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.

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[14] The sources of the comparison complexes were as follows. [Cp*Fe(CO)$_2$]$_2$, Cp$^{*}_2$Fe: Reference 1. [CpFe(CO)$_2$]$_2$, Cp$_2$Ru, Cp$_2$Os: purchased from Strem Chemicals, Inc. Cp*Fe(CO)$_2$I: King, R. B.; Douglas, W. M.; Efraty, A. *J. Organomet. Chem.* **1974**, *69*, 131. CpFe(CO)$_2$I: Eisch, J. J.; King, R. B. *Organomet. Synth.* **1965**, *1*, 175. Cp$_2$Fe: Purchased from Aldrich Chemical Co. Cp$^{*}_2$Os: 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$_2$PPh$_3$: Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. CpRhCl$_2$PPh$_3$: 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.

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[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‡Fe(CO)$_2$]$_2$, 1952, 1776 cm^{-1}; [CpFe(CO)$_2$]$_2$, 1956, 1774 cm^{-1}. For the Fp iodide series: Cp*Fe(CO)$_2$I, 2018, 1971 cm^{-1}; Cp‡Fe(CO)$_2$I, 2039, 1995 cm^{-1}; CpFe(CO)$_2$I, 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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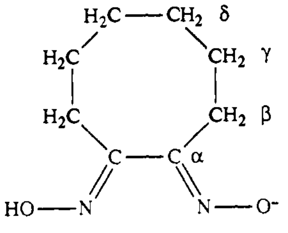
Particular interest in Pt^{III} chemistry[1] arises from the occurrence of mixed-valence, one-dimensional materials,[2] such as the biologically active "platinum blues",[3] and from the participation of Pt^{III} in formally Pt^{II}/Pt^{IV} redox processes.[4] Only a few monomeric Pt^{III} complexes are 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$_8$H$_{12}$(=NO)$_2$H}$^-$, **1a**, and its C$_{12}$ analogue, {C$_{12}$H$_{20}$(=NO)$_2$H}$^-$, **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$_8$doH)$_2$, **2**, or its C$_{12}$ analogue lead to stable binuclear complexes featuring

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0002-7863/92/1514-6944$03.00/0

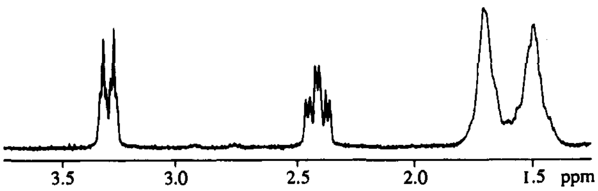

Figure 1. ^{1}H-NMR spectrum of **3** in $CDCl_3$, 293 K.

an unsupported Pt^{III}–Pt^{III} bond. These are typified by the title compound $[Pt(C_8doH)_2Cl]_2$, **3**, which has been fully characterized by both single-crystal X-ray diffraction and solution measurements. The first comparable example of an unsupported Pt^{III}–Pt^{III} bond was recently discovered.[8]

Controlled chlorination of **2** by $PhICl_2$ or p-$ClC_6H_4ICl_2$ in CH_2Cl_2 resulted in a mixture (typically 3:1) of $[Pt^{III}(C_8doH)_2Cl]_2$, **3**, and monomeric $Pt^{IV}(C_8doH)_2Cl_2$, **4**, from which crystalline **3** is readily isolated.[9] Compound **3** has been shown separately to react with further oxidant to form **4**, as in reaction 1.

$$\underset{\mathbf{2}}{2Pt^{II}(C_8doH)_2} \xrightarrow{ArICl_2} \underset{\mathbf{3}}{[Pt^{III}(C_8doH)_2Cl]_2} \xrightarrow{ArICl_2} \underset{\mathbf{4}}{2Pt^{IV}(C_8doH)_2Cl_2} \quad (1)$$

