sometimes observed. We have repeatedly experienced that triphos is not able to stabilize CO_2 adducts either of type A or of type B.[3,8] Thus, whichever species (triphos)Ni$(CO_2)_x$ is on the way of being formed, an easy degradation does follow. (v) The water molecules found in the crystal lattice of **2′** are to be ascribed to the use of reagent grade benzene. We have found that the carbonate–nickel complex is formed regardless of the trace amounts of water in the solvent. In particular, the anhydrous complex **2** is obtained by using dehydrated solvents. Thus, the presence of traces of water in our system does not seem to have the same importance as in the formation of other carbonate complexes from CO_2,[9] but rather serves to improve the crystallization process. By contrast, significant amounts of water in the reaction mixture have been found to inhibit the formation of the carbonate complex. These points suggest an overall process shown in Scheme I.

The above results indicate that none of the pathways (1)–(3) taken separately fully describe the transformation of CO_2 within our system. In fact, not only a carbonate complex and carbon monoxide are formed as in eq 3[10] but also a phosphine group of the ligand is oxidized as in eq 2.[11] Unfortunately, we have not been able to characterize any metal–CO_2 adduct; however, it seems reasonable to accept the idea of the intermediacy of $L_3M(CO_2)_x$ and $L_2M(CO_2)_x$ adducts at different times in the course of the reaction. This agrees well with the assumption that the nature of the metal–ligand fragment is of critical importance in determining not only the coordination mode[8] but also the pattern of CO_2 fragmentation.

Acknowledgment. This work was supported by a grant from the CNR program Chimica Fine e Secondaria.

Registry No. **1**, 60294-99-7; **2′**, 90914-29-7; CO_2, 124-38-9.

Supplementary Material Available: Listings of final positional and thermal parameters with standard deviations for (triphos=O)Ni$(O_2CO)\cdot 0.5H_2O\cdot C_6H_6$ (4 pages). Ordering information is given on any current masthead page.

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Bonding and Conformational Relationships in the "Open Metallocenes": Solid-State Structures of Bis(2,4-dimethylpentadienyl) Compounds of Vanadium and Chromium

Sir:

Recently we have demonstrated that a fairly extensive series of thermally stable, yet chemically reactive, bis(pentadienyl)metal compounds ("open metallocenes") exists.[1] This new series of related molecules clearly affords us a key opportunity to explore structural trends in metal–pentadienyl compounds and thereby gain important insight into their bonding. Structural characterization of the bis(2,4-dimethylpentadienyl) complexes of vanadium and chromium is presented herein and does indeed provide some useful information concerning these "open metallocenes", particularly as a comparison to related cyclopentadienyl and allyl analogues.

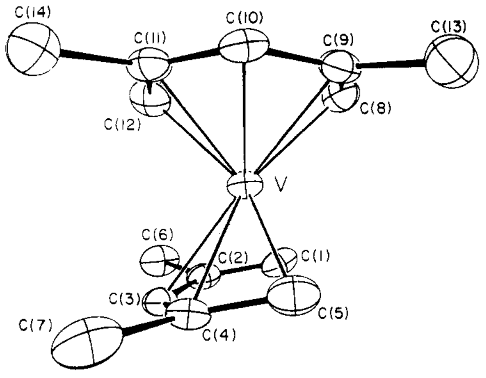

Figure 1. Perspective view of bis(2,4-dimethylpentadienyl)vanadium. The 30% probability ellipsoids are shown.

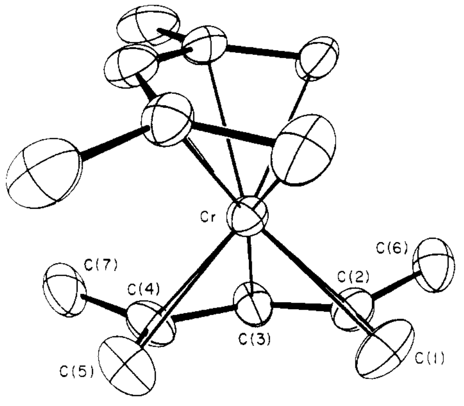

Figure 2. Perspective view of bis(2,4-dimethylpentadienyl)chromium. The 30% probability ellipsoids are shown. The molecule lies on a twofold rotational axis.

