# Deducing Structures of 19-Electron Complexes from Studies of Metal Polyolefin Radicals

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The formation of 19-electron (19e) organometallic adducts from 17e precursors (eq 1) has been studied for radicals generated by thermal, photochemical, and electrochemical means.[1] The 19e complex has, in

$$ML_n + L' \rightleftharpoons ML_nL' \qquad (1)$$
$$\text{17e} \qquad\quad \text{19e}$$
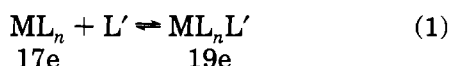
many cases, been shown to be unstable, especially with respect to electron transfer (ET).[2] With the exception of metal sandwich compounds such as cobaltocene and (η^6-arene)FeCp[3] (Cp = η^5-C$_5$H$_5$), very few compounds of this hypervalent electron count have been adequately characterized by physical methods.[1,2a] Given the central role played by these species as reactants and intemediates,[4] questions concerning the structures of 19e species are at the heart of efforts to increase our understanding of the consequences of ET to the structure, reactivity, and physical properties of transition metal organometallic complexes.

The scarcity of well-characterized examples has given rise to a reluctance to assign "genuine" 19e structures to species possessing that formal electron count. This Account discusses some of the reasons why knowledge of the electronic and geometric structures of 19e organotransition metal complexes is relatively underdeveloped and makes some recommendations for future studies. Structural aspects of some nominal 19e metal polyolefin complexes are reviewed, with emphasis on systems studied at the University of Vermont over about the last decade.

As pointed out by both Astruc[2a] and Tyler,[1] formal 19e complexes have often been assumed to undergo molecular distortions which have the effect of lowering the number of valence electrons assigned to the metal to 17 or 18. Figure 1 gives some literature examples.[1,2a] The argument for invoking such distortions is made less compelling if one considers the widespread acceptance of the hypervalent organic counterparts, i.e., organic anion radicals.[5] The delocalization common to stable organic anion radicals has a counterpart in organometallic transition metal radicals, namely, the distribution of spin and charge between the metal and the ligands, i.e., the covalency of the complex.[6]

Bill Geiger was born (1944) and raised in Buffalo, where he studied at Canisius College and did research with Raymond Annino. His Ph.D. was from Cornell University in 1969. His graduate work stressed ESR spectroscopy under the direction of the late David Geske at Cornell and August Maki at the University of California at Riverside. After a postdoctoral year at Northwestern University with the late Donald Smith, he joined the faculty at Southern Illinois University. He moved to the University of Vermont in 1974. Relying primarily on electrochemical and spectroelectrochemical methods, he has been most concerned with defining the ways in which structures and reactivities of organotransition metal complexes are affected by electron transfer reactions.
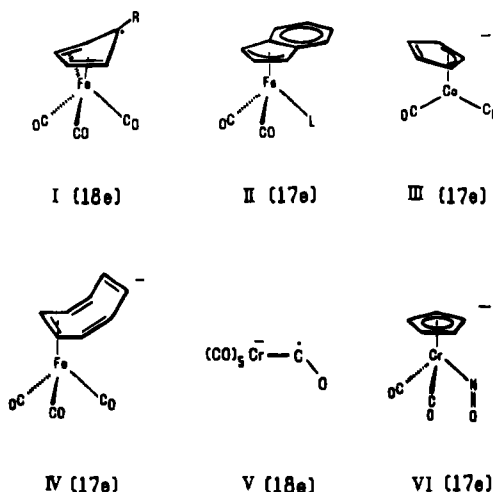

Figure 1. Some structural distortions invoked for nominal 19e complexes, with the resulting formal metal electron counts. (**I**) Tetrahapto Cp: Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694. (**II**) Trihapto indenyl: Wuu, Y.-M.; Zou, C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5861. (**III**) Trihapto Cp: McDonald, R. N.; Schell, P. L. *Organometallics* **1988**, *7*, 1806. (**IV**) Dihapto cyclooctatetraene: Symons, M. C. R.; Wyatt, J. L.; Connelly, N. G. *J. Chem. Soc., Dalton Trans.* **1991**, 393. (**V**) Bent carbonyl: Tyler, D. R. In ref 2b, p 360, commenting on results of Narayanan et al.; Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1986**, *5*, 926. (**VI**) Bent nitrosyl: Geiger, W. E.; Rieger, P. H.; Tulyathan, B.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 7000.

I believe that *genuine 19e complexes are more widespread than commonly assumed*. I hope to identify some impediments to a better understanding of this important problem and to show how some systems studied in our laboratory have yielded fairly firm conclusions about the structures of hypervalent complexes. The vehicles for discussion are "19e" metal polyolefin systems, where the polyolefin is arene, cyclooctadiene (COD), or cyclooctatetraene (COT). I hope that this Account spurs efforts to develop new approaches to the study of structures of 19e complexes.