In the solid, **3** has a characteristic Raman absorption at 139 cm^{-1} assigned to the Pt–Pt stretch. In addition, organosoluble **3** gives the following data: IR(CH_2Cl_2) 374 cm^{-1} (Pt–Cl); UV–vis (cm^{-1}, CH_2Cl_2) 31 400, 36 800, 43 000(sh); ^{13}C-NMR (75.7 MHz, $CDCl_3$, 293 K, TMS) δ = 158.80 (α-C), 26.77, 25.75, 25.05; ^{1}H-NMR (300 MHz, $CDCl_3$, 293 K, TMS) δ = 3.303 (d of t, 1 H, β-CH_2), 2.414 (t of d, 1 H, β-CH_2), 1.782 (m, 2 H, γ-CH_2), 1.546 (m, 2 H, δ-CH_2) (Figure 1). On decoupling the γ-CH_2 protons, the characteristic geminal β-CH_2 resonances become doublets, $^2J_{HH}$ = 13.4 Hz. Complex **3** disproportionates only *slowly* to **2** and **4** (e.g., requires 7 weeks at ambient temperature for 50% disproportionation in $CHCl_3$). Cyclic voltammetry of **3** (CH_2Cl_2, 238 K, 0.5 M n-Bu_4NPF_6, vs Ag/AgCl) showed an electrochemically reversible one-electron oxidation at +1.62 V, and an irreversible reduction at −0.1 V which regenerates **2** as confirmed spectroelectrochemically in a chilled optically transparent thin layer electrode (OTTLE[10]) cell.

X-ray diffraction[11] showed that **3** is a neutral dimer (Figure 2) composed of two crystallographically independent $Pt(C_8doH)_2$ units perpendicularly connected by a Pt–Pt bond and capped by axially coordinated chloride ligands. In the crystal, the two $Pt(C_8doH)_2$ units are mutually rotated by 63.5 (3)°. Each $PtN_4(\alpha\text{-}C)_4(\beta\text{-}C)_4$ moiety is approximately planar (trans N–Pt–N angles: 174 (3)–176.7 (3)°). The extended carbocyclic $(CH_2)_4$ segments not restricted to planarity (C_γ and C_ϵ) fold outward and offer no hindrance to dimerization.

The Pt^{III}–Pt^{III} bond length measured for **3**, 2.6964 (5) Å, coincides with the value of 2.694 (1) Å recently reported[8] for $[Pt_2Cl_6\{HN{=}C(OH)C(CH_3)_3\}_4]$, which contains monodentate imine and chloride equatorial ligands and has a much greater tendency to disproportionation. A length of 2.70 Å may now be regarded as the standard for an unhindered Pt^{III}–Pt^{III} single bond trans to two chloride ligands. However, the axial Pt–Cl bonds are shorter in our pseudomacrocyclic complex, being 2.386 (2) and 2.409 (2) Å for **3** vs 2.458 (3) Å. Our complex makes an interesting comparison with isoelectronic $[Rh(dmgH)_2(PPh_3)_3]_2$, where Rh^{II}–Rh^{II} = 2.936 (2) Å.[12]

