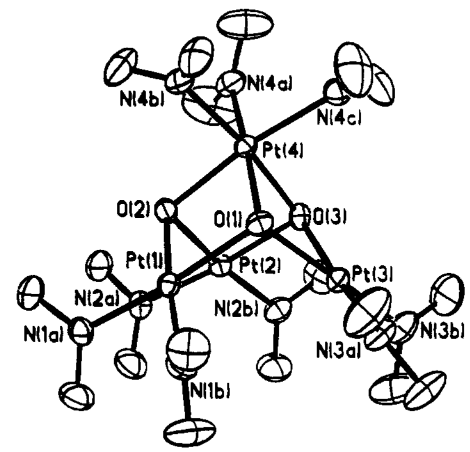

Figure 3. Thermal ellipsoid drawing (50% probability) of the $Pt_4(NO_2)_9O_3^{5-}$ anion.

$(OH)_2]\cdot1^1/_2H_2O$, there is an additional atom involved (Pt–N–O···H–O–Pt and Pt–O–H···O···H–O–Pt). This allows for shorter hydrogen bonds in the anion pair, O–H···O = 2.72 Å (OH to water) and O–H···O = 2.81 Å (OH to nitrito oxygen), than in the cation pair, N–H···O = 2.86 and 3.09 Å, even though the Pt–Pt distance is shorter in the cation pair. It has been proposed that in the carbonate salt there is a charge repulsion between the platinum atoms of the paired dimer units, resulting in a small displacement (0.09 Å) of the platinum atoms from their ligand planes.[9] No significant displacement is seen for the analogous platinum atoms in the anion pair we have studied or for the platinum atoms of the nitrate salt of $[Pt_2(NH_3)_4(OH)_2]^{2+}$. The latter displays chaining of cation complexes by hydrogen bonding in the crystal structure,[8] rather than pairing as described above.

$K_5[Pt_4(NO_2)_9O_3]\cdot3H_2O$. The structure of the tetranuclear anion $[Pt_4(NO_2)_4O_3]^{5-}$ is shown in Figure 3. It features a six-coordinate platinum ion oxo bridged to three four-coordinate platinum ions, which form a triangle bridged by the same three oxygen atoms. There are three nitrito ligands on the unique platinum and two on each of the other three platinums giving the anionic complex approximate C_{3v} symmetry. The coordination geometries and overall charge balance lead to the conclusion that the unique platinum is Pt(IV) and the others are Pt(II). No band is observed in the infrared spectrum that could be assigned to a bridging OH bending mode, in contrast to what is observed for the dimer reported above. Bond lengths and angle are given in Table V.

The Pt(II) part of this complex is analogous to the *cyclo*-tris(μ-hydroxo)tris[*cis*-diammineplatinum(II)] cation whose molecular structure has been reported as the carbonate salt.[9] In this complex, three diammineplatinum(II) units form a ring with bridging by hydroxo groups. In our complex, the hydroxo protons have been replaced by a trinitritoplatinate(IV) group. Interestingly, a second conformation has been reported for the trimer. As the nitrate salt, one hydroxo oxygen is below the plane of the platinum(II) ions.[10]

The observation of a mixed-valence species in these reaction mixtures is of interest because in more acidic solutions $Pt(III)_2^{6+}$ units are formed. Such units could be formed from the reverse disproportionation wherein Pt(IV) reacts with Pt(II) in a mixed-valence compound like the one described above.

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Supplementary Material Available: Listings of crystal data and structure refinement information, thermal parameters, least-squares planes, and nonbonded distances and packing diagrams (7 pages); listings of observed and calculated structure factors (57 pages). Ordering information is given on any current masthead page.

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(10) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Rosenberg, B. *Inorg. Chem.* **1978**, *17*, 1941.

(11) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Rosenberg, B. *Inorg. Chem.* **1977**, *16*, 1192.

Contribution from the Department of Chemistry,
Vanderbilt University, Nashville, Tennessee 37235

Detection of Covalency in Cyclopentadienyl Complexes of the Alkaline-Earth and f Elements: Statistical Evaluation of Structural Data

S. Craig Sockwell and Timothy P. Hanusa*

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Evidence for covalent bonding in cyclopentadienyl complexes of the alkaline-earth and f elements was sought by determining the strength of the linear relationship between metal radii and metal–Cp distances in over 200 structurally characterized compounds. Regression analysis indicates that the metal radius alone is a strong predictor of metal–Cp distances in divalent complexes but that the ligand environment around the metal markedly influences the "effective ionic radius" of the Cp ligand in trivalent and tetravalent compounds. Such steric effects need to be considered before inferences about the presence or absence of covalent bonding are drawn. Revised estimates for the Cp radius in several classes of cyclopentadienyl complexes are presented.

