Inorg. Chem. **2004**, *43*, 622–632

Inorganic Chemistry
Article

Binuclear Rhenium(I) Complexes with Bridging [2.2]Paracyclophane–Diimine Ligands: Probing Electronic Coupling through π–π Interactions

PJ Ball,[†] Tanya Rarog Shtoyko,[†] Jeanette A. Krause Bauer,[†] Warren J. Oldham,[‡] and William B. Connick*,[†]

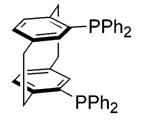
Department of Chemistry, University of Cincinnati, P.O. Box 210172,
Cincinnati, Ohio 45221-0172, and Chemistry Division, MS J-514, Los Alamos National
Laboratory, Los Alamos, New Mexico 87545

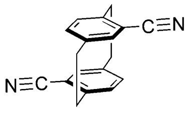
Received July 21, 2003

Two pseudo-*para* substituted *bis*-diimino[2.2]paracyclophane ligands (4,16-bis(picolinaldimine)-[2.2]paracyclophane (BPPc) and 4,16-bis(methyl-picolinaldimine)-[2.2]paracyclophane (BmPPc)) were prepared by the condensation reaction of the appropriate picolinaldimine with 4,16-diamino-[2.2]paracyclophane (**2**). An improved synthesis of **2** from [2.2]paracyclophane also is reported. BPPc (**3a**): monoclinic, $P2_1/c$, $a = 8.2238(11)$ Å, $b = 15.336(2)$ Å, $c = 8.4532(11)$ Å, $\beta = 98.578(3)°$, $V = 1054.2(2)$ Å^3, $Z = 2$. To investigate the binding properties of the *bis*-diimino[2.2]paracyclophane ligands, binuclear rhenium(I) tricarbonyl chloride complexes $[Re(CO)_3Cl]_2(\mu$-BPPc) (**5a**) and $[Re(CO)_3Cl]_2(\mu$-BmPPc) (**5b**) were prepared and fully characterized by infrared spectroscopy, ^{1}H NMR spectroscopy, elemental analysis, UV–visible absorption spectroscopy, and cyclic voltammetry. Two model complexes, Re(tolyl-pyCa)$(CO)_3Cl$ (**4**) (tolyl-pyCa = *N*-(*p*-tolyl)-2-pyridinecarboxaldimine) and $[Re(CO)_3Cl]_2(\mu$-PBP) (**6**) (PBP = *p*-phenylenebis(picolinaldimine)), also are reported. The dimeric compounds **5** and **6** each undergo two one-electron, predominantly diimine-centered reduction processes. Spectroscopic data and comproportionation constants (**5a**, 23 ± 9; **5b**, 23 ± 9; **6**, 2750 ± 540) are consistent with relatively weak interactions between the diimine groups mediated by the paracyclophane bridging group, and these results are consistent with steric and electronic factors.

Introduction

There is growing interest in the incorporation of [2.2]-paracyclophane into the backbone of metal-chelating ligands (e.g., [2.2]PHANEPHOS).[1] In particular, bridging ligands derived from paracyclophane afford the opportunity to investigate the role of π-stacking interactions in mediating electronic communication, as observed for charge-transport in double-stranded DNA[2] and other π-stacked systems.[3] The constrained geometry of [2.2]paracyclophane results in a 2.8 Å separation between the *ipso*-carbon atoms of the stacked rings and a 3.1 Å separation between the planes of the four unsubstituted atoms of each ring.[4] In other words, the inter-ring spacings are considerably shorter than the 3.4 Å interplanar separation between π-stacked bases of DNA, thereby placing an upper limit on the electronic interactions anticipated in double-stranded DNA.


[2.2]PHANEPHOS


PPDCP

The redox potentials of binuclear complexes, composed of two one-electron redox-active units (M^+) and an intervening bridging group, afford a convenient means of assessing electronic interaction. Reduction of one redox center influences reduction of the second, usually unfavorably, and the difference in the observed reduction potentials ($\Delta E = E_1°' - E_2°'$) is reflected in the comproportionation constant, K_c, for the M/M complex:[5]

$$M/M + M^+/M^+ \leftrightarrow 2M^+/M \tag{1}$$

$$K_c = \frac{[M^+/M]^2}{[M/M][M^+/M^+]} = \exp((\Delta E)F/RT) \tag{2}$$

---

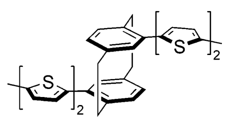
* To whom correspondence should be addressed. E-mail: bill.connick@uc.edu.

[†] University of Cincinnati.

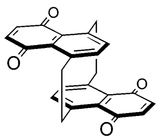
[‡] Los Alamos National Laboratory.

10.1021/ic0348648 CCC: $27.50

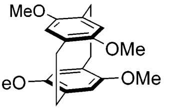
Studies of communication between inorganic,[6,7] as well as organic,[8−15] redox centers mediated by a bridging paracyclophane group indicate varying degrees of coupling, depending on the distance and means of attachment to the bridge. Richardson and Taube[6] examined a series of ruthenium dimers, $(NH_3)_5Ru(\mu\text{-PPDCP})Ru(NH_3)_5^{n+}$, with a pseudo-*para* substituted bridging ligand, PPDCP. The mixed valence Ru^{2+}/Ru^{3+} complex ($n = 5$) exhibits a very weak intervalence band (800 nm, 10 M^{-1} cm^{-1}) associated with Ru(II)-to-Ru(III) charge transfer. The ΔE value for the $Ru^{III/II}$ couples is 38 mV, corresponding to a comproportionation constant of $\sim$4, the statistical limiting value for non-interacting redox centers. Collard and co-workers[8] have observed evidence of stronger interactions for $\mathbf{I}^{2+}$ ($\Delta E = 100$ mV, $K_c \sim 50$), in which the pendant thiophene units are directly attached to the paracyclophane bridge. Not surprisingly, when redox-active groups are directly coupled to the π-system allowing for delocalization of charge over the paracyclophane bridge, as in **II**, **III**, and **IV**, larger ΔE values are observed (**II**, 200; **III**, 290; **IV**, 420 mV).[9] Similarly, very strong coupling is evident in the electrochemistry of bimetallic complexes with [2.2]paracyclophane arene bridging ligands.[7]



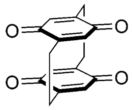
(I)



(II)



(III)



(IV)

As a first step toward developing systems that undergo photoinitiated electron-transfer, we have prepared two novel paracyclophane ligands with pseudo-*para* positioned pyridine carboxaldimine chelating groups. Binuclear rhenium complexes with these ligands are anticipated to provide insight into the influence of $\pi-\pi$ interactions on charge-injection into DNA or conjugated polymers from a metal-to-ligand-(diimine) charge-transfer excited state.[16−18] In the course of these studies, we developed an improved synthesis of pseudo-*para* substituted *bis*-diamino[2.2]paracyclophane (**2**). Here

---

(1) (a) Rozenberg, V.; Kharitonov, V.; Antonov, D.; Sergeeva, E.; Aleshkin, A.; Ikonnikov, N.; Orlova, S.; Belokon, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 91−92. (b) Belokon, Y.; Moscalenko, M.; Ikonnikov, N.; Yashkina, L.; Antonov, D.; Vorontsov, E.; Rozenberg, V. *Tetrahedron: Asymmetry* **1997**, *8*, 3245−3250. (c) Rabaâ, H.; Lacoste, M.; Delville-Desboise, M.-H.; Ruiz, J.; Gloaguen, B.; Ardoin, N.; Astruc, D.; Beuze, A. L.; Saillard, J.-Y.; Linares, J.; Varret, F.; Dance, J.-M.; Marquestaut, E. *Organometallics* **1995**, *14*, 5078−5092. (d) Kay, K. Y.; Baek, Y. G. *Chem. Ber./Recl.* **1997**, *130*, 581−584. (e) Comba, P.; Fath, A.; Huttner, G.; Zsolnai, L. *Chem. Commun.* **1996**, 1885−1886. (f) Comba, P.; Kühner, A. *Eur. J. Inorg. Chem.* **1999**, 509−515. (g) Rossen, K.; Pye, P. J.; Maliakal, A.; Volante, R. P. *J. Org. Chem.* **1997**, *62*, 6462−6463. (h) Pye, P. J.; Rossen, K.; Reamer, R. A.; Tsou, N. N.; Volante, R. P.; Reider, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 6207−6208. (i) Pye, P. J.; Rossen, K.; Reamer, R. A.; Volante, R. P.; Reider, P. J. *Tetrahedron Lett.* **1998**, *39*, 4441−4444. (j) Satou, T.; Takehara, K.; Hirakida, M.; Sakamoto, Y.; Takemura, H.; Miura, H.; Tomonou, M.; Shinmyozu, T. *J. Organomet. Chem.* **1999**, *577*, 58−68. (k) Masterson, D. S.; Hobbs, T. L.; Glatzhofer, D. T. *J. Mol. Catal. A: Chem.* **1999**, *145*, 75−81. (l) Masterson, D. S.; Glatzhofer, D. T. *J. Mol. Catal. A: Chem.* **2000**, *161*, 65−68. (m) Ruzziconi, R.; Piermatti, O.; Ricci, G.; Vinci, D. *Synlett* **2002**, 747−750. (n) Cipiciani, A.; Fringuelli, F.; Piermatti, O.; Pizzo, F.; Ruzziconi, R. *J. Org. Chem.* **2002**, *67*, 2665−2670. (o) Dahmen, S.; Bräse, S. *Chem. Commun.* **2002**, 26−27. (p) Hermanns, N.; Dahmen, S.; Bolm, C.; Bräse, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 3692−3694. (q) Bolm, C.; Wenz, K.; Raabe, G. *J. Organomet. Chem.* **2002**, *662*, 23−33. (r) Bryliakov, K. P.; Talsi, E. P.; Kühn, T.; Bolm, C. *New J. Chem.* **2003**, *27*, 609−614. (s) Zanotti-Gerosa, A.; Malan, C.; Herzberg, D. *Org. Lett.* **2001**, *3*, 3687−3690. (t) Maekawa, M.; Hashimoto, N.; Sugimoto, K.; Kuroda-Sowa, T.; Suenaga, Y.; Munakata, M. *Inorg. Chim. Acta* **2003**, *344*, 143−157.

