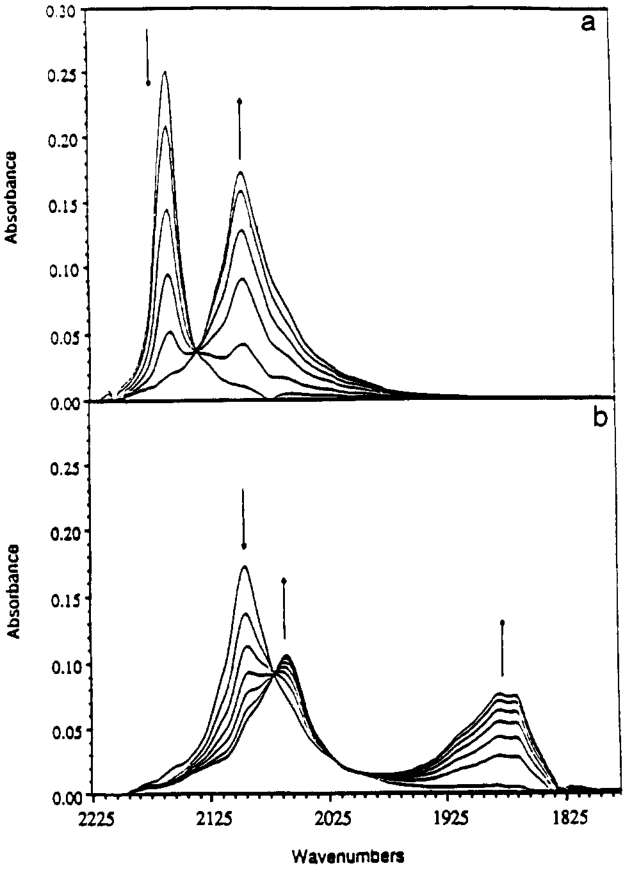

Figure 2. IR spectra recorded during the reduction of $Ir_2(dimen)_4^{2+}$ in 0.1 M $TBA^+PF_6^-/CH_3CN$ (a) during a potential sweep past the $E_{2+/+}°'$ couple, and (b) during a potential sweep past the $E_{+/0}°'$ couple.

remains intact upon $1e^-$ reduction, and that the additional electron is delocalized over both metal centers on the IR time scale.[17]

The spectroscopy of the neutral, $2e^-$ reduced complex, however, is inconsistent with a simple $(d_{z^2}\sigma)^2(d_{z^2}\sigma^*)^2(p_z\sigma)^2$ electronic configuration. The two ν(CN) stretches observed in the IR spectrum of $Ir_2(dimen)_4^0$ indicate that a significant asymmetry in the Ir–Ir core accompanies the addition of a second electron to $Ir_2(dimen)_4^{2+}$. One interpretation is that $Ir_2(dimen)_4^0$ is a mixed-valent, Ir(+)–Ir(–) complex;[19] the stretch at 2058 cm^{-1} arises from the CNR groups coordinated to Ir(+), while the stretch at 1869 cm^{-1} originates from the CNR groups bound to Ir(–). Assignment of the $Ir_2(dimen)_4^0$ electronic structure as formally d^8–d^{10} (rather than d^8–d^8–p^2) suggests that the local symmetry at the d^8 iridium center remains square planar while the ligands at the d^{10} metal distort toward a tetrahedral geometry.[20] The IR spectroscopy of $Ir_2(dimen)_4^0$ in 1,2-difluorobenzene[21] implies that CH_3CN (as well as other coordinating solvents) may bind to the neutral complex.[22,23]