Introduction

Investigation of the degree of covalent bonding in cyclooctatetraenyl and cyclopentadienyl compounds of the pretransition and f elements has been a subject of recurrent interest ever since the isolation of uranocene ($(C_8H_8)_2U$) over 20 years ago.[1] Spectroscopic and physical evidence increasingly suggest that substantial covalent metal–ligand character exists in many organolanthanide and -actinide complexes, especially those in high oxidation states ($\geq$3).[2]

Nevertheless, definitive *structural* evidence for covalency in complexes of the pretransition and f elements has remained more

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(1) Streitwieser, A.; Müller-Westerhoff, U. *J. Am. Chem. Soc.* **1968**, *90*, 7364.

(2) (a) Chang, A. H. H.; Pitzer, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 2500–2507 and references therein. (b) Streitwieser, A. In *Organometallic of the f-Elements*; Marks, T. J., Fisher, R. D., Eds.; Reidel: Dordrecht, Holland, 1979; pp 149–177. (c) Brennan, J. G.; Green, J. C.; Redfern, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 2374–2375. (d) Green, J. C.; Kelley, M. R.; Long, J. A.; Kanellakopulos, B.; Yarrow, P. I. W. *J. Organomet. Chem.* **1981**, *212*, 329–340. (e) Bursten, B. E.; Casarin, M.; Ellis, D. E. A.; Fragalà, I. L.; Marks, T. J. *Inorg. Chem.* **1986**, *25*, 1257–1261. (f) Streitwieser, A., Jr.; Linsley, S. A.; Rigsbee, J. A.; Fragalà, I. L.; Ciliberto, E.; Rösch, N. *J. Am. Chem. Soc.* **1985**, *107*, 7786–7788. (g) Gulino, A.; Casarin, M.; Conticello, V. P.; Gaudiello, J. G.; Mauermann, H.; Fragalà, I.; Marks, T. J. *Organometallics* **1988**, *7*, 2360–2364.

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elusive. In some cases, such as $Cp_3U{=}CHPMe_2Ph$[3] and $(MeC_5H_4)_3U{=}NPh$,[4] multiple metal–ligand bonding has been posited by virtue of unusually short metal–ligand distances and large U–C–P and U–N–C angles. In many other complexes, it is difficult to draw such inferences; e.g., ionic and covalent bonding models may predict the same gross structure,[5] steric effects from bulky ligands may mimic the electronic effects expected from covalent bonding,[6] or satisfactory reference metal–ligand distances and angles may be unavailable.

Considering the ubiquity of the cyclopentadienyl ligand (Cp) in organoalkaline-earth-element and organo-f-element chemistry,[7] a diagnostic criterion for covalency in M–Cp interactions would be extremely useful. Such a test was proposed several years ago in a widely cited review of crystallographic data based on a survey of 23 cyclopentadienyl and cyclooctatetraenyl complexes of the f elements.[8] Because of the apparent invariance of an "effective ionic radius" for the Cp ligand of approximately 1.64 Å, the authors concluded that an ionic bonding model adequately explains the trends in metal–cyclopentadienyl distances in these compounds, i.e., that *no* structural evidence existed for covalent metal–ring bonding. Both we[9] and many others have used this value to analyze the bonding in organoalkaline-earth, organolanthanide, organoactinide, and metallocarborane complexes.[10]

Since that structural survey was completed, however, an enormous increase in the number and variety of structurally characterized ionic cyclopentadienyl complexes has appeared, and the claim has been made that structural data *do* reveal covalent metal–Cp bonding in complexes such as $Cp_2Sm(SiMe_3)_2^-$.[10g] It thus seemed appropriate to reanalyze metal–Cp distances in cyclopentadienyl complexes to determine the validity of structural criteria for bonding in these systems.

Procedure

Single-crystal X-ray and neutron investigations provided the structural information used in this study; structures determined by gas electron diffraction were excluded. Effective ionic radii of the Cp ligands were calculated from the difference between the metal–carbon distance and the metal radius and from the difference between the metal–ring centroid distance and the metal radius. In the subsequent discussion, these two radii will be referred to as R_{M-C} and $R_{M-\Omega}$, respectively. Metal–ring carbon and metal–ring centroid distances, if not given directly in the references, were calculated from the fractional coordinates. Metal radii were taken from Shannon's compilation,[11] and adjustments for other coordination numbers were calculated according to the method outlined in ref 8.

