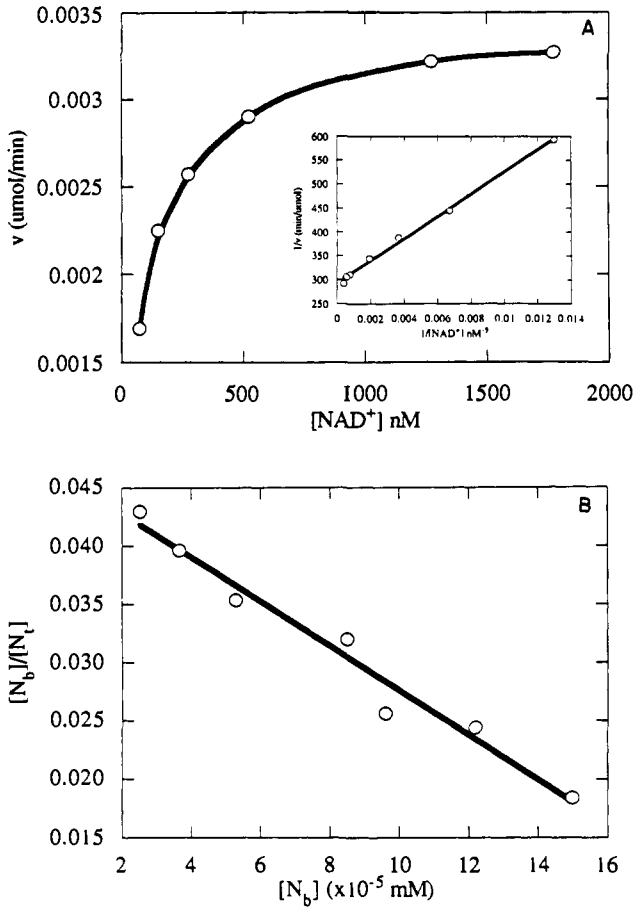

Figure 1. (A) Determination of K_{NAD} under turnover conditions. (B) Determination of K_{NAD} in the absence of substrate. The experiments were carried out by forced dialysis using [^{3}H]NAD$^+$ ([N_f]: 0–500 nM) with E_{od} (250 nM). The extent of bound ([N_b]) and free cofactor was assessed by scintillation counting. The K_{NAD} was deduced from the Scatchard plot (Segal, I. E. *Biochemical Calculations*, 2nd ed.; Wiley: New York, 1976; p 242).

μM, deduced from Figure 1B, was found for the free 4,6-dehydratase.

Since the active-site conformation must play an important role in controlling the binding affinity of coenzyme, the prodigious 2700-fold difference in NAD$^+$ affinity found for the *Yersinia* enzyme may simply reflect a distortion of the nicotinamide binding domain at, or near, the active-site. Comparison of the amino acid sequences and the tertiary structures of many NAD(P)$^+$ or FAD dependent enzymes has led to the identification of a compact ADP-binding domain preserved in most dinucleotide-binding proteins. Homology within this conserved binding region includes a glycine-rich phosphate binding loop, **GXGXXG**, near the N-terminus of the protein, and six predominantly hydrophobic residues forming a hydrophobic core of the dinucleotide binding $\beta\alpha\beta$ fold.[7,8] Contrary to the typical $\beta\alpha\beta$ fold found in most NAD$^+$ binding enzymes, including DHQ synthase,[9] an examination of the sequence of the *Yersinia* enzyme reveals the presence of an extended fold with the sequence of GHTGFKG.[10] The preferred alignment with the typical GXGXXG consensus, **GHTGFKG**, results in the placement of histidine near the N-terminal end of the α-helix which has been recently shown to interfere with the α-helix dipole[11] often thought to be important in ligand (or cofactor) binding.[12] The alternative alignment, **GHTGFKG**, provides a relatively bulky substitution, threonine, for the universally conserved second glycine which is believed to be important to minimize steric interaction with the nicotinamide cofactor.[8] Altering the third conserved glycine to lysine may disrupt the close interaction between the β-strand and α-helix.[8] These primary distinctions from the normal NAD$^+$ binding motif suggest the presence of a second possible cofactor binding consensus for this class of enzyme, which is severely perturbed electronically and/or sterically, resulting in diminished cofactor affinity.[13] These fundamental comparisons may assist in the prediction or tailor-design of desired protein-cofactor interactions of this unique class of nicotinamide binding enzymes as well as possibly many other essential ADP-binding proteins. In addition, assembling a cofactor binding motif(s) for this class of enzyme will help define the common residues important for their overall redox neutral reactions.