(2) For recent reviews, see: (a) Barbara, P. F.; Olson, E. J. C. *Adv. Chem. Phys.* **1999**, *107*, 647−676. (b) Grinstaff, M. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 3629−3635. Giese, B. *Annu. Rev. Biochem.* **2002**, *71*, 51−70. (c) Lewis, F. D. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2001; Vol. 3, Chapter 5. (d) Treadway, C. R.; Hill, M. G.; Barton, J. K. *Chem. Phys.* **2002**, *281*, 409−428. (e) Boon, E. M.; Barton, J. K. *Curr. Opin. Struct. Biol.* **2002**, *12*, 320−329.

(3) For reviews, see: (a) Cornil, J.; Beljonne, D.; Calbert, J.-P.; Bredas, J.-L. *Adv. Mater.* **2001**, *13*, 1053−1067. (b) Miller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417−423. (c) Tolbert, L. M. *Acc. Chem. Res.* **1992**, *25*, 561−568.

(4) Hope, H.; Bernstein, J.; Trueblood, K. W. *Acta Crystallogr.* **1972**, *B28*, 1733−1743.

(5) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278−1285.

(6) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40−51.

(7) (a) Bowyer, W. J.; Geiger, W. E.; Boekelheide, V. *Organometallics* **1984**, *3*, 1079−86. (b) Voegeli, R. H.; Kang, H. C.; Finke, R. G.; Boekelheide, V. *J. Am. Chem. Soc.* **1986**, *108*, 7010−7016. (c) Plitzko, K. D.; Rapko, B.; Gollas, B.; Wehrle, G.; Weakley, T.; Pierce, D. T.; Geiger, W. E., Jr.; Haddon, R. C.; Boekelheide, V. *J. Am. Chem. Soc.* **1990**, *112*, 6546−6556. (d) Gollas, B.; Speiser, B.; Sieglen, J.; Straehle, J. *Organometallics* **1996**, *15*, 260−271.

(8) (a) Salhi, F.; Collard, D. M. *Adv. Mater.* **2003**, *15*, 81−85. (b) Salhi, F.; Lee, B.; Metz, C.; Bottomley, L. A.; Collard, D. M. *Org. Lett.* **2002**, *4*, 3195−3198.

(9) (a) Wartini, A. R.; Staab, H. A.; Neugebauer, F. A. *Eur. J. Org. Chem.* **1998**, 139−148. (b) Wartini, A. R.; Staab, H. A.; Neugebauer, F. A. *Eur. J. Org. Chem.* **1998**, 221−227. (c) Wartini, A. R.; Staab, H. A.; Neugebauer, F. A. *Eur. J. Org. Chem.* **1998**, 1161−1170.

(10) (a) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786−1787. (b) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631−2639.

(11) (a) Staab, H. A.; Rebafka, W. *Chem. Ber.* **1977**, *110*, 3333−3350. (b) Staab, H. A.; Herz, C. P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 392−393. (c) Herz, C. P.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 394. (d) Staab, H. A.; Joerns, M.; Krieger, C. *Tetrahedron Lett.* **1979**, 2513−2516. (e) Staab, H. A.; Krieger, C.; Wahl, P.; Kay, K. Y. *Chem. Ber.* **1987**, *120*, 551−558.

(12) Siegel, M. G.; Liotta, C. L.; Cram, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1387−1391.

(13) Allgeier, H.; Siegel, M. G.; Helgeson, R. C.; Schmidt, E.; Cram, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 3782−3789.

(14) (a) Zyss, J.; Ledoux, I.; Volkov, S.; Chernyak, V.; Mukamel, S.; Bartholomew, G. P.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 11956−11962. (b) Bartholomew, G. P.; Bazan, G. C. *Acc. Chem. Res.* **2001**, *34*, 30−39. (c) Bartholomew, G. P.; Bazan, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 5183−5196.

(15) (a) Bazan, G. C.; Oldham, W. J., Jr.; Lachicotte, R. J.; Tretiak, S.; Chernyak, V.; Mukamel, S. *J. Am. Chem. Soc.* **1998**, *120*, 9188−9204. (b) Oldham, W. J., Jr.; Miao, Y.; Lachicotte, R.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 419−420.

(16) (a) Thornton, N. B.; Schanze, K. S. *Inorg. Chem.* **1993**, *32*, 4994−4995. (b) Stoeffler, H. D.; Thornton, N. B.; Temkin, S. L.; Schanze, K. S. *J. Am. Chem. Soc.* **1995**, *117*, 7119−7128. (c) Thornton, N. B.; Schanze, K. S. *New J. Chem.* **1996**, *20*, 791−800. (d) Yam, V. W.-W.; Lo, K. K.-W.; Cheung, K.-K.; Kong, R. Y.-C. *Chem. Commun.* **1995**, 1191−1193. (e) Yam, V. W.-W. V.; Lo, K. K.-W.; Cheung, K.-K.; Kong, R. Y.-C. *J. Chem. Soc., Dalton Trans.* **1997**, 2067−2072. (f) Metcalfe, C.; Webb, M.; Thomas, J. A. *Chem. Commun.* **2002**, 2026−27.

(17) (a) Walters, K. A.; Ley, K. D.; Cavalaheiro, C. S. P.; Miller, S. E.; Gosztola, D.; Wasielewski, M. R.; Bussandri, A. P.; van Willigen, H.; Schanze, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 8329−8342. (b) Walters, K. A.; Premvardhan, L. L.; Liu, Y.; Peteanu, L. A.; Schanze, K. S. *Chem. Phys. Lett.* **2001**, *339*, 255−262.

we also report the synthesis and spectroscopic properties of a series of rhenium(I) tricarbonyl chloride complexes with these ligands. Electrochemical studies provide evidence of electronic interactions between the pendant diimine groups.

Experimental Section

All chemicals were used as supplied by Strem Chemical (NaO*t*Bu, BINAP, $Pd_2(dba)_3$, $Re(CO)_5Cl$), Fluka (benzophenone imine), Acros, or Aldrich, unless otherwise specified. Tetrahydrofuran (THF) was distilled from Na(s) and benzophenone imine, and benzene was distilled from calcium hydride. Toluene was dried over type 4A molecular sieves. Deuterated solvents were obtained from Cambridge Isotope Laboratories. Dimethyl formamide (DMF) was dried using sieves and magnesium sulfate before distillation under reduced pressure. All other chemicals were used as received. PBP (*p*-phenylenebis(picolinaldimine)),[19] *N*-(*p*-tolyl)-2-pyridinecarboxaldimine (tolyl-pyCa),[20] and 4,16-dibromo[2.2]paracyclophane[10b,21] were synthesized following published procedures. Elemental analyses were performed by Atlantic Microlab. ^1H NMR and ^{13}C NMR spectra were acquired at room temperature using a Bruker AC-250 instrument and are referenced in ppm vs a TMS standard. Proton decoupling experiments were used to make partial assignments. Mass spectra were obtained by electron impact ionization using a Kratos MS-25 instrument or by electrospray ionization using either an Ionspec HiRes ESI-FTICRMS instrument or a Micromass Q-TOF-II instrument. In all cases, the observed isotope patterns agreed well with the predicted patterns based on natural isotopic abundances. GC/mass spectrometry data were collected using a HP6890 GC/MS system with a Restek, Rtx-5 Sil MS column. UV−visible absorption spectra were obtained using a HP8453 diode array spectrometer, and 77 K emission spectra were recorded as previously described.[22] FTIR spectra were collected using a PerkinElmer Spectrum ONE FT-IR spectrometer. Electrochemical measurements were obtained using a standard three-electrode cell and a CV50w potentiostat from Bioanalytical Systems. Samples were dissolved in DMF solutions containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$), which was recrystallized twice from methanol and dried in a vacuum oven prior to use. All scans were recorded at 296 K using a platinum wire auxiliary electrode, a Ag/AgCl reference electrode, and a 0.79 mm^2 gold working electrode. Between scans, the working electrode was polished with 0.05 μm alumina, rinsed with distilled water, and wiped dry using a Kimwipe. The values of $(E_{pc} + E_{pa})/2$, which is an approximation of the formal potential for a redox couple, are referred to as $E^{\circ\prime}$. Reported potentials are referenced against Ag/AgCl, and calculated averages are reported as the average value $\pm 2\sigma$. Confidence limits for potential differences were estimated by propagation of standard deviations. Peak currents (i_p) were estimated with respect to the extrapolated baseline current as described elsewhere.[23] At 0.25 V/s sweep rate, the ferrocene/ferrocenium (FcH/FcH^+) couple occurred at 0.557 V ($\Delta E_p = 70$ mV; $i_{pa}/i_{pc} = 1.1$). Diffusion coefficients of **5** were estimated from chronocoulometry data and used in modeling of the cyclic voltammograms using DigiSim 2.1 from Bioanalytical Systems, assuming slight instability of the reduced complexes, as expected.[24]

4,16-Bis(benzophenone-imine)-[2.2]paracyclophane (1). 4,16-Dibromo-[2.2]paracyclophane (2.00 g, 5.46 mmol), benzophenone imine (2.38 g, 13.1 mmol), NaO*t*Bu (1.47 g, 15.3 mmol), tris-(dibenzylidenacetone)dipalladium ($Pd_2(dba)_3$, 0.025 g, 2.73×10^{-2} mmol), and racemic 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP, 0.0500 g, 8.20×10^{-2} mmol) were refluxed under N_2 or Ar in 22 mL of toluene at 130 °C for 4 days. Additional benzophenone imine, NaO*t*Bu, BINAP, and $Pd_2(dba)_3$ were added at irregular intervals, and the progress of the reaction was monitored by GC/mass spectrometry. Completion was determined by the presence of **1**, as well as the absence of starting materials and the monosubstituted intermediate. The mixture was cooled, diluted with 175 mL of diethyl ether, and filtered to give a gray-green solid. Repeated extraction with CH_2Cl_2 yielded a yellow-orange solution, which was reduced in volume, layered with hexanes, and cooled. The yellow pseudo-*para*-substituted product (2.21 g, 68%) was collected by vacuum filtration. Anal. Calcd for $C_{42}H_{34}N_2$: C, 89.00; H, 6.06; N, 4.94. Found: C, 88.78; H, 6.09; N, 4.95. ^1H NMR ($CDCl_3$,δ): 2.39−2.50 (m, 2H, PC), 2.69−2.78 (m, 2H, PC), 3.07−3.18 (m, 2H, PC), 3.24−3.33 (m, 2H, PC), 5.45 (s, 2H, PC), 6.24 (d, 2H, PC, *J* = 8 Hz), 6.97−7.02 (m, 3H, N−Ph_2, PC), 7.12−7.18 (m, 3H, N−Ph_2), 7.44−7.51 (m, 3H, N−Ph_2), 7.70−7.86 (dd, 3H, *J* = 8 Hz, 3 Hz, N−Ph_2). ^{13}C NMR ($CDCl_3$,δ): 165.14, 148.68, 140.12, 139.99, 136.83, 133.28, 130.88, 130.25, 129.36, 129.19, 128.15, 127.89, 127.59, 126.62, 126.41, 33.71, 32.07. MS (ESI): $m/z = 567.28$ (MH^+).