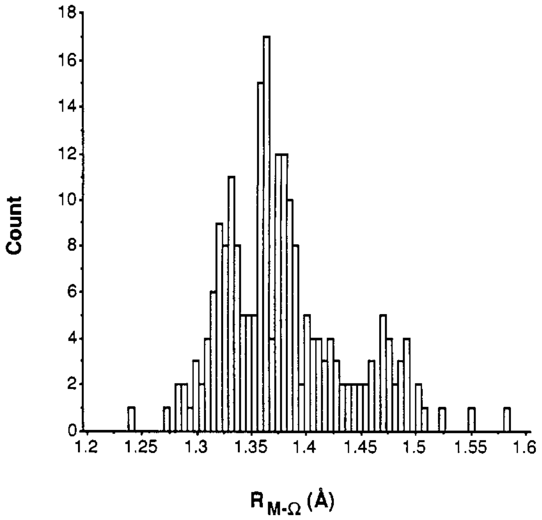

Figure 1. Histogram of $R_{M-\Omega}$ radii for the complete set of cyclopentadienyl complexes, indicating the multimodal nature of the distribution.

Multiple regression analysis and other routine statistical tests were performed by using standard techniques.[12] The form of the multiple regression was $y = \alpha + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3$, where y is the M–C or M–Ω distance, α is the intercept of the regression line, and β_1, β_2, and β_3 are the partial regression coefficients for the metal radius, the oxidation number, and the metal coordination number, respectively. The multiple correlation coefficient R was calculated as $R = [\sum(y - \bar{y})(\hat{y} - \bar{y})]/[\sum(y - \bar{y})^2 \sum(\hat{y} - \bar{y})^2]^{1/2}$ where $\hat{y}$ is the estimated metal–Cp distance. Unless otherwise indicated, the level of significance used in all tests was $\alpha = 0.01$ (99% confidence level).

Results and Discussion

Structural evidence for or against ionic bonding is usually predicated on the ability of the sum of cation and anion radii to reproduce observed metal–ligand distances (i.e., $R = r_+ + r_-$). The basis for establishing such additivity in binary salts and oxides has been through comparisons of compounds considered to be "indisputably" ionic (i.e., those containing group 1 and 2 metals) and those containing metals likely to be more covalent in character (e.g., d-block metals). The systematic shortening of cation–anion distances and the reduction of cell volumes between otherwise isostructural systems are cited as evidence for covalency in these systems.[13]

Despite the wide variety of ionic Cp complexes known, the large range in radii in structurally characterized compounds (e.g., 0.72 Å in 6-coordinate Mg^{2+} to 1.38 Å in 7-coordinate Ba^{2+}) and the variety of observed coordination numbers (6–12) mean that comparatively few have isostructural analogues among the d-block or p-block metals. Such comparisons are thus not a feasible general test for covalency in Cp complexes.

Cyclopentadienyl Radii. The approach used in the earlier survey[8] to identify covalency in cyclopentadienyl complexes was to define an "ionic radius" for the Cp ligand and then to determine whether the addition of metal and Cp radii reproduced observed metal–Cp distances; this is mathematically equivalent to determining whether the Cp radius has a constant value. For any but spherical ligands (halides, hydrides, etc.), however, the ligand "radius" is not a uniquely defined concept, and two approaches are used in the present study: (a) the previously used definition,[8]

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(3) Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1983**, *2*, 1336–1340.

(4) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514–516.

(5) A symmetrical sandwich structure is expected for magnesiocene (Cp_2Mg), for example, whether the structure is considered to be purely ionic ($Cp^-Mg^{2+}Cp^-$) or largely covalent ((π-Cp)Mg(π-Cp)) (Bünder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, *92*, 1–6).

(6) This is a frequent complication in complexes containing M–O–M or M–O–L linkages (L = aryl or bulky alkyl group); see: Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405–409. Evans, W. J.; Hanusa, T. P.; Levan, K. R. *Inorg. Chim. Acta* **1985**, *110*, 191–195 and references therein.

(7) (a) *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalà, I. L., Eds.; Reidel: Dordrecht, Holland, 1985. (b) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds; Pergamon Press: Oxford, England, 1982. (c) *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D., Eds.; Reidel: Dordrecht, Holland, 1979. (d) McCormick, M. J.; Williams, R. A.; Levine, L. J.; Hanusa, T. P. *Polyhedron* **1988**, 7(9), 725–730.

(8) Raymond, K. R.; Eigenbrot, C. W., Jr. *Acc. Chem. Res.* **1980**, *13*, 276–283.

(9) (a) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1045–1046.

(10) See, for example: (a) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115–4119. (b) Tilley, T. D.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1982**, *21*, 2644–2647. (c) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999–3003. (d) Day, C. S.; Day, V. W.; Ernst, R. D.; Vollmer, S. H. *Organometallics* **1982**, *1*, 998–1003. (e) Fagan, P. M.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982**, *1*, 170–180. (f) Wasserman, H. J.; Zozulin, A. J.; Moody, D. C.; Ryan, R. R.; Salazar, K. V. *J. Organomet. Chem.* **1983**, *254*, 305–311. (g) Schumann, H.; Nickel, S.; Hahn, E.; Heeg, M. J. *Organometallics* **1985**, *4*, 800–801. (h) Deacon, G. B.; Fallon, G. D.; Wilkinson, D. L. *J. Organomet. Chem.* **1985**, *293*, 45–50. (i) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 4458–4459.