(6) Bender, S. L.; Mehdi, S.; Knowles, J. R. *Biochemistry* **1989**, *28*, 7555. UDP-galactose-4-epimerase from yeast or *E. coli*[2] and the TDP-D-glucose 4,6-dehydratase from *Salmonella typhimurium* (Romana, L. K.; Santiago, F. S.; Reeves, P. R. *Biochem. Biophys. Res. Comm.* **1991**, *174*, 846) are known to bind NAD$^+$ tightly; however, the dissociation constants have not been determined. The K_{NAD} of *E. coli* TDP-D-glucose oxidoreductase has been estimated in the range of 5–500 μM; however, the authors admit the reported value has a great potential for error (Zarkowsky, H.; Lipkin, E.; Glaser, L. *J. Biol. Chem.* **1970**, *245*, 6599).

(7) Where G refers to glycine, X refers variable amino acids, α designates an α-helix, and β defines a β-sheet.

(8) (a) McKie, J. H.; Douglas, K. T. *FEBS* **1991**, *279*, 5. (b) Wierenga, R. K.; De Maeyer, M. C.; Hol, W. G. J. *Biochemistry* **1985**, *24*, 1346. (c) Rossmann, M. G.; Liljas, A.; Branden, C.-I.; Banaszak, L. J. *Enzymes, 3rd ed.* **1975**, *11*, 61.

(9) Millar, G.; Coggins, J. R. *FEBS* **1986**, *200*, 11.

(10) All the known sequences of UDP-galactose-4-epimerase, CDP-tyvelose epimerase (Verma, N.; Reeves, P. R. *J. Bacteriol.* **1989**, *171*, 5694), TDP-D-glucose 4,6-dehydratase from *Saccharopolyspora erythrea* (Pissowotzki, K.; Mansouri, K.; Piepersberg, W. *Mol. Gen. Genet.* **1991**, *231*, 123), and *Salmonella typhimurium* (Jiang, X.-M.; Neal, B.; Santiago, F.; Lee, S. J.; Romano, L. K.; Reeves, P. R. *Mol. Microbiol.* **1991**, *5*, 695) contain a GGXGXXG fold which still follows the normal consensus.

(11) Sancho, J.; Serrano, L.; Fersht, A. R. *Biochemistry* **1992**, *31*, 2253.

(12) Hol, W. G. J.; van Duijnen, P. T.; Berendsen, H. J. C. *Nature (London)* **1978**, *273*, 443.

(13) The primary GXXGXXG sequence has also been found in the CDP-D-glucose 4,6-dehydratase from *Salmonella typhimurium* (Jiang, X.-M.; Neal, B.; Santiago, F.; Lee, S. J.; Romano, L. K.; Reeves, P. R. *Mol. Microbiol.* **1991**, *5*, 695) and TDP-D-glucose 4,6-dehydratase from *Streptomyces griseus* (Pissowotzki, K.; Mansouri, K.; Piepersberg, W. *Mol. Gen. Genet.* **1991**, *231*, 123); however, no information on cofactor binding in these particular systems is known.

1,2,3,4-Tetramethyl-5-(trifluoromethyl)cyclopentadienide: A Unique Ligand with the Steric Properties of Pentamethylcyclopentadienide and the Electronic Properties of Cyclopentadienide

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Received April 6, 1992

Cyclopentadienide (Cp) and pentamethylcyclopentadienide (Cp*) are two of the most widely used ligands in organometallic chemistry. Since the first synthesis and use of Cp* as a ligand a quarter of a century ago,[1] it has become well established that replacement of the five hydrogens on Cp by five methyl groups results in major changes in both the physical and chemical properties of transition metal complexes which differ only in the substitution of Cp* for Cp.[2] Unfortunately, dissection of the steric

(1) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287.

(2) For selected leading references, see: Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451. Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939. Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265. Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 892. King, R. B. *Coord. Chem. Rev.* **1976**, *20*, 155. Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908. Cramer, R.; Seiwell, L. P. *J. Organomet. Chem.* **1975**, *92*, 245.