Table I. Bonding Parameters[a]

parameter	V	Cr	Fe
A. For $M(2,4\text{-}C_7H_{11})_2$ Compounds			
conformation angle	89.8	82.9	59.7
M–C(1,5)	2.179 (4)	2.166 (6)	2.108 (5)
M–C(2,4)	2.231 (4)	2.162 (5)	2.073 (4)
M–C(3)	2.236 (5)	2.167 (7)	2.084 (3)
M–C (av)	2.211 (2)	2.165 (4)	2.089 (1)
M–CM	1.632 (2)	1.594 (4)	1.508 (2)
C–C (internal)	1.415 (4)	1.414 (8)	1.416 (4)
C–C (external)	1.389 (4)	1.378 (8)	1.406 (4)
C(1)–C(2)–C(3)	124.7 (4)	125.2 (8)	124.1 (3)
C(2)–C(3)–C(4)	130.2 (3)	127.4 (8)	125.5 (3)
C(3)–C(4)–C(5)	125.0 (3)	123.5 (8)	120.7 (3)
C(1)- -C(5)	3.05 (1)	2.93 (1)	2.785 (5)
B. For $M(C_5H_5)_2$ Compounds			
M–C	2.280 (5)	2.169 (4)	2.064 (3)
C–C	1.434 (3)	1.431 (2)	1.440 (2)
M–CM	1.928 (6)	1.798 (4)	1.660 (10)

[a] Angles are given in degrees; distances are given in angstroms.

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[1] (a) Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 1120. (b) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220. (c) Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 3737. (d) Stahl, L.; Ernst, R. D. *Organometallics* 1983, *2*, 1229.

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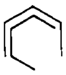
Single crystals of $V(2,4\text{-}C_7H_{11})_2$ and $Cr(2,4\text{-}C_7H_{11})_2$ [$2,4\text{-}C_7H_{11} = 2,4\text{-}(CH_3)_2C_5H_5$] were grown by sublimation and slow-cooling techniques, respectively, and subjected to straightforward X-ray diffraction procedures.[2] The solid-state structural results may be seen in Figures 1 and 2, and selected bonding parameters are contained in Table I. In terms of average M–C bond distances, the situation regarding chromium is the most straightforward. It has already been demonstrated that $Cr(2,4\text{-}C_7H_{11})_2$ has two unpaired electrons,[1a] quite analogous to chromocene itself.[3] In $Cr(2,4\text{-}C_7H_{11})_2$ it can be seen that the Cr–C bond distances are all reasonably similar, ranging from 2.147 (7) to 2.177 (8) Å, averaging[4] 2.165 (4) Å. This distance is essentially identical with that of chromocene, 2.169 (4) Å.[5] In the case of $Fe(2,4\text{-}C_7H_{11})_2$ a reasonable correspondence is also observed with ferrocene, the former having an average Fe–C bond distance of 2.089 (1) Å as compared to 2.064 (3) Å for the latter, less crowded molecule.[1b,6] These data suggest a fundamental relationship between the open and closed systems: *in comparable situations where similar electronic configurations exist, there is a clear correspondence in general bonding parameters.*[7] The designation of the bis(pentadienyl)metal compounds as "open metallocenes" therefore seems to be justified.

In contrast, results for $V(2,4\text{-}C_7H_{11})_2$ demonstrate a notable uniqueness regarding the pentadienyl systems. While vanadocene possesses three unpaired electrons,[3b] $V(2,4\text{-}C_7H_{11})_2$ exists in a low-spin state with only one unpaired electron. This unusual property has led to a very noticeable difference in average V–C bond distances. While the V–C bond distances in vanadocene average 2.280 (5) Å, the average V–C distance for $V(2,4\text{-}C_7H_{11})_2$ is actually much shorter at 2.211 (2) Å![8] This "open vanadocene", then, appears to possess even stronger metal–ligand interactions than vanadocene itself. Of great interest of course is the origin of the low-spin-generating property of the pentadienyl ligands. While the underlying reasons are not completely established yet, some possible contributing factors could be the larger size of the pentadienyl ligand, the more favorable energies of its π molecular orbitals for bonding, and the lower complex symmetries, which can allow for much greater mixing of the metal d orbitals with various ligand orbitals.[10] Further studies to probe more deeply these various possibilities are presently under way.[11]