(11) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

(12) (a) Dowdy, S.; Wearden, S. *Statistics for Research*; Wiley: New York, 1983. (b) McNeil, K. A.; Kelly, F. J.; McNeil, J. T. *Testing Research Hypotheses Using Multiple Linear Regression*; Southern Illinois University: Carbondale, IL, 1975.

(13) Shannon, R. D.; Vincent, H. *Struct. Bonding (Berlin)* **1974**, *19*, 1–43.

i.e., the difference between the metal–carbon distance and the metal radius (R_{M-C}), and (b) the difference between the metal–ring centroid distance and the metal radius ($R_{M-\Omega}$). The latter definition might be of greater use when steric effects are analyzed with the solid angle sum approach of Bagnall[14] and Xing-fu.[15] Both radii were used throughout this work and gave similar indications of trends and differences in groups of compounds.

As a starting point in the present analysis, the average Cp ionic radius was calculated by using the R_{M-C} definition in order to compare it to the value derived from the previous study.[8] For the complete data set of 213 complexes, the radius is 1.651 (0.004, 0.06) Å,[16] a result indistinguishable from the previous value of 1.648 (0.008, 0.04) Å.[8] The analogous $R_{M-\Omega}$ value is 1.378 (0.004, 0.06) Å.

The relatively narrow error limits on the average Cp radii are somewhat misleading, however, as histograms of the radii are distinctly multimodal (Figure 1). In the $R_{M-\Omega}$ radii, for example, three modes are evident in the regions 1.31–1.33, 1.35–1.39, and 1.45–1.50 Å. Inspection of the data suggests that these modes are associated with complexes containing metals in the +2, +3, and +4 oxidation states, respectively. Recalculating the radii with the complexes divided by oxidation state yields values of 1.333 (0.005, 0.03) Å, 1.358 (0.003, 0.04) Å, and 1.440 (0.006, 0.05) Å for $R_{M-\Omega}$ in divalent, trivalent, and tetravalent complexes, respectively. For R_{M-C}, a similar treatment leads to the values 1.607 (0.005, 0.03) Å, 1.632 (0.004, 0.04) Å, and 1.711 (0.006, 0.05) Å, respectively. Analysis of these oxidation-state-specific radii with use of a standard Student *t* or modified *t* test[17] indicates that differences between the means are statistically significant.

The fact that the calculated Cp radius *increases* with higher charge indicates that, on the average, the Cp ligands are progressively farther away from the metal centers in the di-, tri-, and tetravalent complexes, respectively. Purely electrostatic considerations would suggest the opposite; i.e., a higher charge on the metal center should increase the electrostatic field on the metal center, thereby increasing the attraction of the ligand to the metal and *shortening* the distance.[18] Evidently steric influences are responsible for this effect, as the increase in the Cp radius with metal oxidation state parallels a rise in the average coordination number of the complexes, from 6.9 (+2) to 8.4 (+3) to 9.3 (+4). The larger number of ligands required to balance the metal charge in the tri- and tetravalent compounds generates greater interligand van der Waals repulsions, forcing the ligands to remain a farther distance from the metal center than would otherwise be the case. If this explanation for the increase of the Cp radius is valid, it suggests that metal–Cp "covalent shortening" in tri- and tetravalent complexes could be masked by steric effects.

Metal–Ligand Distance vs Metal Radii. An alternate measure of the internal consistency of the data can be obtained from plots of metal-to-ring-centroid or metal-to-carbon distances vs metal radii. In the ionic limit, additivity of radii requires that such plots should have a slope of unity (i.e., $dR_{M-(\Omega \text{ or } C)}/dr_+ = 1$). For the total set of complexes, $dR_{M-\Omega}/dr_+$ is 0.87 ($r^2 = 0.66$) and dR_{M-C}/dr_+ is 0.81 ($r^2 = 0.64$). The value of r^2 indicates that the metal radii account for only two-thirds of the variability in the metal–carbon distances, which would seem to be an unsatisfactorily low correlation for nominally "ionic" compounds. As a comparison, the slope and correlation observed in a plot of metal–Cp distances for the first-row d-block metallocenes ($dR_{M-C}/dr_+ =$ 1.18; $r^2 = 0.83$) were taken as structural evidence that the compounds did *not* fit an ionic model.[8]

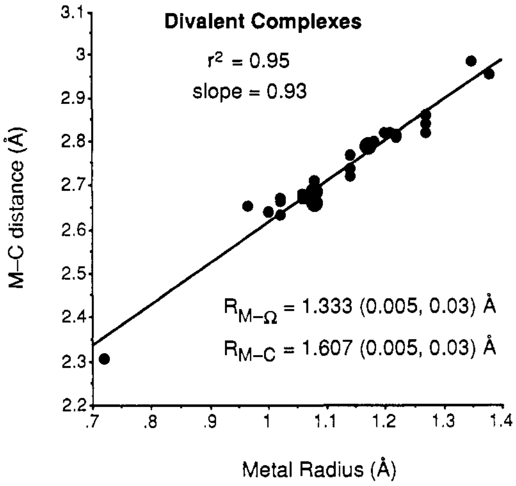

Figure 2. Scatter plot of metal–carbon distances vs metal radii for divalent complexes. Larger dots represent coincident data points. The line is the least-squares fit to the data. The average radius is followed by the standard error and standard deviation.