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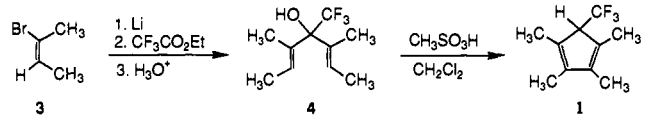
and electronic effects of Cp* has not been accomplished. This problem would be solved by the availability of a substituted cyclopentadienide with the steric bulk of Cp* and the electronic character of Cp. We now report the synthesis and use of such a ligand, 1,2,3,4-tetramethyl-5-(trifluoromethyl)cyclopentadiene (**1**).

Through the use of X-ray photoelectron spectroscopy (XPS), we have demonstrated that the methyl groups on Cp* are very electron donating (relative to hydrogen) to any metal complexed to Cp*. For a series of complexed transition metals, this electron donation was manifest in an approximately 0.08 eV reduction per methyl group in the binding energy of the inner shell electrons of the complexed metal.[3,4] It has also been found that the one trifluoromethyl group on (trifluoromethyl)cyclopentadienide has an electron-withdrawing effect which raises by approximately 0.35 eV the inner shell electron binding energy of a complexed transition metal.[5] Thus, the electron-withdrawing effect of one trifluoromethyl group should cancel the electron-donating effect of four methyl groups if the electronic effects of substituents on cyclopentadienide are additive.[6]

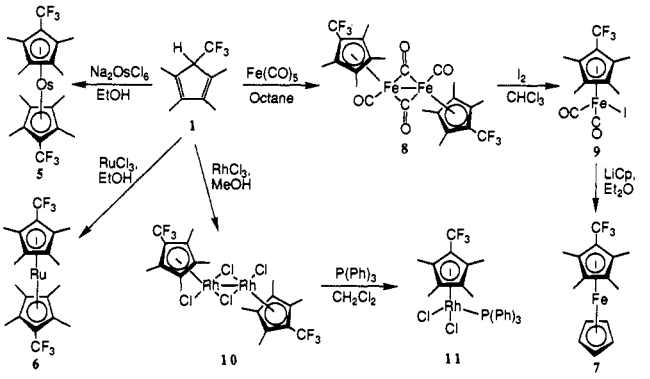
1,2,3,4-Tetramethyl-5-(trifluoromethyl)cyclopentadiene (**1**)[7] was prepared in a three-step process from *trans*-2-butene (**2**). Utilizing literature procedures,[8] commercially available *trans*-2-butene (**2**) was brominated–dehydrobrominated to give **3**.



3 4 1

Treatment of a solution of **3** in diethyl ether at 0 °C with lithium metal resulted in metalation of **3**. Addition of ethyl trifluoroacetate to this lithio derivative at −40 °C gave an 82% yield of **4**.[9] Dehydration of **4** with methanesulfonic acid in methylene chloride at 25 °C resulted in a symmetry-allowed cyclization of the resultant carbocation to produce **1** in 82% yield as a mixture of double-bond isomers.[8a,10-12]

Scheme I



5 1 8 9 6 10 11 7

Table I. X-ray Photoelectron Binding Energies of Pentamethylcyclopentadienide, 1,2,3,4-Tetramethyl-5-(trifluoromethyl)cyclopentadienide,[a] and Cyclopentadienide Complexes of Iron, Ruthenium, Osmium, and Rhodium

compound	binding energy (±0.1 eV)	assignment
trans-$[Cp^*Fe(CO)_2]_2$	707.7	$Fe(2p_{3/2})$
trans-$[Cp'Fe(CO)_2]_2$ (**8**)[a]	708.1	$Fe(2p_{3/2})$
cis,trans-$[CpFe(CO)_2]_2$	708.1	$Fe(2p_{3/2})$
$Cp^*Fe(CO)_2I$	708.5	$Fe(2p_{3/2})$
$Cp'Fe(CO)_2I$ (**9**)	709.0	$Fe(2p_{3/2})$
$CpFe(CO)_2I$	709.0	$Fe(2p_{3/2})$
Cp^*_2Fe	707.0	$Fe(2p_{3/2})$
$Cp'CpFe$ (**7**)	707.8	$Fe(2p_{3/2})$
Cp_2Fe	707.8	$Fe(2p_{3/2})$
Cp^*_2Ru	279.7	$Ru(3d_{5/2})$
Cp'_2Ru (**6**)	280.3	$Ru(3d_{5/2})$
Cp_2Ru	280.3	$Ru(3d_{5/2})$
Cp^*_2Os	49.9	$Os(4f_{7/2})$
Cp'_2Os (**5**)	50.7	$Os(4f_{7/2})$
Cp_2Os	50.6	$Os(4f_{7/2})$
$Cp^*RhCl_2PPh_3$	308.2	$Rh(3d_{5/2})$
$Cp'RhCl_2PPh_3$ (**11**)	308.6	$Rh(3d_{5/2})$
$CpRhCl_2PPh_3$	308.6	$Rh(3d_{5/2})$