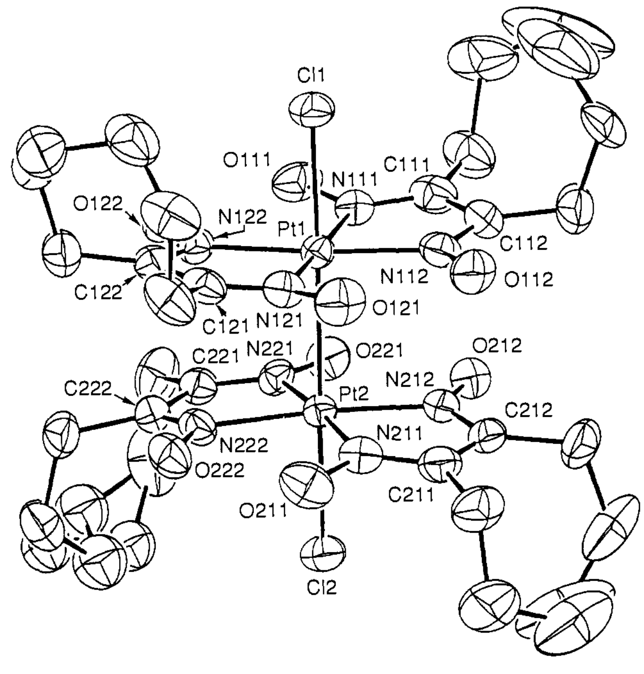

Figure 2. Thermal ellipsoid (50% probability level) diagram of **3** with the crystallographic labeling scheme for selected atoms. C-atoms of each ring are sequentially numbered C(nm1)–C(nm8) in the direction indicated. Both orientations of the disordered (22n) ring shown. Pt–Pt = 2.6964 (5) Å, Pt(1)–Cl(1) = 2.386 (2) Å, Pt(2)–Cl(2) = 2.409 (2) Å, Pt–N = 1.974 (8)–2.012 Å, Cl(1)–Pt(1)–Pt(2) = 177.86 (6)°, Cl(2)–Pt(2)–Pt(1) = 178.84 (7)°.

The face-to-face binuclear structure for "$Pt(C_8doH)_2Cl$" is retained in solution. This is demonstrated by the voltammetric behavior (inappropriate for the hypothetical monomer) and particularly by the continued diamagnetism and intrinsic nonequivalence of the geminally coupled endo and exo protons of the β-CH_2 group. The apparent equivalence of the β-CH_2 groups at positions 3 and 8 in **3** could not be frozen out by cooling to 193 K. This implies a low barrier to alteration of the solid-state conformation with either free rotation around the Pt–Pt bond or adoption of a fully symmetric (eclipsed or staggered) configuration in solution.

Stable $[Pt^{III}(C_8doH)_2F]_2$ has been prepared[13] similarly to **3**, whereas reaction with 0.5 molar equiv of Br_2 yields only mixtures of **2** and $Pt^{IV}(C_8doH)_2Br_2$. In addition, diamagnetic $[Pt^{III}(C_8doH)_2]_2^{2+}$ has been electrosynthesized directly by one-electron oxidation of **2** at −60 °C in CH_2Cl_2/n-Bu_4NBF_4 and characterized in situ by its voltammetry and UV–vis spectrum (similar to, but distinct from, that of **3**) in the OTTLE cell. In contrast, the related cationic complex,[5d] $[Pt(dpgH)_2](ClO_4)$ (dpgH = diphenylglyoximato anion), is essentially monomeric in the crystalline state, with an infinite chain structure of equidistant Pt^{III} centers, with Pt···Pt = 3.259 (4) Å. The ClO_4^- ions are not coordinated, and the phenyl substituents appear to prevent close approach of the d^7-monomeric units, although the bulk material is ESR-silent.

The formation of dimeric Pt^{III} species may be a relatively common, and overlooked, feature of platinum chemistry. For

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(8) Cini, R.; Fanizzi, F. P.; Intini, F. P.; Natile, G. *J. Am. Chem. Soc.* **1991**, *113*, 7805.

(9) To a suspension of 200 mg (0.37 mmol) of **1** in 15 mL of CH_2Cl_2 was added 95 mg (0.34 mmol) of $PhICl_2$ or an equivalent amount of p-$ClC_6H_4ICl_2$. The reaction mixture was stirred for 3 h, and approximately equal amounts of **3** (orange) and **4** (yellow) were separated chromatographically on basic alumina with $CHCl_3$ as eluent; yield: 90 mg (41%). Single crystals appropriate for X-ray study were grown by slow Et_2O diffusion into a CH_2Cl_2 solution of **3**.

(10) Duff, C. M.; Heath, G. A. *Inorg. Chem.* **1991**, *30*, 2528.

(11) Crystal data for **3**: $C_{32}H_{52}Cl_2N_8O_8Pt_2$, M_r = 1137.84, monoclinic $P2_1/n$ (No. 14) a = 17.081 (2) Å, b = 11.992 (2) Å, c = 18.589 (2) Å, β = 90.21 (1)°, V = 3807.7 Å^3, Z = 4, d = 1.985 Mg m^{-3}. Intensity data were collected from an orange crystal, 0.09 × 0.07 × 0.26 mm, with a Phillips PW1100/20 diffractometer, Cu Kα radiation, by θ–2θ scans in the range $0° < 2\theta < 128°$, and were corrected for decay (4%) and absorption (transmission min–max, 0.190–0.434). Structure solution was by the Patterson method. All full-occupancy non-hydrogen atoms were refined anisotropically. Full-matrix refinement, based on F, of 468 parameters, using 5411 observed $[I > 3\sigma(I)]$ reflections, converged to R = 0.037 and R_w = 0.044 with a weighting scheme of $w = [\sigma^2(F) + (0.0006)F^2]^{-1}$. Disorder of the CH_2 carbon atoms was resolved into a 50/50 model for C(225) and C(226) only.