Perhaps most striking, however, are the relative conformations adopted by the dimethylpentadienyl ligands. Given the relatively large barriers to ligand oscillation in these systems,[1,10,11] we believe the observed conformations are due principally to electronic factors in the complexes (as opposed to packing effects). A conformation angle will be defined here as the angle between the M–C(3)–$^1/_2$(C(1) + C(5)) planes (one plane per ligand). This will be taken as 0° for a cis-eclipsed configuration and 180° for an anti-eclipsed configuration. It has already been noted that the iron complex exists in nearly a gauche-eclipsed conformation, I,[1b] as can also be seen by the angle of 59.7° (Table I). On the other hand, the vanadium compond is ideally staggered, as in II (89.8°), while the chromium compound is intermediate (82.9°).[12] In view of the number of very short interligand C--C contacts observed in the eclipsed iron conformation, it is quite clear that the addition of three metal electrons on going from vanadium to iron must be providing a sizable driving force for the conformational changes. If those three electrons are populating molecular orbitals possessing substantial metal d_{xy} and/or $d_{x^2-y^2}$ character, the δ-bonding capability in the system could be greatly enhanced, leading to increased stabilization of the eclipsed conformations (despite the greater interligand repulsions) and thereby to a sequential twisting of the ligands from staggered to eclipsed, as observed.[13] Thus, this simplified model is seen to be consistent with the observed trends. Indeed, recent molecular orbital calculations indicate that this "δ" interaction is greatly enhanced in the open ferrocenes as compared to ferrocene itself[10] and that the related "open titanocenes" should exist in the ideally staggered configuration II.[11] It does appear that a reasonable understanding of the bonding in these systems is emerging, and further efforts are in progress.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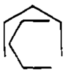
II

Acknowledgment. R.D.E. expresses his appreciation for partial support of this research through grants from the National Science Foundation (CHE-8120683), the University of Utah Research Committee, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank Professor Dr. Rolf Gleiter of the Organisch-Chemisches Institut der Universität Heidelberg and Professor Harry B. Gray of California Institute of Technology for helpful discussions.

Registry No. $V(2,4\text{-}C_7H_{11})_2$, 80703-14-6; $Cr(2,4\text{-}C_7H_{11})_2$, 80732-73-6.

Supplementary Material Available: A listing of positional coordinates for the non-hydrogen atoms of $V(2,4\text{-}C_7H_{11})_2$ and Cr(2,4-

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(2) Sublimation of the vanadium compound above room temperature (ca. 60 °C) leads to an oil (on the 0 °C cold finger) that crystallizes on standing overnight. The chromium compound was crystallized by slowly cooling concentrated solutions in pentane to −78 °C. Single crystals of each compound were mounted in glass capillaries under nitrogen. Data in each case were collected on a Nicolet P$\bar{1}$ autodiffractometer at the University of Utah and subsequently processed and refined at the Nicolet Instrument Corp. For $V(2,4\text{-}C_7H_{11})_2$ the space group is C^6_{2h}-$C2/c$ (No. 15) with a = 13.719 (4) Å, b = 10.838 (4) Å, c = 18.173 (5) Å, and β = 77.74 (2)°. This structure was ultimately refined to agreement indices R = 0.053 and R_w = 0.051 for 1102 independent observed ($I > 3\sigma(I)$) reflections having $2\theta < 45°$. For $Cr(2,4\text{-}C_{(}H_{11})_2$ the space group is D^4_4-$P4_12_12$ (No. 92) with $a = b$ = 8.090 (1) Å and c = 20.847 (3) Å. This structure was ultimately refined to agreement indices R = 0.055, R_w = 0.060 for 589 independent observed ($I > 3\sigma(I)$) reflections having $2\theta < 40°$, with the molecule possessing crystallographic C_2 symmetry. In both cases Mo Kα radiation was used.