Considering the evidence presented above that the radius of the Cp ligand varies with the oxidation state of the metal, a multiple regression analysis was performed with use of both the metal radius and the oxidation state as predictors of the R_{M-C} and $R_{M-\Omega}$ distances. The inclusion of the metal oxidation state provides significantly stronger predictability of the metal–ligand distances ($R^2 = 0.81$ for $R_{M-\Omega}$; $R^2 = 0.79$ for R_{M-C}).

The increase in correlation is not uniform from one oxidation state to another, however. A simple linear regression comparing metal–carbon distances and metal radii was performed on the complexes divided by metal oxidation states. With divalent metal complexes, an excellent correlation (i.e., $dR_{M-C}/dr_+ = 0.93$; $r^2 = 0.95$) is observed between the metal radii and ligand distances (Figure 2). Evidently, the metal radius alone is sufficient to predict metal–Cp distances fairly accurately in *divalent* complexes, a characteristic of highly ionic bonding.[19]

In contrast, the linear correlation for trivalent complexes is weaker ($dR_{M-C}/dr_+ = 0.84$; $r^2 = 0.80$), and for tetravalent complexes there is essentially no correlation between the metal radius and the metal–Cp distance ($dR_{M-C}/dr_+ = 0.29$; $r^2 = 0.07$). Differences between r^2 values for the three oxidation states are statistically significant, evidence that additional factors influencing metal–ring distances are operative in the tri- and especially tet-

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(14) (a) Bagnall, K. W.; Lopez, O. V.; Xing-fu, L. *J. Chem. Soc., Dalton Trans.* **1983**, 1153–1158. (b) Bombieri, G.; Benetollo, F.; Croatto, U.; Castellani, C. B.; Bagnall, K. W.; Xing-fu, L. *Inorg. Chim. Acta* **1984**, *95*, 237–245.

(15) (a) Xing-fu, L.; Xi-Zhang, F.; Ying-Ting, X.; Hai-Iung, W.; Jie, S.; Li, L. *Inorg. Chim. Acta* **1986**, *116*, 85–93. (b) Xi-Zhang, F.; Ao-Ling, G.; Ying-Ting, X.; Xing-fu, L. *Polyhedron* **1987**, *6*(5), 1041–1048.

(16) The first figure in parentheses is the standard error (standard deviation of the mean), and the second is the sample standard deviation. Numbers are rounded on the basis of the standard error.

(17) Behrens-Fisher test; see ref 12a, pp 194–195.

(18) This is especially true since the average metal radii in the data set for trivalent (1.06 Å) and tetravalent complexes (1.07 Å) are smaller than in divalent species (1.12 Å).

(19) Since divalent complexes in general display strong metal radius/metal–Cp distance correlations, the errors on the ionic radius for the Cp ligand are larger than might be expected. Two factors contribute to the apparent discrepancies. The first is that the standard error of the mean (SEM) is sensitive to the size of the sample, i.e., SEM = $\sigma/n^{1/2}$; since the number of divalent complexes is roughly one-half to one-third of the number of trivalent and tetravalent compounds, the divalent set would have a larger standard error even with the same σ. A second reason is that, with their relatively large radii and low coordination numbers, some divalent complexes are sufficiently coordinatively unsaturated that they exist as oligomers or coordination polymers in the solid state (e.g., $(Cp^*)_6Yb_4(\mu\text{-}F)_4$,[20] Cp^*_2Ba[21]). Their formal coordination numbers do not provide accurate gauges to the size of the metal radii, and their calculated Cp radii deviate appreciably from the average values. They consequently have a disproportionately large influence on the standard deviation of the set. For example, because of two close intramolecular $Yb\cdots CH_3$ contacts, the CN of Yb^{2+} in $(Cp^*)_6Yb_4(\mu\text{-}F)_4$ could be regarded as 7 rather than as 5, with a corresponding change in the metal radius and the calculated Cp radius. If this one adjustment were made to the data set, the values for the standard error and standard deviation for R_{M-C} would decrease from 0.005 and 0.03 to 0.004 and 0.02, respectively. Such modifications are inherently arbitrary, however, and we have not attempted to incorporate them.

(20) Burns, C. J.; Berg, David J.; Andersen, Richard A. *J. Chem. Soc., Chem. Commun.* **1987**, 272–273.