4,16-Diamino-[2.2]paracyclophane (2). To a yellow solution of compound **1** (1.98 g, 3.49 mmol) in 160 mL of THF was added 8 mL of 2.0 M HCl (16 mmol), causing the solution to turn bright orange. After refluxing under N_2 or Ar for 4.5 h, the cloudy colorless mixture was treated with 1.0 M HCl and 2:1 hexanes/EtOAc. The isolated aqueous layer was made alkaline by addition of 5.0 M NaOH, resulting in a white precipitate. After extraction with methylene chloride, the organic washings were dried with $MgSO_4$ and reduced to dryness. In some instances, multiple washings were necessary to remove benzophenone impurity. The colorless pseudo-*para*-diamino product (0.554 g, 66.7%) is air sensitive and rapidly turns gray. ^1H NMR ($CDCl_3$,δ): 2.59−3.20 (m, 8H), 3.44 (s, 4H), 5.45 (s, 2H), 6.18 (d, 2H, *J* = 7 Hz), 6.58 (d, 2H, *J* = 7 Hz). MS (EI): $m/z = 238.144$ (M^+).

4,16-Bis(picolinaldimine)-[2.2]paracyclophane(BPPc) (3a). Compound **2** (0.495 g, 2.08 mmol) was stirred with 15 mL of ethanol at 60 °C. 2-Pyridinecarboxaldehyde (1.00 g, 8.32 mmol) was added dropwise, causing the mixture to turn lime green. After addition of 20 mL of ethanol, the mixture was refluxed for 2 h and subsequently cooled overnight. The resulting pale yellow solid (0.726 g, 84%) is stable, but solutions of **3a** are light-sensitive. ^1H NMR ($CDCl_3$, δ): 2.70−2.81 (m, 2H), 3.04−3.14 (m, 2H), 3.22−3.33 (m, 2H), 3.79−3.88 (m, 2H) 6.11 (s, 2H), 6.39 (d, 2H, *J* = 8 Hz), 6.79 (d, 2H, *J* = 7 Hz), 7.40 (dd, 2H, *J* = 6, 6 Hz), 7.88 (dd, 2H, *J* = 8, 8 Hz), 8.39 (d, 4H, *J* = 10 Hz), 8.72 (d, 2H, *J* = 5 Hz). Anal. Calcd for $C_{28}N_4H_{24}$: C, 80.74; H, 5.82; N,13.44. Found C, 80.04; H, 5.81; N, 13.37. MS (EI): $m/z = 416.200$ (M^+).

4,16-Bis(methyl-picolinaldimine)-[2.2]paracyclophane(BmPPc) (3b). 4,16-Diamino-[2.2]paracyclophane (0.210 g, 0.88 mmol)

---

(18) (a) Leidner, C. R.; Sullivan, B. P.; Reed, R. A.; White, B. A.; Crimmins, M. T.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 882−91. (b) Ley, K. D.; Walters, K. A.; Schanze, K. S. *Synth. Met.* **1999**, *102*, 1585−1586. (c) Chan, W. K.; Ng, P. K.; Gong, X.; Hou, S. *J. Mater. Chem.* **1999**, *9*, 2103−2108. (d) Ng, P. K.; Gong, X.; Chan, S. H.; Lam, L. S. M.; Chan, W. K. *Chem. Eur. J.* **2001**, *7*, 4358−4367.

(19) Haga, M.-A.; Koizumi, K. *Inorg. Chim. Acta* **1985**, *104*, 47−50.

(20) Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660−2666.

(21) Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3527−3533.

(22) Jude, H.; Krause Bauer, J. A.; Connick, W. B. *Inorg. Chem.* **2002**, *41*, 2275−2281.

(23) Kissinger, P. T.; Heineman, W. R. *J. Chem. Educ.* **1983**, *60*, 702−706.

(24) Stor, G. J.; Hartl, F.; van Outersterp, J. W. M.; Stufkens, D. J. *Organometallics* **1995**, *14*, 1115−1131.

was stirred with 15 mL of ethanol at 60 °C. 2-Acetylpyridine (0.213 g, 1.76 mmol) was added to the mixture, and approximately 20 mL of ethanol was added. The mixture was refluxed under argon for 24 h, and subsequently the solvent was removed by rotary evaporation. The crude pseudo-*para*-substituted [2.2]paracyclophane product (0.090 g, 23%) was recrystallized from hot ethanol. The compound is stable in the solid state, but light-sensitive in solution. ^{1}H NMR ($CDCl_3$,δ): 2.25 (s, 3H), 2.60−2.65 (m, 2H), 2.95−3.00 (m, 2H), 3.22−3.32 (m, 4H), 5.69 (s, 2H), 6.40 (d, 2H, $J = 8$ Hz), 7.03 (d, 2H, $J = 7$ Hz), 7.40 (t, 2H, $J = 6$ Hz), 7.89 (t, 2H, $J = 6$ Hz), 8.53 (d, 2H, $J = 10$ Hz), 8.68 (d, 2H, $J = 4$ Hz). Anal. Calcd for $C_{30}N_4H_{28}\cdot{}^1/_2H_2O$: C, 79.44; H, 6.44; N, 12.35; Found C, 79.21; H, 6.49; N, 11.94. MS (ESI): $m/z = 445.23$ (MH^+).

Re(tolyl-pyCa)(CO)$_3$Cl (4). A solution of *N*-(*p*-tolyl)-2-pyridinecarboxaldimine (tolyl-pyCa) (1.12 g, 0.61 mmol) and Re(CO)$_5$Cl (0.11 g, 0.30 mmol) in 40 mL of benzene was heated at 60 °C for 6 h. The resulting reaction mixture was reduced in volume, and *n*-pentane was added. The yellow product (0.142 g, 75% yield) was collected by vacuum filtration and recrystallized from CH_2Cl_2/pentane. Anal. Calcd for $Re_2C_{34}N_4H_{24}O_6Cl_2$: C, 38.28; H, 2.41; N, 5.58. Found: C, 38.49; H, 2.49; N, 5.47. ^{1}H NMR (d_6-DMSO, δ): 2.40 (s, 3H), 7.39 (d, 2H), 7.48 (d, 2H), 7.84 (ddd, 1H), 8.36 (m, 2H), 9.06 (d, 1H), 9.31 (s, 1H). MS (ESI, methanol with $NaNO_3$): $m/z = 467.036$ (Re(tolyl-pyCa)(CO)$_3^+$), 524.994 (MNa^+). IR (KBr pellet) ν_{CO}: 2022, 1918, 1894 cm^{-1}.

[Re(CO)$_3$Cl]$_2$(*μ*-BPPc) (5a). **5a** was prepared by the same procedure as for **4**, except substituting the appropriate starting materials: **3a** (0.014 g, 0.035 mmol) and Re(CO)$_5$Cl (0.025 g, 0.069 mmol). The product (0.035 g, 69% yield) was recrystallized from DMF/diethyl ether. Anal. Calcd for $Re_2C_{34}N_4H_{24}O_6Cl_2$: C, 39.75; H, 2.36; N, 5.46. Found: C, 39.87; H, 2.53; N, 5.62. ^{1}H NMR (d_6-DMSO, δ): 2.95−4.02 (m), 6.60 (s, 2H), 6.67 (s, 2H), 6.8−7.0 (m, 8H), 7.89 (m, 4H), 8.45 (m, 4H), 8.62 (m, 4H), 9.10 (m, 4H), 9.40 (m, 4H). IR (KBr pellet) ν_{CO}: 2019, 1911, 1890 cm^{-1}.

[Re(CO)$_3$Cl]$_2$(*μ*-BmPPc) (5b). **5b** was prepared by the same procedure as for **4**, except substituting the appropriate starting materials: **3b** (0.015 g, 0.035 mmol) and Re(CO)$_5$Cl (0.025 g, 0.069 mmol). The product (0.018 g, 50% yield) was recrystallized from DMF/diethyl ether. Anal. Calcd for $Re_2C_{36}N_4H_{28}O_6Cl_2$: C, 40.94; H, 2.68; N, 5.31. Found: C, 40.86; H, 2.85; N, 5.34. ^{1}H NMR (d_6-DMSO, δ): 2.22−3.33 (m, 8H), 2.32 (s, 6H), 2.42 (s, 6H), 6.78 (s, 4H), 7.15 (d, 2H), 7.91 (m, 2H), 8.43 (m, 4H), 9.19 (d, 2H). IR (KBr pellet) ν_{CO}: 2019, 1911, 1890 cm^{-1}.