Ligand-Based Radicals

One group of complexes which deserves separate mention as a subset of 19e compounds is that in which

(1) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325.
(2) (a) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189. (b) Tyler D. R. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 338.
(3) Astruc, D. *Acc. Chem. Res.* **1991**, *24*, 36.
(4) (a) Trogler, W. C. *Int. J. Chem. Kinet.* **1987**, *19*, 1025. (b) Aase, T.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 4974 and references therein. (c) Kochi, J. K. In ref 2b, p 201. (d) Brown, T. L. In ref 2b, p 67. (e) Tyler, D. R.; Mao, F. *Coord. Chem. Rev.* **1990**, *97*, 119.
(5) Kaiser, E. T.; Kevan, L., Eds. *Radical Ions*; Interscience Publ.: New York, 1968. Coordination compounds are less relevant analogues owing to their far greater tendency to exist in open shell configurations.

the "surplus" electron resides *predominantly* on a ligand. The electronic structure of such a system may be designated as "18 + δ", thereby emphasizing its identity as a metal-stabilized ligand radical.[1] In these systems (see **1–3**), radical ions of the metal-free ligands are known separately, e.g., bipyridyl anion,[7a,b] maleic anhydride anion,[1,8] o-benzosemiquinone,[9] tetracyanoethylene anion,[7c] and NO.[10] Since ESR and

1   **2**   **3**
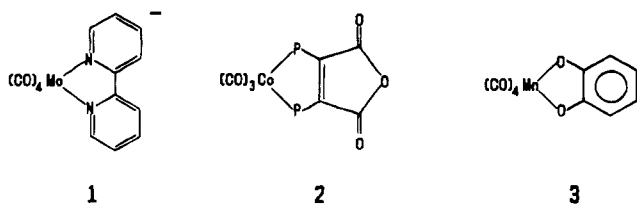
optical absorption spectroscopy are likely to provide a direct answer to the question of spin density distributions in these complexes, 18 + δ complexes suffer less often from electronic ambiguities and, thus, are not treated further in this Account.

Origin of the Problem: A Personal View. A plethora of formally 19e systems has been generated, for example, by electrochemical reduction of 18e precursors.[11,12] An analogous statement may also be made, of course, about the electrochemical production of 17e systems by oxidation of the precursors.[12] Isolation and, especially, X-ray characterization[13] is often more difficult for 19e complexes, however, owing to their common susceptibility to air oxidation. Complexes which undergo oxidation at a formal potential negative of about −1.3 V vs ferrocene (e.g., $Cp_2Co^{0/+}$)[14] are readily oxidized by O_2 in nonaqueous solvents. Air sensitivity may be assumed, therefore, for most 19e systems. The attendant experimental difficulty is compounded by the fact that high-resolution NMR spectroscopy, a method well disposed to the study of air-sensitive materials,[15] is, with some exceptions,[16] not applicable to the study of radicals. With two principal methods of structure analysis (X-ray and NMR) unavailable, the rarity of 19e complexes meeting strict standards of confirmation is rationalized. I

Scheme 1

will return to this point in the context of recommendations for other experimental methods when considering "future directions".

Rationale(s) for Hapticity Lowering. Depending on the relative amount of metal vs ligand character of the singly occupied molecular orbital (SOMO) of the radical, its electronic structure may be represented by relative weights of **A** and **B** which represent the extremes, respectively, of metal- and ligand-localized orbitals. Limiting structure **B** results, of course, in a

$$\overset{\textbf{A}}{\cdot M-L} \leftrightarrow \overset{\textbf{B}}{M-L\cdot}$$
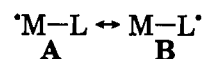
metal electron count that is lower by 1 than that of **A**. Most of the structural changes of Figure 1 allow the surplus electron to be assigned to the ligand. Rational support for such changes has come from observed reaction routes, such as dimerization through ligands and addition of radicals (e.g., H or halogen) to the ligands. However, because product analysis may only reveal the kinetically favored pathway and is in any case nonquantitative, this reasoning must be used with caution.[1,2a]

In some cases, the impetus for proposing molecular distortions in 19e systems is provided from the behavior of 20e analogues. "Slip-fold" distortions of cyclic polyolefin rings (see **I–III**, Figure 1) provide excellent examples of this reasoning. Both arene ligands[17] and Cp ligands[18] are known to undergo ring slippage in lowering the ligand hapticity from, respectively, η^6 to η^4 and η^5 to η^3, to avoid 20e metal configurations. This model accounts nicely for the substitution kinetics of many Cp complexes, in which the η^3 configuration attained by the five-membered rings lowers the transition state energy for associative processes.[19] What would we expect for the structure of the *radical anion* of such a system? Depending on whether or not ring slippage occurs (Scheme 1), the anion would have either the hypervalent 19e form **4** or the hypovalent 17e form **5**.

There is one crystallographically confirmed example of slip-fold distortion in an odd-electron $cyclo$-C_5R_5-type complex, namely, the bis-indenyl complex (η^5-

(6) The amount of metal character in the SOMO of organometallic radicals is most frequently specified by the orbital reduction (or covalency) factor, k', which varies between unity (metal-localized radical) and zero (ligand-localized radical) depending on the degree of spin delocalization. See: Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 190–191.

(7) (a) Kaim, W.; Olbrich-Deussner, B. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 173. (b) Kaim, W.; Moscherosch, M. *Coord. Chem. Rev.* **1994**, *129*, 157.

(8) Mao, F.; Tyler, D. R.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3113.

(9) (a) Baker, P. K.; Broadley, K.; Connelly, N. G. *J. Chem. Soc., Dalton Trans.* **1982**, 471. (b) Lange, C. W.; Pierpont, C. G. *J. Am. Chem. Soc.* **1992**, *114*, 6582. (c) Andrea, R. R.; deLange, W. G. J.; van der Graaf, T.; Rijkhoff, M.; Stufkens, D. J.; Oskam, A. *Organometallics* **1988**, *7*, 1100. (d) Connelly, N. G.; Rieger, P. H. *J. Chem. Soc., Dalton Trans.*, in press.

(10) Lee, K. Y.; Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1990**, *29*, 4196.