[a] For the purpose of formula representation in this table, 1,2,3,4-tetramethyl-5-(trifluoromethyl)cyclopentadienide is represented as Cp'.

Neither the lithium nor thallium salts of the anion of **1** were sufficiently stable for their use as intermediates in the preparation of transition metal complexes of **1**.[5] Thus, as shown in Scheme I, various other synthetic approaches were used to prepare a series of complexes of **1** with iron, ruthenium, osmium, and rhodium.[7]

The osmocene **5** and ruthenocene **6** were prepared in a straightforward manner. Treatment of excess **1** with sodium hexachloroosmate hexahydrate in refluxing ethanol for 24 h under argon gave a 26% yield of **5**. In a similar manner, ruthenium trichloride hydrate reacted with an excess of **1** in refluxing ethanol to give a 65% yield of **6**. The synthesis of the unsymmetrical ferrocene **7** was less direct. Treatment of excess iron pentacarbonyl with **1** in refluxing octane gave a 34% yield of the trans dimer **8**.[13] On reaction with 1.1 equiv of iodine in chloroform, **8** was converted into **9** in 60% yield. Exposure of **9** to a large excess of lithium cyclopentadienide gave **7** in 18% yield. The dimeric

(3) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470.

(4) See, also: Calabro, D. C.; Hubbard, J. L.; Blevins, C. H., II; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839. Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130. Lichtenberger, D. L.; Kellogg, G. E. *Acc. Chem. Res.* **1987**, *20*, 379.

(5) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228.

(6) For discussions of the additivity of the electronic effect of methyl groups, see: Gassman, P. G.; Winter, C. H. *Organometallics* **1991**, *10*, 1592. Sowa, J. R., Jr.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2537.

(7) Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds. All compounds discussed in this paper gave spectral data that were consistent with the assigned structures.

(8) (a) Campbell, P. H.; Chiu, N. W. K.; Deugau, K.; Miller, I. J.; Sorensen, T. S. *J. Am. Chem. Soc.* **1969**, *91*, 6404. (b) Bordwell, F. G.; Landis, P. S. *J. Am. Chem. Soc.* **1957**, *79*, 1593.

(9) To 6.94 g (1 mol) of lithium wire and 350 mL of anhydrous diethyl ether under a dry argon atmosphere at 0 °C was added dropwise 67.5 g (0.50 mol) of 2-bromo-*cis*-2-butene in 50 mL of anhydrous diethyl ether, and the reaction mixture was stirred at 0 °C for an additional 2 h. The reaction mixture was cooled to −40 °C, and 32.7 g (0.23 mol) of ethyl trifluoroacetate in 50 mL of anhydrous diethyl ether was added dropwise. The reaction mixture was stirred for 1.5 h after the addition was complete. The supernatant liquid was decanted from the excess lithium wire and neutralized with 500 mL of 2 N aqueous hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with three 75-mL portions of diethyl ether. The combined ethereal extracts were washed successively with 50 mL of saturated sodium bicarbonate solution, 50 mL of water, and 50 mL of brine and dried over anhydrous magnesium sulfate. After filtration, the filtrate was concentrated on a rotary evaporator and the residue was vacuum distilled to afford 36.4 g (82%) of **4** as a colorless liquid: bp 78 °C (19 mm).