[Re(CO)$_3$Cl]$_2$(*μ*-PBP) (6). **6** was prepared by the same procedure as for **4**, except substituting the appropriate starting materials: PBP (0.020 g, 0.0069 mmol) and Re(CO)$_5$Cl (0.050 g, 0.138 mmol). Yield: 0.057 g, 96%. Anal. Calcd for $Re_2C_{24}N_4H_{14}O_6C_{l2}\cdot 2H_2O$: C, 30.87; H, 1.94; N, 6.00. Found: C, 30.35; H, 1.52; N, 5.67. ^{1}H NMR (d_6-DMSO, δ): 7.80 (s, 4H), 7.89 (m, 2H), 8.41 (m, 4H), 9.11 (d, 2H), 9.48 (s, 2H). ^{1}H NMR (d_6-acetone, δ): 7.86 (s, 4H), 7.95 (dd, 2H), 8.38−8.53 (m, 4H), 9.19 (d, 2H), 9.48 (s, 2H). MS (ESI, acetonitrile): $m/z = 920.0$ (MNa^+), 936.9 (MK^+). MS (ESI, acetonitrile/methanol with $NaNO_3$): $m/z = 890.959$ ([Re(CO)$_3$(CH_3CO)]$_2$(PBP)$^+$), 903.985 ([Re(CO)$_3$]$_2$(PBP)(Cl)(CH_3CN)$^+$). IR (KBr pellet) ν_{CO}: 2024, 1916, 1894 cm^{-1}.

X-ray Crystallography. Experimental and metrical data for crystals of **1** and PBP are provided in the Supporting Information. A yellow plate of **3a** was obtained by slow evaporation of a CH_2Cl_2/hexanes solution. Diffraction data were collected at 150 K on a standard Bruker SMART 1K CCD diffractometer with graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å. Data frames were processed using the program SAINT.[25] The data were corrected for decay, Lorentz, and polarization effects. An absorption correction based on the multiscan technique was applied using SADABS.[26] The structure was solved by a combination of direct methods using SHELXTL v5.03[27] and the difference Fourier technique, and the solution was refined by full-matrix least squares on F^2 for reflections diffracting out to 0.75 Å resolution. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were calculated based on geometric criteria and treated with a riding model. The isotropic temperature factors for the H atoms were defined as 1.2 times U_{eq} of the adjacent atom. A final difference Fourier map was featureless, with the highest residual electron density peak of 0.427 e Å^{-3}. Experimental data are summarized in Table 1.

Table 1. Crystallographic Data for **3a**

formula	$C_{28}H_{24}N_4$	Z	2
fw, g/mol	416.51	ρ_{calc}, g cm^{-3}	1.312
space group	$P2_1/c$	T, K	150(2)
a, Å	8.2238(11)	radiation, Å	0.71073
b, Å	15.336(2)	no. of reflcns collcd	6759
c, Å	8.4532(11)	no. of indep reflcns	2590
α, deg	90	GOF on F^2	1.050
β, deg	98.578(3)	R_1/wR_2 [$I > 2\sigma(I)$]^a	0.0645/0.1671
γ, deg	90	R_1/wR_2 (all data)^a	0.1017/0.1858
V, Å^3	1054.2(2)		

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Results and Discussion

Synthesis. Though several examples of N-substituted imino-[2.2]paracyclophane derivatives are known,[1k−m,28] disubstituted varieties have not been reported. A convenient route to the targeted pseudo-*para* substituted *bis*-diimino-[2.2]paracyclophane ligands (**3**) was devised based on the preparation of the pseudo-*para* diamino precursor **2**, followed by condensation with the appropriate picolinaldimine. Previous syntheses of **2** suffered from low yields and required extensive chromatography. Cram and co-workers[13,29] reported a 5-step procedure starting from [2.2]paracyclophane and giving **2** in 0.7% overall yield. Subsequently, Neugebauer and Fischer[30] reported a two-step procedure, involving nitration to give pseudo-*para* dinitro[2.2]paracyclophane, followed by reduction to give **2**. Though the second step gives good yields (67%), the dinitro precursor is obtained in low yields after chromatography (1.4%),[21] and the overall yield of **2** is estimated to be 0.9%. Recently, Langer and co-workers[31] reported a similar two-step procedure; however, even after chromatography following each step, the product (91%) was found to be a 1:3 mixture of 4-amino[2.2]-

---

(25) Bruker SMART v5.051 and SAINT v5.A06 programs were used for data collection and data processing, respectively. Bruker Analytical X-Ray Instruments, Inc., Madison, WI.

(26) SADABS was used for the application of semiempirical absorption and beam corrections for the CCD data. G. M. Sheldrick, University of Göttingen, Göttingen, Germany, 1996.

(27) SHELTX v5.03 was used for the structure solution and generation of figures and tables. G. M. Sheldrick, University of Göttingen, Göttingen, Germany, and Siemens Analytical X-ray Instruments, Inc., Madison, WI.

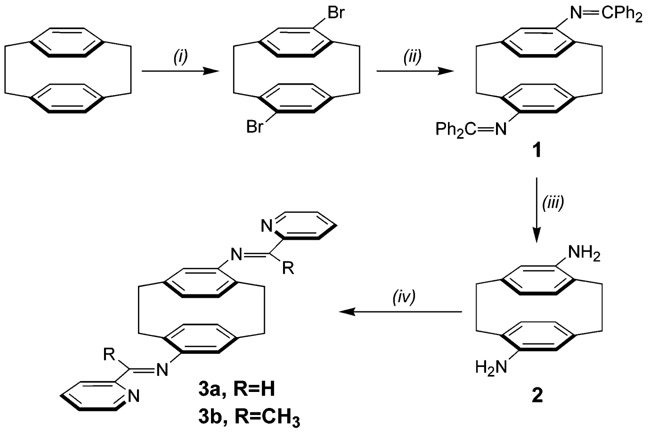
(28) Aly, A. A.; Mourad, A.-F. E.; El-Shaieb, K. M.; Hopf, H. *Synth. Commun.* **2001**, *31*, 637−644.

(29) Singer, L. A.; Cram, D. J. *J. Am. Chem. Soc.* **1963**, *85*, 1080−1084.

(30) Neugebauer, F. A.; Fischer, H. *J. Chem. Soc., Perkins Trans. 2* **1981**, 896−900.

(31) Lahann, J.; Hocker, H.; Langer, R. *Angew. Chem.* **2001**, *40*, 726−728.

Scheme 1. Synthesis of Paracyclophane Diimine Ligands, **3a** and **3b**[a]



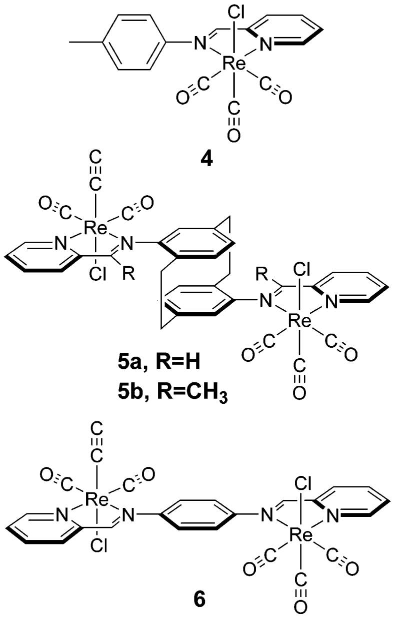
[a] (i) Br_2, CCl_4; (ii) NaO^{t}Bu, benzophenone imine, toluene; (iii) HCl, THF; (iv) 2-pyridinecarboxaldehyde (a) or 2-acetylpyridine (b), EtOH.

paracyclophane and the disubstituted product, and compound **2** was not isolated.

To overcome these limitations, we adopted a strategy based on Buchwald's[32] method of palladium-catalytic amination of aryl bromides (Scheme 1). A somewhat similar procedure was reported for the preparation of a pseudo-*ortho*-aminobromo[2.2]paracyclophane.[1g] Pseudo-*para* dibromo-[2.2]paracyclophane (27%)[10b,21] was allowed to react with benzophenone imine in the presence of base and catalyst to produce **1**, which was characterized by mass spectrometry, elemental analysis, ^1H and ^{13}C NMR spectroscopies, and X-ray crystallography. In contrast to pseudo-*ortho* substitution reactions,[1g] analytically pure product was readily isolated without chromatography. Hydrolysis using HCl in THF gave exclusively the pseudo-*para* diamino product (**2**) in 12.2% unoptimized overall yield without chromatography. The compound was characterized by ^1H NMR and mass spectrometry, but because of its instability in air, the product was typically used immediately in the subsequent step. Condensation with pyridinecarboxaldehyde or 2-acetylpyridine gave the picolinaldimino bridging ligands, **3a** or **3b**, respectively. The products were characterized by mass spectrometry, elemental analysis, and ^1H NMR spectroscopy, as well as X-ray crystallography in the case of **3a**. For the purpose of comparison, additional N-substituted pyridine carboxaldimine ligands tolyl-pyCa[20] and PBP[19] also were prepared.

The rhenium(I) complexes **4**, **5**, and **6** (Scheme 2) were prepared from $Re(CO)_5Cl$ by the general method of Wrighton and Morse.[33] The complexes were isolated as yellow-orange solids, and all four compounds gave satisfactory elemental analyses. The paracyclophane-bridged complexes are only moderately soluble in DMSO and DMF, whereas **4** and **6** also are soluble in less polar solvents. Infrared spectra of samples contained in KBr pellets exhibit three ν(CO) stretching bands, as expected for *fac*-tricarbonyl complexes.[34]

Scheme 2



The band maxima for the paracyclophane-bridged complexes (**5**) occur at slightly lower frequencies than those of **4** and **6**, suggesting increased electron density on the metal centers. Mass spectra were recorded using the approach of Hori and Ishianti,[35] whereby a small amount of sodium ions was added to a solution of the analyte prior to volatilization by electrospray injection. Under these conditions, compound **4** gave the expected spectrum composed of two sets of mass peaks corresponding to loss of halide ($Re(tolyl\text{-}pyCa)(CO)_3^+$) and to formation of a Na^+ adduct, $[Re(tolyl\text{-}pyCa)(CO)_3Cl + Na]^+$. For dimers **5** and **6**, this procedure and variations gave spectra with multiple sets of peaks, including $[M + Na]^+$.