(11) Early indications of the general reducibility of organotransition metal complexes are found in the papers of Dessy et al.; for example: Dessy, R. E.; Stary, F. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 471.
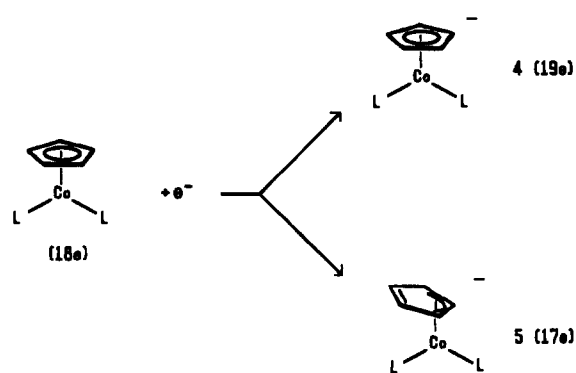
(12) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 1.

(13) (a) Connelly, N. G. *Chem. Soc. Rev.* **1989**, *18*, 153. (b) Baird, M. C. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 49.

(14) Geiger, W. E. *J. Am. Chem. Soc.* **1974**, *96*, 2632.

(15) Roe, D. C. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1987; Chapter 8.

(16) Leading references: (a) Heck, J.; Rist, G. *J. Organomet. Chem.* **1988**, *342*, 45. (b) Blümel, J.; Hebendanz, N.; Hudeczek, P.; Köhler, F. H.; Strauss, W. *J. Am. Chem. Soc.* **1992**, *114*, 4223.
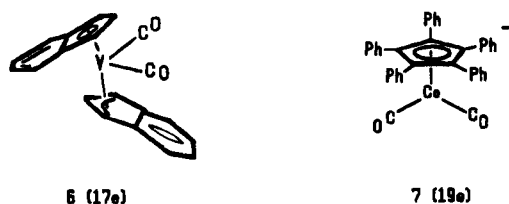
(17) Zhang, S.; Shen, J. K.; Basolo, F.; Ju, T. D.; Lang, R. F.; Kiss, G.; Hoff, C. D. *Organometallics* **1994**, *13*, 3692 and references therein.

(18) (a) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307. (b) Merola, J. S.; Kacmarcik, R. T.; van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 329.

(19) Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740 and references therein.

Scheme 2
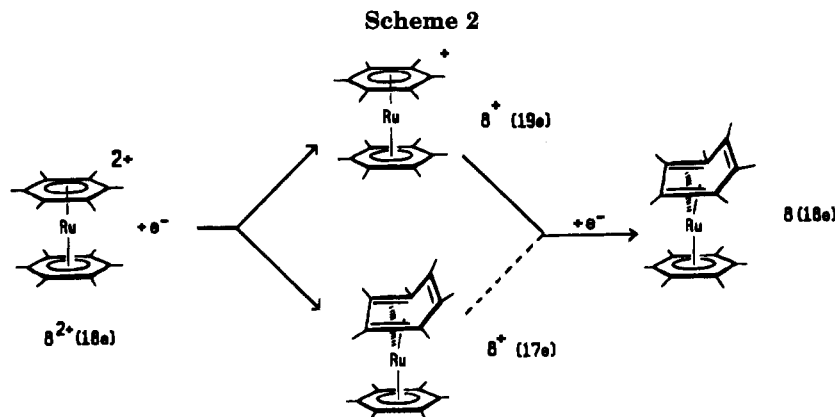
$C_9H_7)(\eta^3\text{-}C_9H_7)V(CO)_2$, **6**.[20] Trihapto coordination of

6 (17e)   **7 (19e)**

one indenyl ligand results in a formal 17e complex. The isoelectronic *cyclopentadienyl* complexes cannot, however, be assumed to undergo the same distortion, because the indenyl ligand is particularly susceptible to a slip-fold effect.[18] In fact, ESR spectra of a relevant 19e anion, $[(\eta^5\text{-}C_5Ph_5)Co(CO)_2]^-$, **7**, are completely explained by symmetric bonding to all five ring carbons, implying a planar C_5 ring in the radical.[21] Although indenyl metal complexes possess interesting redox properties and systematic distortions with increasing electron count,[22] they should be viewed with caution as models for the analogous Cp complexes. Ring slippage in hypervalent radicals with ordinary Cp ligands must still be considered to be undemonstrated. More definitive structural results for radicals are available for arene complexes, to which the discussion now turns.

Nineteen-Electron Ruthenium and Rhodium Arene Complexes

In 1970, Fischer and Elschenbroich[23] reported that a bis-hexamethylbenzene complex of ruthenium can be isolated in two different 18e forms which are related by a formal two-electron transfer. In this groundbreaking work, the Ru(0) complex, **8**, was assigned one planar (η^6) ring and one bent (η^4) ring on the basis of ^1H NMR spectra (three Me resonances for the bent ring). The hinge angle was later shown by crystallography to be 42°.[24] The corresponding Ru-(II) dication, 8^{2+}, has two planar (η^6) arenes. The Ru-(I) intermediate implied by these results is a 17e complex if it possesses a bent arene ligand or a 19e complex if the arene ring is planar (Scheme 2).

(20) Kowaleski, R. M.; Rheingold, A. L.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1986**, *108*, 2460.

(21) Connelly, N. G.; Geiger, W. E.; Lane, G. A.; Raven, S. J.; Rieger, P. H. *J. Am. Chem. Soc.* **1986**, *108*, 6219.

(22) (a) Lovelace, S. Ph.D. Thesis, University of Pittsburgh, 1992. (b) O'Hare, D.; Murphy, V. J.; Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1993**, 383. (c) Westcott, S. A.; Kakkar, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777.

(23) Fischer, E. O.; Elschenbroich, C. *Chem. Ber.* **1970**, *103*, 162.