(21) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1045–1046.

ravalent species which are not important in the divalent complexes.[22]

Correction for Steric Effects. Since the trivalent and tetravalent compounds have higher coordination numbers and greater opportunities for ligand–ligand repulsions than do the divalent compounds, it is natural to focus attention on steric interactions in their metal coordination spheres. The varied and often irregular sizes of ligands make such interactions difficult to quantify, although progress in this direction is being achieved.[14,15] We attempted here a simple, "global" estimate of the effect ligand–ligand repulsions might have on metal–ligand distances.

One approach to approximating the correction for steric influences is to select classes of the complexes with as similar a coordination environment as possible; this should minimize variations due to different ligand sets on the metals. A search was made of the data base for classes of complexes that displayed strong ($r^2 \geq 0.95$) metal radius/metal–Cp correlations and for which $dR_{M-\Omega(C)}/dr_+$ was 1.0 ± 0.1. Other than the divalent complexes already discussed, the only compounds meeting these criteria were neutral trivalent species containing three Cp or two Cp* (Cp* = Me_5C_5) ligands; evidently these bulky sets occupy a large fraction of the coordination spheres of the metals and minimize the steric influences of other ligands. Figure 3 presents least-squares plots and optimal radii of the Cp ligands in trivalent Cp_3ML_n complexes, where L_n represents 0, 1, or 2 terminal or bridging ligands, and in mononuclear trivalent $Cp^*_2ML_2$ complexes (CN = 8). No other classes of trivalent complexes were found that possessed values within the above limits for both the slope and the correlation coefficient. The next best category of compounds contained the common $[Cp_2M(\mu\text{-}X)]_2$ dimers (CN = 8), where Cp = C_5H_5 or various mono- or disubstituted rings (Figure 3). The greater scatter around the regression line and the value of the slope substantially above 1 indicate that the bulk of two Cp rings does not sufficiently dominate the coordination sphere of the metals so that the steric properties of X can be ignored.

Just as important as the determination of those classes of complexes for which workable values of the Cp radius can be found is the identification of types of compounds for which the "effective Cp radius" is *not* a useful concept. No classes of tetravalent complexes were discovered that even approach the above criteria for both r^2 and the slope. The most promising candidate was the set of Cp_3AnL_2 and Cp_4An complexes (Cp = C_5H_5 or indenyl; CN = 11 or 12), for which $r^2 = 0.98$. The slope of the regression line is 2.23, however, indicating that the metal–Cp distance increases at over twice the rate of the metal radii; i.e., an additive relationship does not exist between the metal radius and the Cp radius. It is also interesting to note that the strong dR_{M-C}/dr_+ correlation found for trivalent tris(cyclopentadienyl) complexes does not extend to their tetravalent counterparts. The class of Cp_3UL_n complexes, for example, has a dR_{M-C}/dr_+ correlation of ~0; in particular, metal–Cp distances for the Cp_3UL complexes (CN = 10) range from 2.68 to 2.82 Å, even though they all are constructed around the same metal with a nominal radius of 1.08 Å. Similarly, the set of mono- or dinuclear complexes containing the 8-coordinate tetravalent $Cp^*_2ML_n$ unit has a coefficient of determination of $r^2 = 0.77$; the trivalent equivalent has $r^2 = 0.98$.