Crystal Structure of 3a. An ORTEP diagram is shown in Figure 1, and selected bond lengths and angles are given in Table 2. The constrained [2.2]paracyclophane core induces characteristic puckering of the paracyclophane phenylene groups to give a boatlike conformation.[36] The nonbonded C···C distance between the *ipso* carbons, C3 and C6A (2.82 Å), is significantly shorter than the distance (3.07 Å) between the mean planes defined by the remaining four C atoms comprising the phenylene ring (C1−C2−C4−C5). These distances are similar to those found for **2**, as well as those reported for other pseudo-*para* substituted compounds (2.76 and 3.07 Å).[4,15,36] The bent geometry of the phenylene rings is reflected in the 11.8(3)° and 12.5(3)° dihedral angles formed by the C1−C2−C4−C5 with the C2−C3−C4 plane and the C1−C6−C5 plane, respectively.

The crystal structure also confirms the expected *E* configuration of the imine. The C9═N1(imine) double bond (1.258(3) Å) is slightly shorter than observed for PBP (1.273-

---

(32) Wolfe, J. P.; Ahman, J.; Sadighi, J. P.; Singer, R. A.; Buchwald, S. L. *Tetrahedron Lett.* **1997**, *38*, 6367−6370.

(33) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998−1003.

(34) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

(35) (a) Hori, H.; Ishihara, J.; Koike, K.; Takeuchi, K.; Ibusuki, T.; Ishitani, O. *Chem. Lett.* **1997**, *3*, 273−274. (b) Hori, H.; Ishihara, J.; Koike, K.; Takeuchi, K.; Ibusuki, T.; Tanabe, J.; Ishitani, O. *Anal. Sci.* **1998**, *14*, 287−292.

(36) Keehn, P. M. *Cyclophanes*; Academic Press: New York, 1983; Vol. 1.

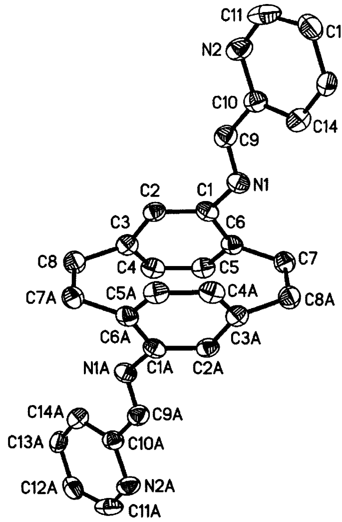


Figure 1. ORTEP diagram with 50% probability ellipsoids showing the geometry of **3**. H atoms are not shown for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3a**[a]

N(1)−C(9)	1.258(3)	N(1)−C(1)	1.425(3)
C(3)−C(8)	1.518(3)	C(6)−C(7)	1.516(3)
C(7)−C(8)#1	1.583(3)	C(9)−C(10)	1.476(3)
C(9)−N(1)−C(1)	118.2(2)	N(1)−C(9)−C(10)	122.1(2)
C(6)−C(7)−C(8)#1	112.5(2)	C(3)−C(8)−C(7)#1	112.7(2)
N(1)−C(1)−C(6)	116.9(2)	N(1)−C(1)−C(2)	121.8(2)
C(1)−C(6)−C(7)	121.1(2)	C(2)−C(3)−C(8)	120.9(2)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1$, $-y$, $-z + 1$.

(2) Å). Though the difference is on the edge of statistical significance, the trend is consistent with the expected decrease in bond length with increasing electron-donating character of the phenyl substituent, as noted for benzylideneanilines.[37] The pyridyl ring and the imine group (C1−N1−C9−C10) are nearly coplanar, forming a 6.4(2)° torsion angle (α) and a short intermolecular contact between the N(imine) and a H(pyridyl) atom (N1···H14, 2.63 Å). The imine group is canted with respect to the phenylene groups of the paracyclophane, as defined by C1−C2−C4−C5, forming a 44.8(2)° torsion angle (β). This orientation results in a short intramolecular contact between the N(imine) and a methylene proton (N1···H7A, 2.65 Å). In the case of **1**, similar short contacts are observed for the N(imine) with H(phenyl) (2.54 Å) and H(methylene) (2.57 Å) atoms. For comparison, Ph-pyCa crystallizes with two molecules in the asymmetric unit, each disordered in a head-to-tail arrangement; the resulting α and β dihedral angles are equal within each molecule with values of 8.9(8) and 17.9(7)°. Evidently, the conformational energy surface is relatively shallow along the β coordinate, since the related PBP ligand adopts a nearly planar structure in the solid state with α and β angles of 2.8(2)° and 15.9(2)°, respectively. However, the 34.1° dihedral angle observed[38] for Re(Ph-pyCa)(CO)$_3$Cl is consistent with the notion that, upon metal binding, steric factors will favor a twisted geometry and decreased π coupling.

NMR Spectroscopy. ^{1}H NMR spectra of **1**−**3** in CDCl$_3$ exhibit patterns of resonances consistent with the inversion symmetry of pseudo-*para* substituted [2.2]paracyclophanes.[13,29,39] A set of four multiplet resonances, corresponding to the eight bridging paracyclophane protons, occurs between 2.4 and 3.9 ppm. The three aromatic paracyclophane resonances, each corresponding to two protons (*ortho*, singlet; *meta*, doublet; *para*, doublet), occur between 5.4 and 7.0 ppm. In the case of the benzophenone−imine product (**1**), the ^{13}C NMR spectrum shows seventeen resonances, as expected from the inequivalency of the phenyl groups.[40] The aromatic region of the ^{1}H NMR spectrum is complicated by overlapping resonances of the phenyl protons (7.0−7.9 ppm). The *ortho* (5.45 ppm) and *meta* (6.24 ppm) paracyclophane proton resonances are shifted upfield relative to [2.2]-paracyclophane (6.37 ppm), whereas the *para* resonance occurs further downfield, buried under a phenyl imine resonance (7.0 ppm). Reich and Cram have previously noted that chemical shifts of *ortho*, *meta*, and *para* resonances exhibit a characteristic pattern in pseudo-*para* substituted [2.2]paracyclophanes, with the *para* proton resonance downfield of the *meta* and a large upfield shift of the *ortho* resonance with increasingly electron-donating substituents.[39] The relatively small *para* upfield shift with electron-releasing substituents has been ascribed to damping of electron delocalization due to the nonplanar geometry of the phenylene rings.[13,39] In the case of **1**, the large upfield shift of the *ortho* proton resonance relative to [2.2]paracyclophane (6.37 ppm) is consistent with substantial shielding by the imine group. The large downfield shift (−0.6 ppm) of the *para* resonance is characteristic of pseudo-*gem* deshielding by the transannular substituent.[13]

The ^{1}H NMR spectrum of the diamino derivative (**2**) confirms the previous assignment of these resonances in the spectrum of a mixture of the pseudo-*para* and pseudo-*meta* isomers.[31] A broad singlet due to the amine protons occurs at 3.44 ppm, and three aromatic resonances, each corresponding to two protons, occur at 5.45 (*ortho*), 6.18 (*meta*), and 6.58 ppm (*para*). The *ortho* and *meta* chemical shifts are within 0.07 ppm of those estimated using Cram's substituent chemical shift values (5.37 and 6.25 ppm, respectively) and remarkably similar to those of **1**. However the *para* chemical shift is 0.27 ppm upfield of the estimated value (6.85 ppm). Using these data and those for nine previously reported compounds,[13] we find there exists a satisfactory empirical correlation ($R^2 = 0.949$) between the *meta* chemical shifts (δ_m) of 10 pseudo-*para* substituted [2.2]-paracyclophanes and the Hammett *para*-substituent parameter (σ_p),[41] according to

$$\delta_m = 0.308(\sigma_p) + 6.38 \qquad (3)$$

Not surprisingly, correlations for *ortho* and *para* chemical shifts are poor, most likely in part because these protons are

---

[37] Bürgi, H. B.; Dunitz, J. D. *Helv. Chim. Acta* **1971**, *54*, 1255−1260.

[38] Dominey, R. N.; Hauser, B.; Hubbard, J.; Dunham, J. *Inorg. Chem.* **1991**, *30*, 4754−4758.

[39] Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3534−3543.

[40] Spencer, L.; Euler, W. B.; Traficante, D. D.; Kim, M.; Rosen, W. *Magn. Reson. Chem.* **1998**, *36*, 398−402.

[41] Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328−4337.

situated closer to the transannular substituent. In the case of the δ_m values, the fortuitous correlation with σ_p suggests that both resonance and field contributions to the chemical shift are significant. Correlations with σ_m (which emphasizes electrostatic effects with respect to σ_p) and with σ_p^+ (which emphasizes resonance effects with respect to σ_p and typically correlates better with δ)[42] are significantly weaker. Similarly, correlations with Swain and Lupton[41] field (×*c1*, $R^2 = 0.783$) and resonance ($\mathscr{R}$, $R^2 = 0.758$) parameters also are weaker, and a best-fit model based on both parameters suggests approximately equal weighting of these effects with only slight improvement ($R^2 = 0.958$) over the single σ_p parameter model. This result contrasts with Ewing's observation that aromatic chemical shift correlations, even those for δ_m, tend to weight resonance effects more heavily than electrostatic effects.[42] It is tempting to simply conclude that mesomeric effects are dampened in bent paracyclophane rings. However, it also should be noted that *meta* and pseudo-*meta* substituent chemical shift values for [2.2]paracyclophanes are small and of roughly similar magnitude,[13] indicating that transannular effects, which are reasonably dominated by electrostatic interactions,[12] also have a significant influence on δ_m.