(24) Huttner, G.; Lange, S. *Acta Crystallogr.* **1972**, *B28*, 2049.

The Ru(I) monocation 8^+ was first detected during voltammetry studies by the Finke and Boekelheide groups at the University of Oregon, as part of a cleverly designed study of (η-arene)Ru^{II} (η^6-arene′) complexes involving cyclophanes which have a geometry predisposed to tetrahapto coordination.[25] This study established that the Ru(I) ion, 8^+, is unstable with respect to disproportionation (eq 2) in most solvents, an exception being CH_2Cl_2. The character-

$$2\,8^+ \rightleftharpoons 8 + 8^{2+} \tag{2}$$

ization of 8^+ is difficult owing to both its thermodynamic instability and its tendency to undergo radical side reactions.[26] Although the voltammetry of this system is fascinating in its own right[26] [and is ultimately more consistent with a 19e Ru(I) intermediate], the d^7, Ru(I), ion is an unlikely candidate for spectroscopic investigations designed to settle the question of its geometry.

On the basis that the d^7 electronic configuration is better known for Rh(II) than for Ru(I), we turned to the isoelectronic sandwich complex, $[(\eta^6\text{-}C_6Me_6)Rh\text{-}Cp^*]^{2+}$ (Cp* = η^5-C$_5$Me$_5$), 9^{2+}, in the hope that its one-electron reduction product would be persistent.

Complex 9^{2+} exhibits two reversible voltammetric waves.[27] Moreover, it is possible to isolate the product of the *second* reduction, **9**, and to demonstrate by NMR spectroscopy[27] and by crystallography[28] that its arene ligand is bent to virtually the same extent as that in **8**, adding weight to the analogy between 8^+ and 9^+. Even though 9^+ was stable with respect to disproportionation, it eluded our attempts at its isolation.[28] We were able, however, to produce persistent deep blue solutions of the Rh(II) intermediate either by 1e electrolysis of 9^{2+} or by comproportionation of **9** and 9^{2+}. These solutions were ESR *silent* at temperatures between ambient and 77 K. This result implied rapid electronic relaxation of the radical and suggested the applicability of NMR spectroscopy, which has been profitably employed in the study of other paramagnetic sandwich complexes with short relaxation times.[29] Sharp proton resonances are indeed observed for solutions of 9^+ in CD_2Cl_2 (Figure 2) in the temperature range 183 K < T < 300 K.

(25) (a) Laganis, E. D.; Voegeli, R. H.; Swann, R. T.; Finke, R. G.; Hopf, H.; Boekelheide, V. *Organometallics* **1982**, *1*, 1415. (b) Finke, R. G.; Voegeli, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* **1983**, *2*, 347.

(26) Pierce, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 6063.

(27) Bowyer, W. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5657.

(28) Bowyer, W. J.; Merkert, J.; Geiger, W. E.; Rheingold, A. L. *Organometallics* **1989**, *8*, 191.
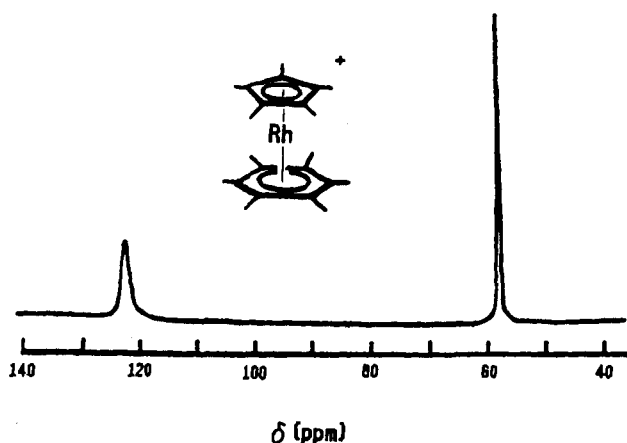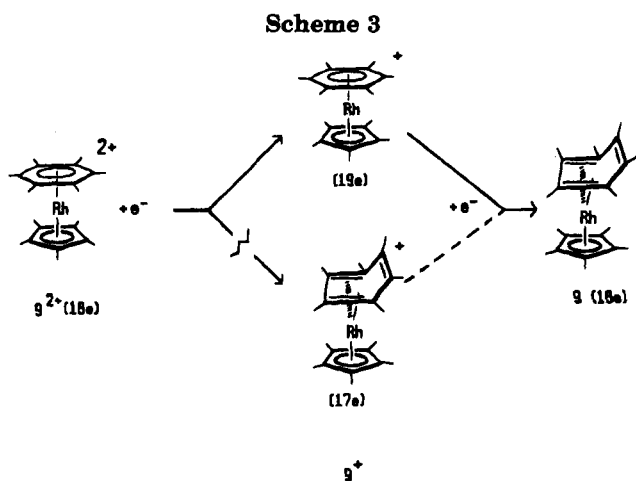
Figure 2. ¹H NMR spectrum of **9⁺** in acetone-d_6 at 298 K vs TMS. Reprinted with permission from Merkert, J.; Nielson, R. S.; Weaver, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7084. Copyright 1989 American Chemical Society.