Although we have not been able to confirm the mixed-valent nature of $Ir_2(dimen)_4^0$ by crystallographic means, we note that the flexibility and large range of bridging distances available to the dimen ligand are compatible with an unsymmetrical structure.[24] We also note that the potential difference between the two $1e^-$ reductions ($\Delta E°' = (E°'_{2+/+} - E°'_{+/0} = 0.19$ V) is considerably smaller than that predicted by purely electrostatic considerations.[27] As with other transition metal complexes that undergo multiple oxidation state changes at a discrete (or nearly discrete) thermodynamic potential,[28] the small $\Delta E°'$ value observed for $Ir_2(dimen)_2^{2+}$ implies that a large geometry change is involved in the net $2e^-$ transfer depicted in Scheme I. The structural change stabilizes $Ir_2(dimen)_4^{2+}$ and/or $Ir_2(dimen)_4^0$ relative to $Ir_2(dimen)_4^+$, resulting in a smaller separation between $E°'_{2+/+}$ and $E°'_{+/0}$ than would otherwise be observed. The reversibility of both processes on the CV time scale suggests these structural changes are rapid.

Finally, a d^8–d^{10} electronic description of $Ir_2(dimen)_4^0$ is supported by the observations of Eisenberg et al. concerning the solution chemistry of $Rh(dppe)_2$ (where dppe = 1,2-bis(diphenylphosphino)ethane).[30] In polar solutions and/or at low temperatures, $Rh(dppe)_2$ is unstable, yielding solutions that exhibit NMR and UV–vis spectra and reactivity patterns consistent with a disproportionated $Rh(dppe)_2^+$ (d^8)/$Rh(dppe)_2^-$ (d^{10}) ion pair.

As expected, these low-valent reduced species are highly reactive. Preliminary data suggest $Ir_2(dimen)_4^+$ undergoes oxidative addition reactions with CH_2Cl_2. A complete report concerning the spectroscopy, structure, and reactivity of $Ir_2(dimen)_4^{n+}$ will be presented elsewhere.

Acknowledgment. We wish to thank Johnson Matthey for a generous loan of iridium trichloride, Professor John E. Ellis for the use of his FTIR spectrometer, and the 3M Co. for partial support of this research. M.G.H. acknowledges the University of Minnesota for a Stanwood Johnston Memorial Fellowship.

---

(18) Caldararu, H.; DeArmond, M. K.; Hanck, K. W.; Sahini, V. E. *J. Am. Chem. Soc.* **1976**, *98*, 4455.

(19) Mixed-valence binuclear rhodium complexes have been previously described: (a) Dulebohn, J. I.; Ward, D. L.; Nocera, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 4054. (b) Ladd, J. A.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1984**, *23*, 2318 and referenced therein.

(20) A recently prepared mixed-metal Rh(I)–Ir(–I) complex adopts a similar asymmetric geometry. The crystal structure shows that the Rh(I) center is square-planar while the Ir(–I) center is tetrahedral. McDonald, R.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 1564.

(21) O'Toole, T. R.; Younathan, J. N.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 3923.

(22) In the noncoordinating 1,2-difluorobenzene, the ν(CN) stretches of $Ir_2(dimen)_4^0$ are shifted approximately 10 cm^{-1} to higher energy than in CH_3CN or acetone.

(23) Five-coordinate Ir(I) complexes are well-known. See, for example: Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335.

(24) A range of nearly 2.3 Å in metal–metal distance is spanned by known structures of binuclear iridium complexes containing the dimen ligand. For example, the Ir–Ir distance in $Ir_2(dimen)_4Ag^{3+}$ is 5.284 Å,[25] while the Ir–Ir distance in $Ir_2(dimen)_4(PPh_3)_2Au^{3+}$ is 2.986 Å.[26]

(25) Sykes, A. G.; Mann, K. R. *J. Am. Chem. Soc.* **1988**, *110*, 8252.

(26) Sykes, A. G.; Mann, K. R. *J. Am. Chem. Soc.* **1990**, *112*, 7247.

(27) Bowyer, W. J.; Geiger, W. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *239*, 253.

(28) (a) Pierce, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 6063 and references therein.

(29) (a) Kunin, A. J.; Nanni, E. J.; Eisenberg, R. *Inorg. Chem.* **1985**, *24*, 1852. (b) Mueller, K. T.; Kunin, A. J.; Greiner, S. Henderson, T.; Eisenberg, R. *J. Am. Chem. Soc.* **1987**, *109*, 6313.