The ^{1}H NMR spectrum of the bridging ligand **3a** exhibits eight aromatic resonances with four pyridyl protons and the imine proton occurring between 7.4 and 8.7 ppm. The *ortho*, *meta*, and *para* resonances (6.11, 6.39, and 6.79 ppm, respectively) are shifted downfield of those observed for **1** and **2**, reflecting somewhat increased electron-accepting character of the imine substituents. The ^{1}H NMR spectrum of the methylated diimine ligand (**3b**) exhibits a similar pattern, except the imine proton resonance (8.38 ppm) is replaced by a singlet at 2.25 ppm, attributable to the methyl protons. The pyridyl and the *meta* paracyclophane proton chemical shifts are nearly identical to those of **3a**. Assuming the value of σ_p for a benzylideneamino substituent (0.0),[43] the *meta* chemical shifts for **3a** and **3b** are in excellent agreement with eq 3. However, the *ortho* and *para* resonances (5.69 and 7.03 ppm) for **3b** are shifted from those of **3a**, most likely as a result of the closer approach of the imino methyl group to these protons as compared to the imino hydrogen.

The ^{1}H NMR spectrum of the monomeric rhenium(I) complex (**4**) exhibits the expected pattern for the tolyl-pyCa ligand, consisting of seven resonances between 7.3 and 9.3 ppm and a singlet at 2.40 ppm due to the methyl protons. As observed for related complexes,[38,44,45] substantial deshielding of the imine proton results in a characteristic downfield shift of this resonance (9.31 ppm) from that observed for free tolyl-pyCa. NMR studies of rhenium dimers **5a** and **5b** were hampered by poor solubility. The aromatic region of the ^{1}H NMR spectrum of **5a** is consistent with sixteen resonances of approximately equal intensities, twice as many as for the free ligand. Notably, two *ortho* resonances occur as singlets at 6.60 and 6.67 ppm. The accumulated data are consistent with the presence of enantiomeric and meso forms of the dimer in a 1:1 ratio, though the possibility of rotational isomers of one of these forms cannot be entirely discounted. The downfield shift of the pyridyl resonances from those of the free ligand is diagnostic of metal coordination. Though the imine proton resonances could not be conclusively assigned, they most likely overlap with paracyclophane resonances near 7.0 pm, indicating a substantial upfield shift with respect to related Re(I) complexes,[38,44,45] possibly as a result of shielding via through-space interaction with the paracyclophane group. In support of this notion, molecular models of **5** suggest that a coplanar arrangement of the diimine groups and the attached paracyclophane phenylene rings is unfavorable. The spectrum of **5b** is qualitatively similar; however, the two sets of resonances occur in an approximately 2:1 ratio, as might be expected if one enantiomer is slightly more favored than the other. The imine methyl proton resonances occur at 2.32 and 2.42 ppm. In contrast, the ^{1}H NMR spectrum of **6** exhibits six aromatic resonances and gives no indication of the presence of isomers. However, it is reasonable to expect rotation about the N−C(phenylene) bond to be fast on the NMR time scale[44,46] and proton environments of the meso and enantiomeric forms to be very similar.

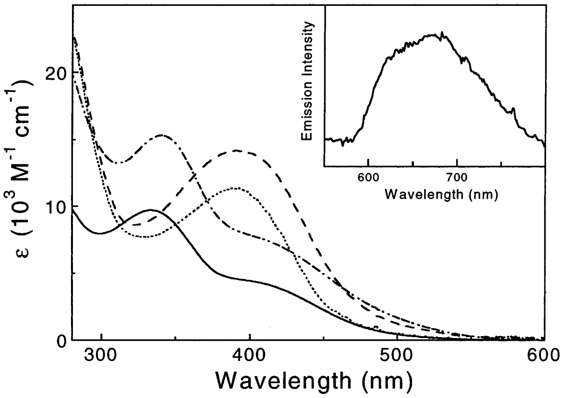


Figure 2. UV−visible absorption spectra of **4** (—), **5a** (− − −), **5b** (···), and **6** (·· − −) in DMF solution. Inset shows emission from **4** in 77 K butyronitrile glassy solution ($\lambda_{ex} = 415$ nm).

Electronic Structures and Electronic Coupling. The UV−visible absorption spectra of **4**, **5**, and **6** in DMF (Figure 2, Table 3) exhibit intense, short-wavelength absorption bands below 300 nm. Spectra of the free diimine ligands indicate that ligand-centered transitions contribute significant intensity in this region. Compounds **4** and **6** also exhibit intense absorption bands near 335 nm, and a similar feature occurs in the spectra of related Re(I) R-pyCa complexes,[38,47] as well as Mo(0) and Rh(III) PBP-bridged dimers.[19,48] The

---

(42) Ewing, D. F. In *Correlation of NMR Chemical Shifts with Hammett σ Values and Analogous Parameters*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; p 546.

(43) Ryan, J. J.; Humffray, A. A. *J. Chem. Soc. B* **1966**, 842−845.

(44) Creber, M. L.; Orrell, K. G.; Osborne, A. G.; Sik, V.; Bingham, A. L.; Hursthouse, M. B. *J. Organomet. Chem.* **2001**, *631*, 125−134.

(45) (a) Yam, V. W.-W.; Wang, K.-Z.; Wang, C.-R.; Yang, Y.; Cheung, K.-K. *Organometallics* **1998**, *17*, 2440−2446. (b) Yam, V. W.-W.; Yang, Y.; Zhang, J.; Chu, B. W.-K.; Zhu, N. *Organometallics* **2001**, *20*, 4911−4918.

(46) (a) Granifo, J.; Bird, S. J.; Orrell, K. G.; Osborne, A. G.; Sik, V. *Inorg. Chim. Acta* **1999**, *295*, 56−63. (b) Orrell, K. G.; Osborne, A. G.; Sik, V.; Webba da Silva, M.; Hursthouse, M. B.; Hibbs, D. E.; Abdul Malik, K. M.; Vassilev, N. G. *J. Organomet. Chem.* **1997**, *538*, 171−183.

(47) Rossenaar, B. D.; Stufkens, D. J.; Vlcek, A., Jr. *Inorg. Chem.* **1996**, *35*, 2902−2909.

Table 3. UV−Visible Absorption Data and Reduction Potentials[a] for **4**, **5a**, **5b**, and **6**

compound	abs (DMF) λ_{max}, nm (ϵ, cm^{-1} M^{-1})	$E_1°'$, V (ΔE_p, mV)	$E_2°'$, V (ΔE_p, mV)	ΔE, mV	K_c
4	334 (9700), 408sh (4300)	−0.833 (70)			
5a	392 (14200)	−0.81[b]	−0.89[b]	80 ± 10	23 ± 9
5b	388 (11400)	−0.94[b]	−1.02[b]	80 ± 10	23 ± 9
6	341 (15300), 411sh (7450)	−0.654 (58)	−0.856 (56)	202 ± 5	2750 ± 540

[a] Cyclic voltammograms were recorded in 0.1 M TBAPF$_6$/DMF at 0.25 V/s and referenced vs Ag/AgCl. [b] From modeling of cyclic voltammetric data.

free ligands, tolyl-pyCa (325 nm, 19400 M^{-1} cm^{-1}) and PBP (359 nm, 22800 M^{-1} cm^{-1}), exhibit $\pi-\pi^*$ transitions in this vicinity, confirming that the bands observed in the spectra of the metal complexes also are attributable to ligand-centered absorption. Interestingly, the decrease in absorption energy from tolyl-pyCa to PBP is qualitatively consistent with expected increased delocalization and stabilizing inductive effects. Along these lines, it is tempting to make inferences about the electronic properties of the paracyclophane ligands **3a** and **3b**, which exhibit similar bands maximizing at intermediate wavelengths (~350 nm).[49,50] However, the precise relationship between the band energies and *N*-aryl amine substituents is not fully understood.[51] In the spectra of **5a** and **5b**, these ligand-centered absorptions are evidently obscured by an overlapping longer wavelength band.

Compounds **4**, **5**, and **6** also exhibit broad and intense absorption bands centered near 400 nm. The involvement of the diimine in these transitions is suggested by the observation that neither [2.2]paracyclophane nor Re([2.2]-PHANEPHOS)(CO)$_3$Cl exhibits bands more intense than 1600 M^{-1} cm^{-1} for $\lambda > 340$ nm.[52] As noted for Re(Ph-pyCa)(CO)$_3$Cl and related complexes,[33,38,47,53−57] the charge-transfer character of the absorption band for **4** is evident from its negative solvatochromic behavior. Though the band appears as a shoulder in DMF and acetonitrile, it shifts to longer wavelengths with decreasing solvent polarity and the absorption maximum is well-resolved (λ_{max} (nm): 405, MeOH; 428, CH$_2$Cl$_2$; 428, THF). Though poor solubility limited similar investigations of **5** and **6**, the accumulated evidence suggests that the low-energy absorptions for all four complexes arise from transitions with significant metal-to-ligand charge-transfer (MLCT) character involving the diimine ligand, in keeping with studies of related compounds.[33,38,45,47,57,58] The charge-transfer absorption manifold of **5b** is shifted to shorter wavelength with respect to **5a**, as expected for the destabilization of the diimine π^* level by the methyl substituent. Similarly, the MLCT bands for **5a** and **5b** are shifted to the blue of those for **4**, **6**, and other complexes with R-pyCa ligands[47] (e.g., Re(Ph-pyCa)(CO)$_3$-Cl 398 nm, 4420 M^{-1} cm^{-1}; Re(Cy-pyCa)(CO)$_3$Cl, 410 nm, 3480 M^{-1} cm^{-1}),[38] apparently reflecting the relative electron-donating character of the attached [2.2]paracyclophane as also suggested by the infrared spectra. The MLCT transitions of all four complexes occur at longer wavelengths than observed for rhenium tricarbonyl complexes with 1,10-phenanthroline and 2,2′-bipyridine ligands.[33] These results are in accord with the relatively strong π-acceptor properties of the N-substituted pyridine carboxaldimine ligands.[51,59] Interestingly, the MLCT band for the PBP-bridged dimer **6** is shifted slightly to the red of that of **4** because of perturbation by the remote rhenium center. Stabilization of the π^* level of the bridging ligand is consistent with the electrochemistry of **6** (vide infra) and studies of polypyridyl-bridged rhenium dimers,[60−64] though the effect is evidently small in the case of **6**. It also is noteworthy that the charge-transfer bands of all three dimers are approximately 1.3 to 1.6 times more intense than might be expected on the basis of spectra of monomeric complexes, presumably as a consequence of overlap with the aforementioned ligand-centered absorption. In summary, the relative energies of the MLCT maxima can be understood in terms of the electronic properties of the diimine ligands, and there is no firm evidence of electronic interactions mediated by the paracyclophane bridging ligands.