Scheme 3

The key finding of a *single* resonance (57 ppm) for the arene methyl groups in **9⁺** establishes the chemical equivalence of each position in the six-membered ring. This evidence is consistent with the presence of a planar arene, but it does not rule out a structure having a *bent* but *fluxional* arene ligand. At about this time we learned that Nielson and Weaver had also recorded NMR spectra of **9⁺** at Purdue University. Comparison of the two sets of results led to an important conclusion about the possibility of fluxionality in this system. Analysis of the spectral line widths under different magnetic field strengths set an upper limit for activation barrier to fluxionality of about 20 kJ/mol, which is only about one-fourth of the value typical of fluxional arenes in 18e complexes.[30] If the arene ring in **9⁺** is bent, the metal must shift around its periphery at an unprecedented rate. A structure with the metal bound centrosymmetrically to a *planar* arene is a preferable explanation of the NMR data. This rationale is the primary basis on which a 19e structure is assigned to the Rh(II) radical,[31] with the *second* step of the electron transfer

series (Scheme 3) being the one involving the planar-to-bent arene distortion.

A Twist of Good Fortune

ESR spectroscopy is generally the method of choice for characterization of paramagnetic systems. If only ESR data had been available for **9⁺** (ESR spectra should be obtainable at liquid He temperature), one might have reasonably expected to diagnose the type of metal orbital involved in the SOMO and to obtain an estimate of the metal spin density from the orbital reduction factor.[32] Only in the unlikely event that proton superhyperfine splittings were resolved would one be able to make a direct argument about the arene conformation.

The quasi-degenerate ground state of **9⁺** (d_{xz}, d_{yz}) and concomitant rapid electronic relaxation[33] rendered the radical ESR-silent, however, at temperatures accessible to us ($T \geq 77$ K). The sharp-line NMR spectra of **9⁺** which arise from the radical being subject to very rapid electronic relaxation[29a,c] allowed us to spectroscopically probe the arene conformation.

How General Are Planar Arene Ligands in 19e Complexes?

Planar arenes are found (X-ray evidence) for the 19e first-row complexes (η^6-C₆Me₆)FeCp[2a] and [η^6-C₆Me₆)₂-Fe]⁺,[34] and they are highly probable for [(η^6-C₆R₆)Co-(η^5-C₅R₅)]⁺ with certain R groups.[35,36] Even some *20e* versions of the latter do not appear to undergo arene bending, which is less common for complexes of first-row metals than for those of the second and third rows.[37] There are also data, however, which suggest that odd-electron complexes of earlier transition metals are better described as having *bent* arene ligands. The strongest argument is based on ESR spectra assigned to the one-electron reduction product of bis-(benzene)chromium. The observation of three sets of two equivalent proton hyperfine splittings for one ring is consistent with the formulation [(η^6-Bz)Cr(η^4-Bz)]⁻, **10**, which has 17 electrons.[38]
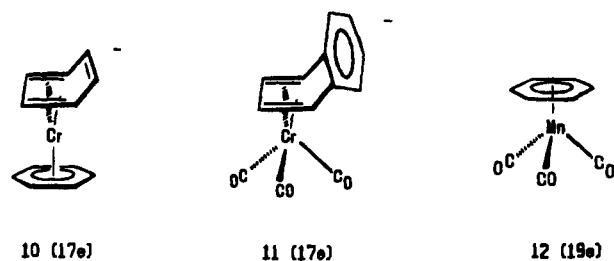
Two other relevant studies focus on arene metal carbonyl complexes. The voltammetric behaviors of the 18e complexes (η^6-naphthalene)Cr(CO)₃[39] and [(η^6-

(29) (a) Poole, C. P.; Farach, H. A. *Theory of Magnetic Resonance*, 2nd ed.; Wiley: New York, 1987; Chapter 11. (b) Clack, D. W.; Warren, K. D. *Struct. Bonding (Berlin)* **1980**, *39*, 1. (c) Rettig, M. F. In *NMR of Paramagnetic Molecules*; LaMar, G. N., Horrocks, W., Jr., Holm, R. H., Eds.; Academic Press: New York, 1973; p 220 ff.

(30) The 18e complex, **9²⁺**, is fluxional at elevated temperatures, the motion resulting in equivalency of all CH₃ groups: Darensbourg, M. Y.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 7425.

(31) Merkert, J.; Nielson, R. M.; Weaver, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7084.

(32) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; McGraw-Hill: New York, 1972; p 326.

(33) Ammeter, J. H. *J. Magn. Reson.* **1978**, *30*, 299.

(34) Ward, M. D.; Calabrese, J. C. *Organometallics* **1989**, *8*, 593.

(35) Kölle, U.; Fuss, B.; Rajasekharan, M. V.; Ramakrishna, B. L.; Ammeter, J. H.; Böhm, M. C. *J. Am. Chem. Soc.* **1984**, *106*, 4152.

(36) Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716.

(37) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

(38) Elschenbroich, C.; Bilger, E.; Koch, J.; Weber, J. *J. Am. Chem. Soc.* **1984**, *106*, 4297.

arene)Mn(CO)$_3$]$^{+}$ [40] reveal single *two-electron* reduction waves. Since the waves were nearly Nernstian, they lacked suitable diagnostic criteria to distinguish the $E°$ values or heterogeneous ET rates of the individual one-electron steps. It is not known how to distinguish the sequence of ET and structure changes in such two-electron Nernstian waves.[27b] The *chemistries* of the *doubly-reduced* products are, however, consistent with the presence of bent arenes.

Rieke[39] has postulated that arene bending occurs at the one-electron stage in the Cr system (hence a 17e metal in **11**), whereas Cooper[40] favors arene bending in the second stage for the Mn system (a 19e metal in **12**). The naphthalene ligand in **11** is more likely to undergo the slip-fold distortion than is a monocyclic arene ligand for reasons entirely analogous to the indenyl effect for five-membered-ring ligands. Reduction of (benzene)Cr(CO)$_3$ itself is an irreversible, apparently one-electron, reaction[39] which has not been studied in depth. Both **11** and **12** are unstable with respect to disproportionation, so that their spectroscopic characterization will be difficult to accomplish.