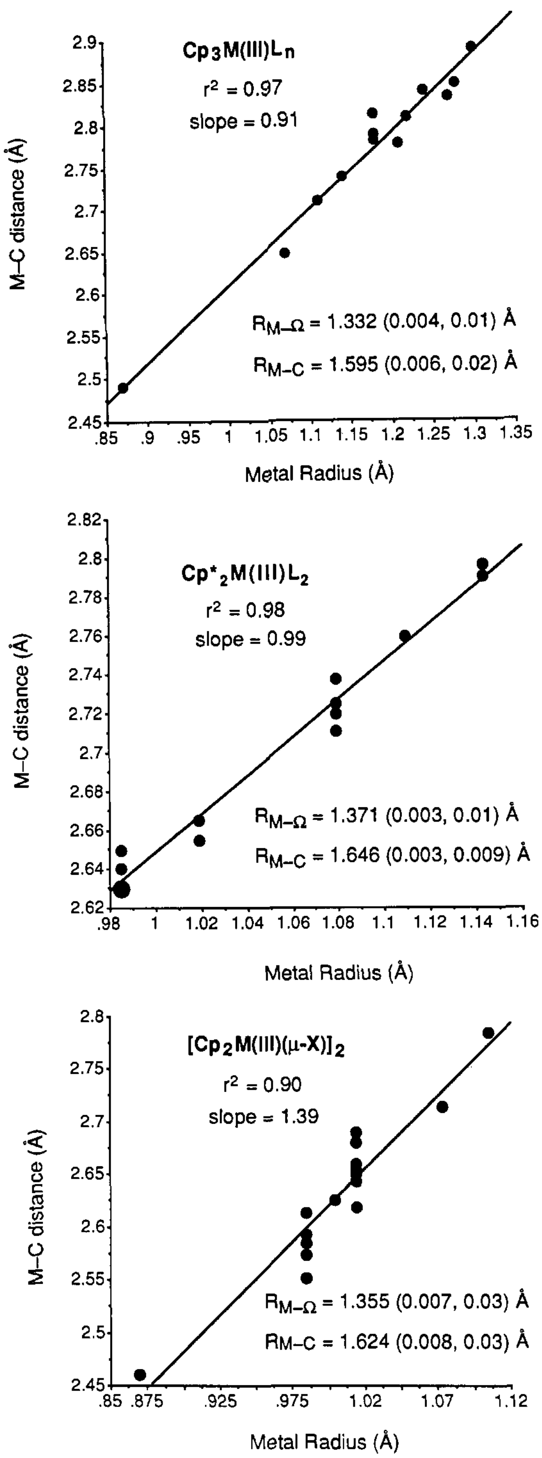

Figure 3. Scatter plots of metal–carbon distances vs metal radii for the neutral trivalent complexes Cp_3ML_n, where L_n represents 0, 1, or 2 terminal or bridging ligands, mononuclear $Cp^*_2ML_2$ compounds, and the $[Cp_2M(\mu\text{-}X)]_2$ dimers. The average radius for each class of complexes is followed by the standard error and standard deviation.

Use of Coordination Number as a Predictor of Metal–Ligand Distances. As an alternative to selecting actual subsets of complexes for analysis, we examined the effect the CN of a complex has on metal–ligand distances by adding it as a variable in a multiple regression analysis that included the metal radius and oxidation state. The multiple regression coefficient for $dR_{M-\Omega}/dr_+$ (dR_{M-C}/dr_+) of the complete data set rose from $R^2 = 0.81$ (0.79), with the metal radius and oxidation state as variables, to $R^2 = 0.88$ (0.87) when the coordination number was included; the improvement is significant at the 99% confidence level.

The effect of using the CN with the metal radius as predictors of metal–Cp distances in complexes divided by oxidation states is instructive. The change in R^2 for divalent complexes is a negligible increase from 0.95 to 0.96, underscoring the comparative unimportance of steric effects on the structures of these complexes. For trivalent compounds the increase in R^2 is also small (0.80 to 0.84) and not significant at even the 90% confidence level. R^2 for the tetravalent complexes, however, rose from 0.07 for the entire data set to 0.45, an improvement significant at the 99% confidence level. The large enhancement in correlation confirms that ligand–ligand interactions in tetravalent cyclopentadienyl systems play a major role in determining their Cp–metal distances.

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(22) One of these factors could be the net charge on the complexes; all of the divalent species are neutral compounds, for example, whereas the charge on tetravalent complexes ranges from 1+ to 5−. Since only 6% of the total number of complexes is charged, too few examples are available to test any trends adequately.

The fact that with the present analysis a combination of the metal radius and coordination number accounts for slightly less than half of the metal–ligand distance variability in tetravalent systems, whereas these factors can compensate for >80% of the variation in divalent and trivalent compounds, *might* be taken as an indication that covalent effects are introducing significant nonlinear deviations from the trends expected from an ionic bonding model. Just as reasonably, however, the poor correlation in tetravalent complexes may indicate that ligand–ligand contacts in the highly coordinated compounds are sufficiently complicated that a detailed analysis of steric interactions will be required for the interpretation of the geometries of these systems. Only then should covalency be introduced as an explanation for structural anomalies in such cyclopentadienyl complexes.

Conclusions

Analysis of metal–cyclopentadienyl distances in a large number of alkaline-earth-element and f-element complexes makes it evident that a unique value for the cyclopentadienyl radius does not exist. Metal–Cp distances are a function of both the radius of the metal center and amount of ligand–ligand contact on the coordination sphere of the metal, which can be correlated with the oxidation state and, to a lesser extent, the coordination number of the metal center. The concept of an "effective ionic radius" for the Cp ligand is still useful in the case of divalent complexes, however, and can be used with certain classes of trivalent species if complexes with similar ligand sets are used as the basis for comparison. No consistent value for the Cp radius can be found for tetravalent cyclopentadienyl compounds.

A rigorous analysis of ligand–ligand repulsions is obviously of paramount importance for the prediction of structures of ionically bonded organometallic compounds. Attempts toward modeling these interactions in a quantitative fashion for both cyclopentadienyl systems and other ionic complexes are in progress.