The luminescence properties of these rhenium(I) tricarbonyl diimine complexes were examined to gain additional insight into their electronic structures. In 77 K frozen butyronitrile solution, compounds **4** and **6** exhibit very weak red emission maximizing near 680 and 690 nm, respectively (Figure 2).[65] The emission profiles are characteristically broad, unstructured, and somewhat asymmetric, reminiscent

---

(48) Chandra, M.; Sahay, A. N.; Mobin, S. M.; Pandey, D. S. *J. Organomet. Chem.* **2002**, *658*, 43−49.

(49) Free [2.2]paracyclophane does not absorb strongly in this region ($\epsilon < 100$ M^{-1} cm^{-1}, $\lambda > 300$ nm).

(50) Iwata, S.; Fuke, K.; Sasaki, M.; Nagakura, S.; Otsubo, T.; Misumi, S. *J. Mol. Spectrosc.* **1973**, *46*, 1−15.

(51) Crociani, B.; Granozzi, G. *Inorg. Chim. Acta* **1987**, *132*, 197−206.

(52) Kunkely, H.; Vogler, A. *Inorg. Chem. Commun.* **2002**, *5*, 391−394.

(53) Sullivan, B. P. *J. Chem. Phys.* **1989**, *93*, 24−26.

(54) Walters, K. A.; Kim, Y.-J.; Hupp, J. T. *Inorg. Chem.* **2002**, *41*, 2909−2919.

(55) Knor, G.; Leirer, M.; Keyes, T. E.; Vos, J. G.; Vogler, A. *Eur. J. Inorg. Chem.* **2000**, 749−751.

(56) Leirer, M.; Knoer, G.; Vogler, A. *Z. Naturforsch.* **1999**, *54b*, 341−344.

(57) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888−2897.

(58) Stufkens, D. J.; Vlcek, A., Jr. *Coord. Chem. Rev.* **1998**, *177*, 127−179.

(59) Reinhold, J.; Benedix, R.; Birner, P.; Hennig, H. *Inorg. Chim. Acta* **1979**, *33*, 209−213.

(60) (a) Vogler, A.; Kisslinger, J. *Inorg. Chim. Acta* **1986**, *115*, 193−196. (b) Lin, R.; Guarr, T. F. *Inorg. Chem.* **1990**, *29*, 149−152. (c) Lin, R.; Duesing, R.; Guarr, T. F. *Inorg. Chem.* **1990**, *29*, 4169−4172. (d) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1990**, *29*, 2909−2914. (e) Braterman, P. S.; Song, J. I.; Kohlmann, S.; Vogler, C.; Kaim, W. *J. Organomet. Chem.* **1991**, *411*, 207−213. (f) Lin, R.; Fu, Y.; Brock, C. P.; Guarr, T. F. *Inorg. Chem.* **1992**, *31*, 4346−4353. (g) Ruminski, R. R.; Lehmpuhl, D. *Inorg. Chim. Acta* **1993**, *204*, 45−51.

(61) Juris, A.; Campagna, S.; Bidd, I.; Lehn, J. M.; Ziessel, R. *Inorg. Chem.* **1988**, *27*, 4007−4011.

(62) Ruminski, R.; Cambron, R. T. *Inorg. Chem.* **1990**, *29*, 1575−1578.

(63) Baiano, J. A.; Carlson, D. L.; Wolosh, G. M.; DeJesus, D. E.; Knowles, C. F.; Szabo, E. G.; Murphy, W. R., Jr. *Inorg. Chem.* **1990**, *29*, 2327−2332.

(64) Yoblinski, B. J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* **1992**, *31*, 5−10.

of MLCT emissions from related complexes.[58,66] The maxima are slightly blue-shifted with respect to that observed for Re(Ph-pyCa)(CO)$_3$Cl (709 nm),[38] and the observed lifetimes (**4**, 0.15; **6**, 0.08 μs) are consistent with emissions originating from a lowest predominantly spin-forbidden MLCT state. The band maxima exhibit a relatively large Stokes shift from the spin-allowed MLCT absorptions for each compound, because promotion of a dπ(Re) bonding electron to the pyCa-centered π^* LUMO, having significant imine antibonding character, results in considerable inner-sphere reorganization.[47,58,67,68] For both complexes, the luminescence intensity is much weaker than observed for shorter wavelength emitting complexes with 2,2′-bipyridine and 1,10-phenanthroline ligands,[33] and the accumulated data are qualitatively consistent with energy gap law considerations that account for an increase in nonradiative decay rate with decreasing emission energy.[58,66,69,70]

In contrast to **4** and **6**, emissions from frozen solid and solution samples of **5** are vanishingly weak. While there are other examples of nonluminescent rhenium(I) tricarbonyl complexes,[55,56] compounds **5a** and **5b** are the first examples of halide derivatives with N-substituted pyridine carboxaldimine ligands. It is evident that MLCT emissions from **5** should occur within an easily measurable wavelength range, similar to **4** and **6**, since the absorption spectra and first reduction potentials (vide infra) for all four complexes are similar and these observables are known to correlate with emission energy.[61,63,64,71] In addition, it should be noted that there is no evidence for photodecomposition of samples of **5**, and the relatively high energy of the lowest triplet state (~24600 cm^{-1})[72] and relatively unfavorable redox potentials[73,74] of [2.2]paracyclophane argue against the intramolecular energy- or electron-transfer quenching. Therefore, we conclude that relatively fast nonradiative excited-state relaxation and/or slow radiative relaxation in **5a** and **5b** account for the absence of emission. It is reasonable to expect that the excited-state decay, as observed for many rhenium(I) tricarbonyl diimine complexes,[58] is dominated by weak coupling to the ground state. However, the similar MLCT absorption energies for these complexes do not support an energy gap law explanation for the absence of emissions from **5**. One plausible explanation is that the paracyclophane group enhances coupling between the ground and excited states by introducing additional vibrational modes and/or improving vibrational coupling to the medium, as has been argued for several Re and Ru complexes.[58,64,75,76] Alternatively, a low-lying ligand-centered triplet state would be expected to perturb the emission properties of **5**;[17,77−79] however, this possibility is difficult to assess since the energies of the lowest triplet states of R-pyCa ligands bonded to Re(I) are not known.

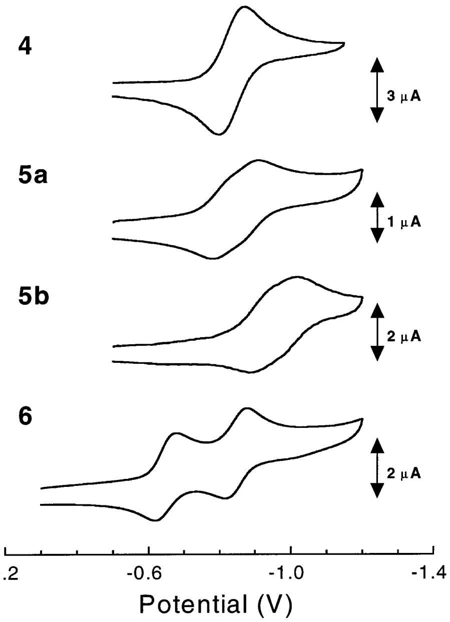


Figure 3. Cyclic voltammograms of **4**, **5a**, **5b**, and **6** recorded in 0.1 M TBAPF$_6$/DMF at 0.25 V/s vs Ag/AgCl. Traces are scaled and offset along the vertical axis for purposes of comparison.

To better understand the role of the paracyclophane bridge in mediating electronic communication, the cyclic voltammograms of **4**, **5**, and **6** were recorded in DMF solution (0.1 M TBAPF$_6$) (Figure 3, Table 3). None of the complexes is oxidized at potentials <1.5 V, and this is consistent with the high oxidation potentials of other rhenium tricarbonyl diimine complexes[24,71,80] as well as [2.2]paracyclophane (1.5 V, 0.1 M NBu$_4$(ClO$_4$)/MeCN)[73] in the case of **5**. At 0.25 V/s, the cyclic voltammogram of **4** exhibits a nearly reversible one-electron reduction at −0.83 V vs Ag/AgCl ($\Delta E_p = 70$ mV) corresponding to reduction of the diimine ligand.[38,62,71,81] The value of ΔE_p (70 ± 6 mV) was approximately constant for six measurements from 0.01 to 0.5 V/s, and the cathodic peak current (i_{pc}) exhibited a linear dependence on the square root of the scan rate ($\nu^{1/2}$) from 0.01 to 10 V/s, as expected for a diffusion controlled process.

---

(65) A very weak blue-green emission also was observed, similar to the fluorescence reported for (CO)$_5$Re-Re(^{i}Pr-pyCa)(CO)$_3$ (Rossenaar, B. D.; Lindsay, E.; Stufkens, D. J.; Vlcek, A., Jr. *Inorg. Chim. Acta* **1996**, *250*, 5−14); the emission was not further characterized.

(66) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711−743.

(67) Maruyama, M.; Kaizu, Y. *Inorg. Chim. Acta* **1996**, *247*, 155−159.

(68) Maruyama, M.; Matsuzawa, H.; Kaizu, Y. *Inorg. Chem.* **1995**, *34*, 3232−3240.

(69) Worl, L. A.; Duesing, R.; Chen, P.; Della Ciana, L.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849−858.

(70) Abbott, L. C.; Arnold, C. J.; Ye, T.-Q.; Gordon, K. C.; Perutz, R. N.; Hester, R. E.; Moore, J. N. *J. Chem. Phys. A* **1998**, *102*, 1252−1260.