Interlude I: Implications of Nernstian Voltammetric Behavior

In a Nernstian[42] redox couple, any structural changes between the oxidized and reduced forms of the couple must be *rapid and reversible* on the electrochemical time scale. An inference that no appreciable structure changes occur between two Nernstian redox partners is not necessarily correct, as has been emphasized elsewhere.[43] Still, there are situations in which this inference makes a reasonable working hypothesis to help assign isomeric structures in redox pairs, as I believe the next example will show. We will discuss isomers of polyolefin complexes in which the gross structures of the 19e systems are identified by NMR spectroscopy of *the 18e complexes that complete the Nernstian redox couple.*

Redox Interconversions of Cobalt Cyclooctatetraene Isomers

Some years ago, we investigated the reduction of a complex which was denoted in the literature as CpCo-(1,5-C$_8$H$_8$), **13**. This study marked an effort to probe the fate of an 18e metal "diolefin" complex (two double bonds of the COT ring are not metal-bound) when it is reduced to a hypervalent state. We found that one-electron reduction of **13** produces an anion radical with a different isomeric makeup, but still containing a diolefin-bound C$_8$H$_8$ ring: [CpCo(1,3-C$_8$H$_8$)]$^-$, **14**$^-$. The equilibria and kinetics of the redox-induced isomerization have been detailed,[44] and here we just attend to the queries of (1) how the structure of the radical

(39) (a) Rieke, R. D.; Arney, J. S.; Rich, W. E.; Willeford, B. R., Jr.; Poliner, B. S. *J. Am. Chem. Soc.* **1975**, *97*, 5951. (b) Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420.
(40) Thompson, R. L.; Geib, S. J.; Cooper, N. J. *J. Am. Chem. Soc.* **1991**, *113*, 8961.
(41) Bowyer, W. J.; Geiger, W. E. *J. Electroanal. Chem.* **1988**, *239*, 253.
(42) Bard, A. J.; Faulkner, L. F. *Electrochemical Methods*; John Wiley and Sons: New York, 1980; p 215 ff.
(43) Geiger, W. E. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1985; Vol. 33, pp 276–281.
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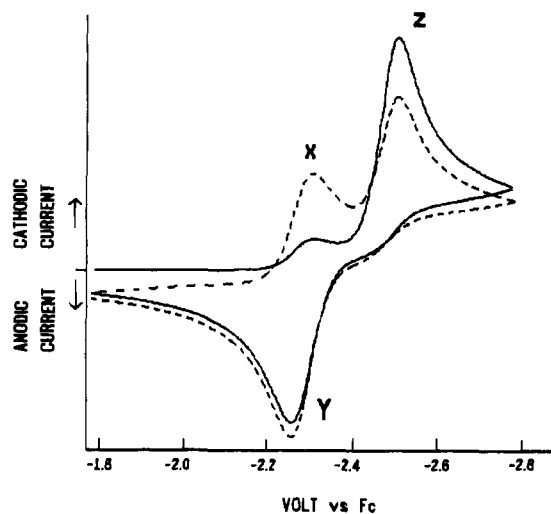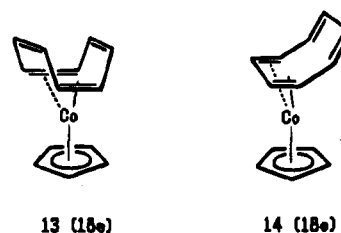

Figure 3. Two successive CV scans of CpCO(C$_8$H$_8$) at $v = 100$ V/s taken without pause. Isomers **13** and **14** are responsible for the cathodic features Z and X, respectively. The solid line gives the response of the first scan, the dashed line the response of the second scan.

anion, **14**$^-$, was assigned and (2) whether **14**$^-$ is a genuine 19e complex.


13 (18e)   **14 (18e)**

A cyclic voltammetric scan (solid line in Figure 3) displays, in addition to the major cathodic wave (Z) for **13**, two other features at more positive potentials, one cathodic (X) and one anodic (Y), which are separated by the Nernstian value of 60 mV. The presence of X and Y suggests (a) that solutions of **13** contain a previously unaccounted-for minor component and (b) that the reduced form of the minor component is the immediate product of the reduction of **13**. The enhanced cathodic wave (X) of the minor component on an immediate second scan (dashed line in Figure 3) reveals that the solution near the electrode is enriched in the minor component after the reduction/reoxidation cycle. Bulk cathodic electrolysis converted the sample to a product with an $E°$ of -2.27 V vs ferrocene (the X/Y couple). The ESR spectrum of the reduction product gave important information about the amount of Co character in the SOMO (vide infra), but offered no direct information about the metal–cyclooctatetraene geometry. That information came from study of the *oxidized* (18e) form of the minor (X/Y) component.

Examination of ^{1}H NMR spectra of fresh, unelectrolyzed, solutions of CpCo(COT) shows that the minor feature arises from the 1,3-COT isomer, **14**, which is present in a ratio of ca. 1:4 to **13** at ambient temperatures. This fact completed the puzzle and told us that when **13**, the isomer with a tub-shaped COT ring, is reduced by one electron, it rearranges to the isomer with the lawnchair-shaped COT ring, **14**$^-$, or at least to a closely related structure. There is no evidence that the COT ring is not still tetrahapto-bonded to Co

in the anion **14⁻**, although some flattening of the ring may accompany the electron addition.[45] It is worth noting that the structure of the 19e product might have remained uncertain if the equilibrium between neutral **13** and **14** had so heavily favored the former that the latter was below NMR detection limits. Just such a situation occurs in the studies of the reduction of the analogous *cyclooctadiene* complex, as we will later discuss.