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Supplementary Material Available: Tables of multiple regression coefficients for M–Ω and M–C distances vs metal radius, oxidation number, and coordination number and of regression coefficients for M–Ω and M–C distances vs metal radius for complexes divided by oxidation states and a complete listing of and literature references for all complexes used in this study (17 pages). Ordering information is given on any current masthead page.

Contribution from the Institute of Chemistry,
Academia Sinica, Taipei, Taiwan, ROC

Electron Delocalization in Mixed-Valence Biferrocenium Salts: Nuclear Magnetic Resonance Contact Shift Studies

Teng-Yuan Dong,* Ming-Yhu Hwang, Tsui-Ling Hsu, Chi-Chang Schei, and Show-Kei Yeh

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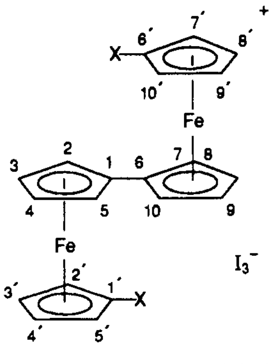
1′,6′-Diethenylbiferrocenium triiodide (**6**) was prepared, and the intramolecular electron-transfer rate was determined. The X-ray structure of 1′,6′-diethenylbiferrocene at 300 K has been determined: monoclinic, $P2_1/n$, a = 5.7977 (4) Å, b = 17.2970 (20) Å, c = 9.1994 (13) Å, and β = 90.210 (15)°; ρ_{calcd} = 1.520 g cm^{-3}, Z = 2, R_F = 0.04, and R_{wF} = 0.03. The ^{1}H and ^{13}C NMR contact shifts have been observed for a series of mixed-valence biferrocenium triiodides. Analysis of the sign of contact shifts suggests that the electron delocalization is based on competing σ and π delocalization mechanisms. It appears that the σ skeleton in the delocalization of spin density is strongly favored in the cyclopentadienyl moiety. The unpaired spin delocalization in π-type orbitals is found to predominate in the fulvenide moiety.

Introduction

Discoveries made in the last few years have shown that the solid-state environment plays a crucial role in determining the rate of intramolecular electron transfer in various mixed-valence complexes.[1] In the case of binuclear mixed-valence biferrocenium compounds, it has been found that the nature of the solid-state environment about a mixed-valence cation can dramatically affect the rate of intramolecular electron transfer.[2-8] Several important observations have been made on the mixed-valence compounds **1**–**5**.[3,4,8] Compounds **2**–**5** give unusual temperature-dependent Mössbauer spectra. At temperatures below 200 K they each show two doublets, one for the Fe^{II} and the other for the Fe^{III} site. Increasing the sample temperature in each case causes the two doublets to move together with no discernible line broadening and eventually to become a single "average-valence" doublet at temperatures of 275, 245, 275, and 260 K, respectively. Furthermore, pronounced sample history dependencies of rates of electron transfer have been noted for compounds **1**, **4**, and **5**. For example, a microcrystalline sample of **5** gives a 300 K Mössbauer spectrum which is dominantly that of a valence-localized species (i.e., two



X = H (**1**), C_2H_5 (**2**), C_3H_7 (**3**), C_4H_9 (**4**), $CH_2C_6H_5$ (**5**), $CH{=}CH_2$ (**6**)

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(1) Hendrickson, D. N.; Oh, S. M.; Dong, T.-Y.; Moore, M. F. *Comments Inorg. Chem.* **1985**, *4*(6), 329.

(2) Dong, T.-Y.; Cohn, M. J.; Hendrickson, D. N.; Pierpont, C. G. *J. Am. Chem. Soc.* **1985**, *107*, 4777.

(3) Cohn, M. J.; Dong, T.-Y.; Hendrickson, D. N.; Geib, S. J.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1985**, 1095.

(4) (a) Dong, T.-Y.; Hendrickson, D. N.; Iwai, K.; Cohn, M. J.; Reingold, A. L.; Sano, H.; Motoyama, I.; Nakashima, S. *J. Am. Chem. Soc.* **1985**, *107*, 7996. (b) Konno, M.; Hyodo, S.; Iijima, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2327. (c) Nakashima, S.; Masuda, Y.; Motoyama, I.; Sano, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1673. (d) Nakashima, S.; Katada, M.; Motoyama, I.; Sano, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2253.

(5) (a) Dong, T.-Y.; Hendrickson, D. N.; Pierpont, C. G.; Moore, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 963. (b) Motoyama, I.; Suto, K.; Katada, M.; Sano, H. *Chem. Lett.* **1983**, 1215. (c) Kai, M.; Motoyama, I.; Katada, M.; Masuda, Y.; Sano, H. *Chem. Lett.* **1988**, 1037.

(6) Dong, T.-Y.; Kambara, T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 4423.

(7) Dong, T.-Y.; Kambara, T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 5857.

(8) Sorai, M.; Nishimori, A.; Hendrickson, D. N.; Dong, T.-Y.; Cohn, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 4266.