(12) Caulton, K. G.; Cotton, F. A. *J. Am. Chem. Soc.* **1971**, *93*, 1914.

(13) Heath, G. A.; Lee, S. B.; Raptis, R. G. To be published.

example, a diamagnetic intermediate is observed[13] by ^{1}H-NMR spectroscopy in the reaction of $Pt(acac)_2$ with p-$ClC_6H_4ICl_2$ but has yet to be isolated as it disproportionates rapidly to Pt^{II} and Pt^{IV} at room temperature.

Acknowledgment. We thank Dr. E. Krausz for the Raman spectrum and S. B. Lee for technical assistance.

Supplementary Material Available: For **3**, Tables SI–SVII listing crystallographic data, bond lengths, bond angles, torsion angles, positional isotropic and anisotropic displacement parameters for non-hydrogen atoms, and hydrogen positional parameters (14 pages); Table SVIII listing observed and calculated structure factors for **3** (17 pages). Ordering information is given on any current masthead page.

*Book Reviews**

Inclusion Aspects of Membrane Chemistry. Edited by T. Osa and J. L. Atwood (Tohoku University and University of Alabama, respectively). Kluwer: The Netherlands. 1991. vi + 292 pp. $99.00. ISBN 0-7923-1123-X.

This book has six fairly good reviews from the 1987–1988 period about various topics in membrane chemistry. They include ion extraction and transport in crown ethers, ion transport in synthetic ionophores and liquid/liquid interfaces, electrochemical and photochemical properties of bilayer lipid membranes, photocontrol of ion permeation through membranes, and liquid crystal composite membranes.

Unfortunately, this book typifies a product that has become, in my opinion, all too common in scientific publishing: a photo-offset collection of disparate articles with little or no value added by the editors. There is no foreword to the book, nor is there any indication by the editors that the articles were subject to any significant review process. The articles are printed in different type—a common attribute of the photo-offset process when the editors fail to require a consistent format. There is a 3.5 page subject index, which I found to be of little use, as well as an afterword of 57 words on the back cover, which does little to summarize the book.

I believe the articles would be of some interest to the reader who wants a survey of the subject area. Each article has a number of references dating from about 1988 and earlier, and each provides the reader with sufficient information to begin a serious study of her/his own. However, if one wanted to begin a study of any of these areas, the use of Chemical Abstracts online on CD-ROM or in plain text would probably have been a faster, and perhaps less expensive, way of obtaining the required information. The book will be less interesting to the non-serious scientist or student.

In conclusion, I must say that I was frustrated with this book. The subject of technical applications of membranes needs a good reference book suitable for the advanced graduate student and senior researcher entering the field. The reader needs to be told of the connections between the various topics in this book and other relevant areas of membrane science, surface science, and biophysics. A comprehensive foreword and decent editing job could have made this book something more than just another of the many books containing collections of good reviews.

Joel M. Schnur, *Naval Research Laboratory*

The Chemistry and Technology of Pectin. Edited by Reginald H. Walter (Cornell University). Academic Press: San Diego. 1991. xi + 276 pp. $95.00. ISBN 0-12-733870-5.

Two previous summaries of that class of polymers referred to as pectins have been published: *The Pectic Substances* by Z. I. Kertesz (1951) and *Chemistry and Function of Pectins* edited by M. L. Fishman and J. J. Jen (1986). This book is presented as a textbook that "attempts to explain the scientific and technical basis of many of the practices followed in processing and preparing foods fabricated with or containing pectin". That it does, but it contains some deficiencies that will limit its usefulness as either a text or reference book.