Interlude II. Is 14⁻ a Genuine 19e Complex? How Does Metal–Ligand Covalency Influence This Description?

The surplus electron in **14⁻** occupies an orbital which is delocalized over both the metal and the ligands. EHMO calculations[45] and a detailed ESR study[46a] are in agreement that the SOMO is 30–40% Co d_{xy} and about 60% COT, with the majority of the ligand charge residing on the four uncomplexed carbons (see **14a**):

14a⁻ (as 18 + δ)   **MO of 14a**
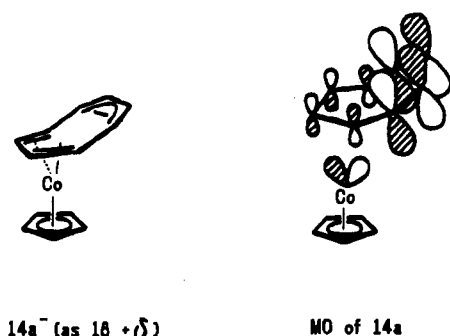
In the isoelectronic 19e nickel group complexes, $(\eta^5\text{-}C_5R_5)M(COT)$, M = Ni, Pd, the C_8H_8 ring appears to retain the tub configuration.[46a] Since the SOMO of the Ni group complexes is apparently highly metal based,[46] the contrast in the isomeric preferences of the Co and Ni group complexes strongly implicates the highly delocalized orbital in the former as being the key factor in the ring tub-to-chair conversion in the couple $CpCo(C_8H_8)^{0/1-}$. Complex **14⁻** is midway in electronic character between the two extremes of "metal-based" and "18 + δ" radicals and is perhaps best termed a "delocalized 19e complex". It represents only one point on a continuum between the two extremes of metal- and ligand-spin localization.

The amount of metal character in the SOMO of organometallic radicals is most frequently specified by the orbital reduction (or covalency) factor, k, which varies between unity (metal-localized radical) and zero (ligand-localized radical) depending on the degree of spin delocalization.[33,47] Table 1 gives a sampling of results on some organometallic radicals with a range of covalency (i.e., SOMO delocalization) in nominally metal-centered radicals.

Hypervalent Metal–Cyclooctadiene Complexes: 19e or 17e Compounds?

Complexes of first-row metals with simple diolefins such as norbornadiene, COD, and butadiene are

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(46) (a) Geiger, W. E.; Rieger, P. H.; Corbato, C.; Edwin, J.; Fonseca, E.; Lane, G.; Mevs, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 2314. (b) Kölle, U.; Ting-Zhen, D.; Keller, H.; Ramakrishna, B. L.; Raabe, E.; Krüger, C.; Raabe, G.; Fleischhauer, J. *Chem. Ber.* **1990**, *123*, 227.

(47) Rieger, P. H. In ref 2b, pp 290–294.

Table 1. Values of the Covalency Parameter, k', Reported for Selected 17e and 19e Organometallic Complexes

radical	17e/19e	nominal metal orbital	k'	ref
$Mn(dmpe)_2(\eta^2\text{-}(CH_2)_2C_6H_4)$	17e	$d_{x^2-y^2}$	0.59	a
$[CpMn(dppe)(CO)]^+$	17e	$d_{x^2-y^2}$	0.68	b
$[CpMn(PPh_3)(CO)_2]^+$	17e	$d_{yz} + d_{xy}$	0.38	b
$[Fe(CO)_5]^+$	17e	e_z^-	0.55	c
$CpFe(\eta^5\text{-}C_2B_9H_{11})$	17e	$d_{x^2-y^2}, d_{xy}$	0.86	d
$[Cp_2Fe]^+$	17e	$d_{x^2-y^2}, d_{xy}$	0.82	e
$[CpCo(\eta^2\text{-}R_2N_4)]^-$	19e	d_{xz}	0.60	f
Cp_2Co	19e	d_{xz}, d_{yz}	0.85	g
$[CpCo(CO)_2]^-$	19e	d_{yz}	0.56	h
$[(C_5Ph_5)Rh(CO)_2]^-$	19e	d_{yz}	0.45	i
$Cp^*Ni(\eta^4\text{-}C_4Ph_4)$	19e	$d_{xz} + d_{yz}$	0.86	j

^{a} Howard, C. G.; Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2631. ^{b} Pike, R. D.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Faraday Trans. 1* **1985**, 3913. ^{c} Lionel, T.; Morton, J. r.; Preston, K. F. *J. Chem. Phys.* **1982**, *76*, 234. ^{d} Maki, A. H.; Berry, T. E. *J. Am. Chem. Soc.* **1965**, *87*, 4437. ^{e} Prins, R. *Mol. Phys.* **1970**, *19*, 603. ^{f} Maroney, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 4144. ^{g} Ammeter, J. H. *J. Magn. Reson.* **1978**, *30*, 299. ^{h} Symons, M. C. R.; Bratt, S. W. *J. Chem. Soc., Dalton Trans.* **1979**, 1739. ^{i} Connelly, N. G.; Geiger, W. E.; Lane, G. A.; Raven, S. J.; Rieger, P. H. *J. Am. Chem. Soc.* **1986**, *108*, 6219. ^{j} Kölle, U.; Ting-Zhen, D.; Keller, H.; Ramakrishna, B. L.; Raabe, E.; Krüger, C.; Raabe, G.; Fleischauer, J. *Chem. Ber.* **1990**, *123*, 227.