(71) Van Wallendael, S.; Shaver, R. J.; Rillema, D. P.; Yoblinski, B. J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* **1990**, *29*, 1761−1767.

(72) (a) Hillier, I. H.; Glass, L.; Rice, S. A. *J. Chem. Phys.* **1966**, *45*, 3015−3021. (b) Goldacker, W.; Schweitzer, D.; Dinse, K. P.; Hausser, K. H. *Chem. Phys.* **1980**, *48*, 105−111.

(73) (a) Sato, T.; Torizuka, K. *J. Chem. Soc., Perkins Trans. 2* **1978**, 1199−1204. (b) Sato, T.; Torizuka, K.; Shimizu, M.; Kurihara, Y.; Yoda, N. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2420−2423.

(74) Jund, R.; Lemoine, P.; Gross, M. *Angew. Chem.* **1982**, *94*, 315−13.

(75) Braunstein, C. H.; Baker, A. D.; Strekas, T. C.; Gafney, H. D. *Inorg. Chem.* **1984**, *23*, 857−864.

(76) Fuchs, Y.; Lofters, S.; Dieter, T.; Shi, W.; Morgan, R.; Strekas, T. C.; Gafney, H. D.; Baker, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 2691−2697.

(77) Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415−7417.

(78) Sacksteder, L.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1990**, *29*, 4335−4340.

(79) Shaw, J. R.; Schmehl, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 389−394.

(80) Connick, W. B.; Di Bilio, A. J.; Hill, M. G.; Winkler, J. R.; Gray, H. B. *Inorg. Chim. Acta* **1995**, *240*, 169−174.

(81) Wallace, L.; Rillema, D. P. *Inorg. Chem.* **1993**, *32*, 3836−3843.

The ratio of peak currents ($i_{pa}/i_{pc} = 0.9$) is slightly less than one, as expected for loss of Cl^- from the reduced complex.[24] In acetonitrile solution (−0.92 V vs Ag/AgCl, $\Delta E_p = 62$ mV; $i_{pa}/i_{pc} = 0.9$), the process shows an expected slight cathodic shift with respect to that observed for Re(Ph-pyCa)$(CO)_3Cl$ (−0.94 V vs SCE).[38] In DMF, a second and irreversible wave occurs near −1.4 V, and similar behavior is observed for **5** and **6**. This process is attributed to reduction coupled with chloride dissociation, as reported for related compounds.[24,82]

The voltammograms of **5a** and **5b** at 0.25 V/s each exhibit two closely spaced reversible reductions near −0.85 V and −0.98 V, respectively, as anticipated for consecutive one-electron reductions of weakly interacting pyridine carboxaldiimine groups (Figure 3). The [2.2]paracyclophane group is not directly involved in these processes since it is reduced at −3.0 V.[74] For **5a**, the ratio of peak currents (0.75 ± 0.03) and the separation between the peaks of the cathodic and anodic waves (122 ± 7 mV) showed little variation for nine measurements from 0.02 to 3 V/s. The cathodic peak current also exhibits a linear dependence on $\nu^{1/2}$ as expected for a Nernstian process. The reduction potentials and ΔE were estimated from modeling of the cyclic voltammograms (Table 3). The relative potentials for **5a** and **5b** are consistent with destabilization of the diimine π^* level by the imine methyl substituent, and the slight cathodic shift with respect to reduction of **4** is consistent with the electron-donating properties of the paracyclophane. In contrast, **6** undergoes two well-separated reversible one-electron reductions at $E_1°' = -0.65$ V ($\Delta E_p = 57$ mV; $i_{pa}/i_{pc} = 1.0$) and $E_2°' = -0.85$V ($\Delta E_p = 58$ mV; $i_{pa}/i_{pc} = 0.6$), reflecting significantly stronger interaction between the carboxaldiimine groups. The ratios of peak currents (0.9 and 0.6) and ΔE (202 ± 5 mV) are insensitive to scan rate from 0.02 to 0.5 V/s. The cathodic peak current (i_{pc}) shows a linear dependence on the square root of the scan rate ($\nu^{1/2}$) as expected for a Nernstian process.

From eq 2, comproportionation constants were determined for the general reaction

$$M/M + M^-/M^- \leftrightarrow 2M^-/M$$

where the reduction processes involve a predominantly diimine-localized orbital. The resulting values (Table 3), reflecting stronger interactions between the pyCa groups in **6** than in **5**, can be understood in terms of the factors contributing to stabilization of symmetrical mixed-valence dimers, including inductive, electrostatic, and resonance effects.[6,83] The anodic shift of $E_1°'$ for **6** with respect to **4** and **5** is consistent with stabilization of the diimine π^* level by the inductive influence of the remote acidic Re(I) metal center. The effect is attenuated for the second reduction process, and in the case of **6**, $E_2°'$ is nearly coincident with the first reduction potential of **4**. The stabilization of the π^* level is more pronounced than observed for the MLCT absorption maxima (though 0−0 energies have not been determined), possibly because the charge-transfer energies also are dependent on ligand σ-donation, which is attenuated by similar inductive effects and would tend to compensate for π^* stabilization. Interestingly, the value of K_c for **6** is comparable, but less than that observed for the reduction of $(CO)_4Mo(\mu\text{-PBP})Mo(CO)_4$ (7.8×10^3),[19] as might be expected for increased metal orbital character in the rhenium system. Inductive effects are much smaller for **5** because the diimine π-systems are weakly coupled. In fact, Cram and co-workers[12] previously found that the acidity constants of transannularly substutited 4-carboxy- and 4-amino-[2.2]-paracyclophanes can be described using an electrostatic model. Though quantative treatment of electrostatic interactions requires currently unavailable knowledge of charge distribution on the reduced dimers, it is likely that the valence electrons reside in orbitals with significant imine π^* character.[68] Thus, the relative values of K_c are qualitatively consistent with electrostatic repulsion and the intramolecular N(imine)···N(imine) distances for **5** (6.0 Å) and **6** (5.7 Å). A third contributor to K_c is resonance stabilization of the mixed-valence complex associated with delocalization of the valence electron over the entire molecule, which is a tantalizing possibility for **6**. However, for **5** it is likely that this contribution is smaller than either inductive or electrostatic effects.

Table 4. Comproportionation Constants for Bridged Paracyclophane Redox Systems

compound	ΔE, mV	K_c
$(NH_3)_5Ru(\mu\text{-PPDCP})Ru(NH_3)_5^{6+}$	38[a]	∼4[a]
5a	80 ± 10	23 ± 9
5b	80 ± 10	23 ± 9
$\mathbf{I}^{2+}$	100[b]	∼50

[a] Data from ref 6. [b] Data from ref 8.

In summary, the K_c values for **5a** and **5b** are consistent with weak interactions between the pendant redox groups, as observed for other pseudo-*para* substituted paracyclophane-bridged systems.[6,8] However, these results should not be construed to indicate that coupling via $\pi-\pi$ interactions of the [2.2]paracyclophane unit is necessarily weak. Strong electronic interactions mediated by arene paracyclophane bridging ligands[7] indicate that the nature of the coupling of the redox centers *to the bridging* π-stack strongly influences electronic communication. For weakly coupled pseudo-*para* substituted systems, electronic interaction increases along the series $(NH_3)_5Ru(\mu\text{-PPDCP})Ru(NH_3)_5^{6+}$ < **5a**, **5b** < $\mathbf{I}^{2+}$ (Table 4). The increased interaction with respect to the ruthenium dimer is entirely consistent with electrostatic considerations (Ru···Ru, 12.0 Å), as well as variations in coupling to the π-system of the bridging group. A larger interaction for $\mathbf{I}^{2+}$ might be expected if steric congestion in **5** disfavors a coplanar arrangement of the diimine group and the attached paracyclophane phenylene group, and consequently, reduces π-overlap. It also has been suggested that the strong donor properties of [2.2]paracyclophane, as reflected by its relatively low oxidation potential, may allow

---

[82] (a) Breikss, A. I.; Abruna, H. D. *J. Electroanal. Chem.* **1986**, *201*, 347−358. (b) O'Toole, T. R.; Sullivan, B. P.; Bruce, M. R. M.; Margerum, L. D.; Murray, R. W.; Meyer, T. J. *J. Electroanal. Chem.* **1989**, *259*, 217−239. (c) Christensen, P.; Hamnett, A.; Muir, A. V. G.; Timney, J. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1455−1463.

[83] Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125−3134.

for partial delocalization of charge onto the bridge of **I**$^{2+}$, thereby increasing electrostatic interactions.[8] In contrast, delocalization is likely attenuated in the case of **5** because of the relatively unfavorable reduction potential of [2.2]-paracyclophane.

Acknowledgment. Diffraction data on the Bruker 1K CCD diffractometer were collected through the Ohio Crystallographic Consortium, funded by the Ohio Board of Regents 1995 Investment Fund (CAP-075) and located at the University of Toledo, Instrumentation Center in A&S, Toledo, OH 43606. J.A.K.B. thanks Dr. Alan Pinkerton (Department of Chemistry, University of Toledo) for the use of the Smart 2K diffractometer. W.B.C. thanks the National Science Foundation (CHE-0134975) for their generous support and the Arnold and Mabel Beckman Foundation for a Young Investigator Award. P.J.B. and W.B.C. are grateful to the University of Cincinnati University Research Council for summer research fellowships. P.J.B. thanks the University of Cincinnati for a Neff Scholarship, the Department of Chemistry Research Associates Program for support, and the UC Women in Science and Engineering Program for an REWU fellowship. We thank Ms. Jean Paddock and Drs. T. H. Ridgway, W. R. Heineman, M. J. Baldwin, and E. Brooks for helpful discussions and expert technical assistance.

Supporting Information Available: Plot of δ_m vs σ_p for pseudo-*para* substituted [2.2]paracyclophanes, tables of crystallographic data, structure refinement details, atomic coordinates, interatomic distances and angles, anisotropic displacement parameters, and calculated hydrogen parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0348648