This book is a collection of twelve chapters that address major topics related to pectin, written by key experts in the field. A disturbing aspect to this reviewer is a lack of integration between chapters, an absence of cross-referencing, and a poor index. As one example, so-called amidated pectins are mentioned in passing in a sentence in four different chapters and determination of the degree of amidation in one, but nowhere does one learn what amidated pectin is, how it is made, what are its properties, and why and how it is used.

Those wishing to learn about the structural and organic chemistry of pectin will be disappointed. The one general structure (on p 88) is incorrect, showing the glycosyl units joined by peroxy linkages and containing mixed notations for the bonding of ring carbon atoms. The less than 1-page descriptions of the molecule in Chapters 1 and 5 leave much to be desired. The 2-page description of sugar beet pectin in Chapter 7 is a little more complete, but it still does not describe adequately the differences between native and commercial pectins in terms of the rhamnogalacturonan core, poly(galacturonic acid) stretches, and arabinan, galactan, and arabinogalactan side chains. Phrases such as the ones that indicate that 1,2-linked L-rhamnosyl residues are inserted in the galacturonan chain leave one wondering if a L-rhamnopyranosyl unit is attached to O-2 of a D-galactopyranosyluronic acid unit or if a D-galactopyranosyluronic acid unit is attached to O-2 of a L-rhamnopyranosyl unit. Reaction schemes would have been very helpful in Chapter 9, especially to indicate what is meant by bond 1, bond 2, etc. While it is common in the food industry to report the methyl ester content as "degree of methoxylation", this is incorrect chemical terminology and probably should have been pointed out. The concept of β-elimination seems to have been overlooked.

This book could be a helpful resource to chemists wishing to learn about the properties of pectins that make them useful in food applications, but a glossary would have been extremely helpful and the lack of introductory material, good structural chemistry, and integration of topics will restrict its usefulness.

James N. BeMiller, *Purdue University*

Advances in Organobromine Chemistry I. Edited by J.-R. Desmurs (Rhône-Poulenc Recherches) and B. Gérard (Potasse et Produits Chimiques). Elsevier: Amsterdam. 1991. xiv + 299 pp. $151.50. ISBN 0-444-89274-5.

This volume contains the very diverse principal contributions to "Orgabrom '89", the first international symposium on brominated organic compounds held at Mulhouse in 1989. The editors wisely chose an organization in five sections: "Preparation of Organobrominated Compounds; Synthesis"; "Preparation of Organobrominated Compounds; Mechanisms"; "Use of Organobrominated Compounds; Synthesis"; "Use of Organobrominated Compounds; Mechanisms"; and, most important, "Economic Aspects and Applications".

This is a book about a unique industry at a time of rapid and competitively driven change. Roughly half the contributions (15 out of 27) come from academia, and so this book also bridges the interface of misunderstanding between the industrial and academic cultures.

The industrial culture emerged from geology. Three companies—the Dead Sea Bromine Group, the Ethyl Corporation, and the Great Lakes Chemical Corporation—produce 85% of the world's bromine, their relative contributions diminishing in that order. Through no coincidence, the sodium bromide concentration in the Dead Sea amounts to 12 g/L, whereas those in the underground brine reservoirs of Arkansas and Michigan amount to 3.0–3.5 and 2.0–2.5 g/L.

But it is only through chemistry that the industry can prosper. It is better to brominate exhaustively e.g. diphenyl ether and then to ship the flame-retardant decabromo derivative than it is to ship liquid bromine. It is better still to exploit the preparatively valuable combination of selectivity and moderate reactivity, both of bromine and of its derivatives, in multistep syntheses of bromine-free targets from bromine-free starting materials. A classic example in this volume comes from the Farmitalia group of A. Longo et al. in their syntheses of three steroidal aromatase inhibitors.

The debt which synthetic design owes to reaction mechanistic understanding is explicit in the organization of this volume. Less immediately obvious is the lesson that subtle experimental variables can distort the consequences of even well-known mechanisms (viscosity effects in aliphatic radical bromination by D. D. Tanner et al.; pH in phenol bromination by O. Tee). The practical importance of less-well-known mechanisms is illustrated in the B. R. Langlois review of perhalofluoro-

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*Unsigned book reviews are by the Book Review Editor.