known to form formal 19e complexes. [CpCo(diolef)]⁻ radicals are sufficiently persistent to be characterized by ESR spectroscopy,[48] and when diolef = 1,5-COD, the radical (**15⁻**) appears to isomerize to diolef = 1,3-COD (**16⁻**),[48] being thereby qualitatively analogous to the COT complexes discussed above. On the other

15⁻ (19e)   **16⁻ (19e)**

17⁻ (17e)   **18⁻ (17e)**
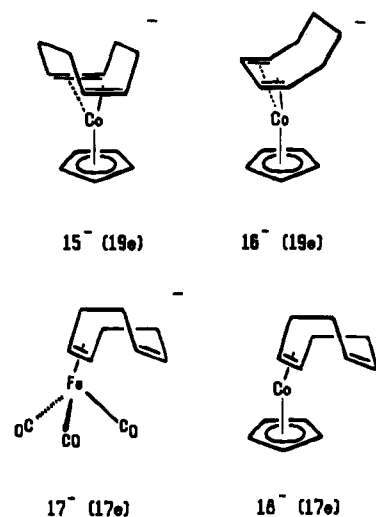
hand, the isoelectronic 19e anions $[(CO)_3Fe(diolef)]^-$ are suggested to partially decoordinate the diolefin, so that one of the double bonds is no longer bonded to the metal, thus reducing the formal electron metal count to 17 (see **17⁻**).[49] The grounds for the conclusions in these two different systems are worthy of examination.

The reduction of **15** was studied predominantly by electrochemical methods.[48] The 19e anion, **15⁻**, transforms over a period of several minutes to a new product with an $E°$ about 1 V positive of that of **15**. We argued for the structure **16⁻** for the new product

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(49) Krusic, P. J.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 2645.

on the basis of three facts: (1) its ESR spectrum is consistent with a Co-based SOMO, (2) its 1e *anodic oxidation* re-forms **15** in good yield, and (3) its *oxidative demetalation* [e.g., by Ce(IV)] produces free 1,3-COD, as opposed to 1,5-COD similarly released from **15⁻**. These observations give *indirect* evidence for **16⁻**, but the lack of direct spectroscopic evidence lends uncertainty to the nature of the rearranged reduction product.

Among the other structural candidates for [Cp-Co(COD)]⁻ is **18⁻**, in which the partially decomplexed COD ring acts as a *dihapto* ligand. In this structure, the hapticity change lowers the metal electron count from 19e to 17e. An argument in favor of such partial deligation is found in the results mentioned above of Krusic and co-workers on [(CO)₃Fe(diolef)]⁻ analogues.[49] When $(CO)_3Fe(\eta^4$-butadiene) (**19**) is reduced with 1 equiv of sodium naphthalenide, a high-resolution ESR spectrum of a radical with proton hyperfine splittings consisting of a doublet of triplets is obtained.

19 (18e)   **20⁻ (17e)**
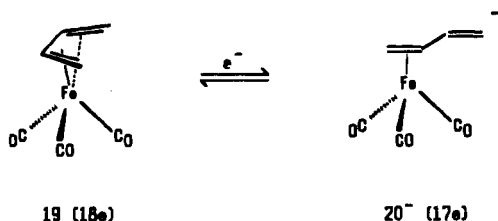
This evidence is consistent with the presence of a dihapto-bound butadiene ligand in the anion **20⁻**.[49] Support for concerted electron transfer and tetra- to dihapto rearrangement of (CO)₃Fe(diolef) comes from measurements of vapor-phase electron attachment rates for these compounds.[50] Further studies on these and related complexes are needed to clarify the nature of the rearrangement processes in these ions.

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(56) (a) Blackburn, D. W.; Britton, D.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1495. (b) Jonas, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520.

Future Directions

Nineteen-electron complexes are increasingly recognized as playing a central role in important processes such as ET chain catalysis and ligand substitution reactions.[4] Electrochemistry[12] and photochemistry[51] are at the center of studies of organometallic radicals, even though neither is inherently a structure tool. This Account suggests that our knowledge of the real structures of 19e systems lags far behind our knowledge of their reactivity. The pace at which this gap is closed may well be aided by new applications of spectroscopic and spectroelectrochemical methods. The techniques of paramagnetic NMR spectroscopy and electron-nuclear double resonance spectroscopy (ENDOR)[52] continue to be grossly underutilized in organometallic chemistry. Each of these methods has the potential to provide access to ligand (especially, proton) hyperfine splittings[52b] which can help deduce metal−ligand geomtries. Deuterium NMR spectroscopy of paramagnetic organometallics holds promise in minimizing problems arising from broad proton resonance lines.[53] Infrared spectroelectrochemistry[54] has undergone a rebirth,[55] but most applications to organometallic compounds have been limited to the carbonyl stretching energy region. Specially-chosen solvent/electrolyte combinations will open spectral windows to monitor other functional groups (alkynes, olefins, nitrosyls, etc.) to supplement the tools available for investigation of structures of hypervalent complexes. Increased use of synthetic methodologies[56] for the isolation of highly reduced complexes could also have a significant impact on progress in this important area of research.

Summary

Where formal 19e transition metal organometallic compounds are concerned, we are much more knowledgeable about reactivity than structure at this stage. This situation is understandable for a class of compounds that is highly reactive. The reluctance to assign genuine 19e structures to radicals may not, however, be justified in many cases. Metal−polyolefin complexes, in particular, have been shown as able to sustain "true" 19e structures. Increased attention to the problem of hypervalent radical structures is warranted, and some suggestions for future studies and directions have been made.