(10) Deno, N. C.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 1871. Sorensen, T. S. *Can. J. Chem.* **1964**, *42*, 2768. Sorensen, T. S. *Can. J. Chem.* **1965**, *43*, 2744. Deno, N. C.; Pittman, C. U., Jr.; Turner, J. O. *J. Am. Chem. Soc.* **1965**, *87*, 2153. Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395. Sorensen, T. S. *J. Am. Chem. Soc.* **1967**, *89*, 3782, 3794. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press Inc.; Verlag Chemie GmbH: Weinheim/Bergstr., 1970; pp 58–59. Sorensen, T. S. In *Carbonium Ions*; Olah, G., Schleyer, P. v. R., Eds.; John Wiley and Sons: New York, 1970; Vol. II, Chapter 19.

(11) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1. Gassman, P. G.; Ray, J. A.; Wenthold, P. G.; Mickelson, J. W. *J. Org. Chem.* **1991**, *56*, 5143.

(12) To 9.65 g (46.3 mmol) of **4** in 250 mL of dry methylene chloride was added 25 mL (385 mmol) of methanesulfonic acid, and the reaction mixture was stirred for 20 s at room temperature, followed by quenching into 300 mL of water. The organic phase was separated, and the aqueous layer was extracted three times with 50-mL portions of methylene chloride. The combined organic layers were washed twice with 50-mL portions of saturated sodium bicarbonate solution, 50 mL of water, and 50 mL of brine and dried over anhydrous magnesium sulfate. After filtration, the filtrate was concentrated on a rotary evaporator and the residue was vacuum distilled to afford 7.2 g (82%) of **1** as a colorless liquid: bp 42–45 °C (4.5 mm).

(13) For a previous report of **8**, see: Bond, A.; Bottrill, M.; Green, M.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 2372.

rhodium complex **10** was obtained in 65% yield when rhodium trichloride hydrate was treated with excess **1** in refluxing methanol. The conversion of **10** into **11** was achieved in 92% yield through treatment of **10** with a slight excess of triphenylphosphine in methylene chloride at ambient temperature.

Table I lists the inner shell electron binding energies of compounds **5–9** and **11**. For comparison purposes, the corresponding Cp and Cp* complexes were purchased or prepared by literature methods,[14] and their binding energies were measured and included in Table I. The binding energy data firmly establish that 1,2,3,4-tetramethyl-5-(trifluoromethyl)cyclopentadienide (Cp‡) is electronically equivalent to Cp. The difference between Cp‡ and Cp* in electron donation to complexed transition metals ranges from 0.3 eV/Cp‡ for **6** to 0.5 eV/Cp‡ for **9**. For the six series studied, the difference between Cp‡ or Cp and Cp* averaged 0.4 eV. Thus, it is obvious that the Cp‡ and Cp ligands are electronically similar, and that they are both electronically very different from Cp* when used as ligands for transition metals.

While the electronic equivalence of Cp‡ and Cp has been established, the question of the steric equivalence of Cp‡ and Cp* requires examination. The literature[15] permits the generalization that the trifluoromethyl group is larger than methyl and smaller than *tert*-butyl. Rotational studies[15] suggest that trifluoromethyl is comparable in size to isopropyl or smaller than isopropyl. However, comparison of bis(trifluoromethyl)methyl with isopropyl suggests that they are very similar in size,[16] which would imply that trifluoromethyl and methyl are close in steric effects. Clearly, Cp‡ is not a *perfect* steric substitute for Cp*. It is probably slightly larger. It seems likely that this difference will be sufficiently small that, for all practical purposes, Cp‡ can be viewed as sterically equivalent to Cp*.

In summary, we have prepared various transition metal complexes of 1,2,3,4-tetramethyl-5-(trifluoromethyl)cyclopentadienide and demonstrated that they are electronically equivalent[17] to the corresponding complexes of cyclopentadienide and approximately sterically equivalent to the analogous complexes of pentamethylcyclopentadienide. The availability of this ligand should permit detailed studies which will dissect the electronic effects from the steric effects of the methyl groups of Cp* and lead to a thorough understanding of the role of Cp* versus Cp. We are currently pursuing such studies.

Acknowledgment. We are indebted to the National Science Foundation for a grant that supported this investigation.

Supplementary Material Available: The physical properties of compounds **1** and **4–11** and the experimental procedures for **5–11** (6 pages). Ordering information is given on any current masthead page.

(14) The sources of the comparison complexes were as follows. $[Cp^*Fe(CO)_2]_2$, Cp^*_2Fe: Reference 1. $[CpFe(CO)_2]_2$, Cp_2Ru, Cp_2Os: purchased from Strem Chemicals, Inc. $Cp^*Fe(CO)_2I$: King, R. B.; Douglas, W. M.; Efraty, A. *J. Organomet. Chem.* **1974**, *69*, 131. $CpFe(CO)_2I$: Eisch, J. J.; King, R. B. *Organomet. Synth.* **1965**, *1*, 175. Cp_2Fe: Purchased from Aldrich Chemical Co. Cp^*_2Os: Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E.; Wiege, M. B.; Boeyens, J. C. A.; Levendis, D. C. *Organometallics* **1986**, *5*, 2321. $Cp^*RhCl_2PPh_3$: Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. $CpRhCl_2PPh_3$: Bresler, L. S.; Varshavskii, Y. S.; Kormer, V. A.; Marasanova, N. N.; Cherkasova, T. A. *Koord. Khim.* **1981**, *7*, 421. See also: Faraone, F.; Pietropaolo, R.; Troilo, G. G.; Piraino, P. *Inorg. Chim. Acta* **1973**, *7*, 729.

(15) Bott, G.; Field, L. D.; Sternhell, S. *J. Am. Chem. Soc.* **1980**, *102*, 5618. Cosmo, R.; Sternhell, S. *Aust. J. Chem.* **1987**, *40*, 35. Datta, D.; Sharma, G. T. *J. Chem. Res., Synop.* **1987**, 422. Della, E. W. *Tetrahedron Lett.* **1966**, 3347. It has also been reported that trifluoromethyl is larger than isopropyl: Nagai, T.; Nishioka, G.; Koyama, M.; Ando, A.; Miki, T.; Kumadaki, I. *Chem. Pharm. Bull.* **1991**, *39*, 233. MacPhee, J. A.; Panaye, A.; Dubois, J.-E. *Tetrahedron* **1978**, *34*, 3553.

(16) Dawson, W. H.; Hunter, D. H.; Willis, C. J. *J. Chem. Soc., Chem. Commun.* **1980**, 874.

(17) Additional evidence for the electronic equivalence of Cp‡ and Cp is provided by an examination of the carbonyl stretching frequencies of **8** and **9**. For the Fp dimer series, the values are as follows: $[Cp^*Fe(CO)_2]_2$, 1923, 1749 cm^{-1}; $[Cp^{\ddagger}Fe(CO)_2]_2$, 1952, 1776 cm^{-1}; $[CpFe(CO)_2]_2$, 1956, 1774 cm^{-1}. For the Fp iodide series: $Cp^*Fe(CO)_2I$, 2018, 1971 cm^{-1}; $Cp^{\ddagger}Fe(CO)_2I$, 2039, 1995 cm^{-1}; $CpFe(CO)_2I$, 2042, 1997 cm^{-1}.

Synthesis and Characterization of a Diplatinum(III)-Tetrakis(α-dioximato) Complex Containing an Unsupported Metal-Metal Bond

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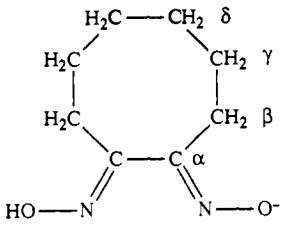
Particular interest in Pt^{III} chemistry[1] arises from the occurrence of mixed-valence, one-dimensional materials,[2] such as the biologically active "platinum blues",[3] and from the participation of Pt^{III} in formally Pt^{II}/Pt^{IV} redox processes.[4] Only a few monomeric Pt^{III} complexes are known,[5] while several dinuclear ones containing a metal-metal bond, supported by two or four bridging ligands, have been characterized.[6]



1a

In contrast to dimethylglyoxime, and all other familiar α-dioximes, the C_8 carbocyclic α-dioximato ligand $\{C_8H_{12}(=NO)_2H\}^-$, **1a**, and its C_{12} analogue, $\{C_{12}H_{20}(=NO)_2H\}^-$, **1b**, confer pronounced organosolubility on their complexes,[7] which opens up many new opportunities for physical and chemical studies. Here we report that oxidative coupling reactions of planar $Pt^{II}(C_8doH)_2$, **2**, or its C_{12} analogue lead to stable binuclear complexes featuring

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