(3) (a) Fritz, H. P.; Schwarzhans, K. E. *J. Organomet. Chem.* **1964**, *1*, 208. (b) Gordon, K. R.; Warren, K. D. *Inorg. Chem.* **1978**, *17*, 987.

(4) When average values of bonding parameters are cited, the accompanying number in parentheses is the standard deviation of the mean value. It should be noted that these deviations will not reflect the distribution of the individual values but rather the actual uncertainty for the average value.

(5) Gard, E.; Haaland, A.; Novak, D. P.; Seip, R. *J. Organomet. Chem.* **1975**, *88*, 181.

(6) Haaland, A.; Nilsson, J. E. *Acta Chem. Scand.* **1968**, *22*, 2653.

(7) Indeed, we have also observed a correspondence between ruthenocene and bis(2,3,4-trimethylpentadienyl)ruthenium.[1d]

(8) It is interesting to note that the vanadium atom is closest to the (charged) carbon atoms in positions 1 and 5, whereas the iron structure is exactly the opposite, while chromium is intermediate. Also, even though the open vanadium complex has much shorter metal–carbon distances than vanadocene itself, the former value is still longer than that in the "open chromocene", so that an "electron-imbalance" relationship[9] still exists in these compounds.

(9) Haaland, A. *Acc. Chem. Res.* **1979**, *12*, 415.

(10) Böhm, M. C.; Eckert-Maksič, M.; Ernst, R. D.; Wilson, D. R.; Gleiter, R. *J. Am. Chem. Soc.*, **1982**, *104*, 2699.

(11) Gleiter, R., private communication.

(12) Actually, because the interior C-C-C-bond angles are greater than 120°, the chromium compound is closer to being staggered, even though it is the vanadium compound which has a virtually perpendicular twist occurring between its two ligands.

(13) One could reason that the large girth of the pentadienyl ligand could lead to stabilization of the d_{z^2} orbital, while the closer proximity of the metal atom to the ligand plane (as compared to the cyclopentadienyl systems) could lead to destabilization of the d_{xy} and $d_{x^2-y^2}$ orbitals, thus giving rise to an orbital pattern essentially as described. It is, however, hard to imagine these influences being sufficient to bring about the low spin configurations by themselves, and it is probable that greater orbital (d-d and metal-ligand) mixing is also important.[12] Nevertheless, while this is only a crude model, it is consistent with the observed conformational and electronic trends.

$C_7H_{11})_2$ and a tabulation of bonding parameters (2 pages). Ordering information is given on any current masthead page.

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(14) NSF Predoctoral Fellow, 1980–1983.

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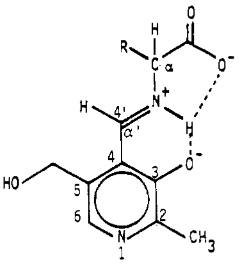
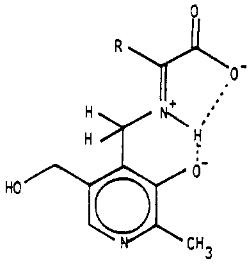
NMR Evidence for the Delocalized α,α′ Carbanion of Pyridoxal and Pyridoxamine Schiff Bases as the Intermediate in Vitamin B_6 Catalyzed Transamination

Sir:

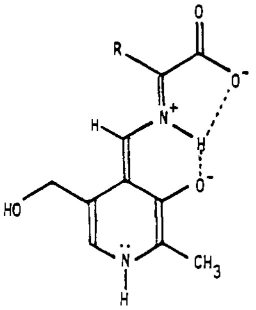
The mechanism of enzymatic and nonenzymatic vitamin B_6 catalyzed transamination of α-amino and α-keto acids proposed by Metzler et al.[1] involves the formation and interconversion of aldimine and ketimine Schiff bases **1** and **2**. The intermediate obtained by dissociation of the α proton of the amino acid moiety of the aldimine was first suggested by Metzler et al. to be the dihydropyridine type tautomer **3**. This intermediate was later suggested by Schirch and Jenkins[2] as the absorbing species with a maximum near 505 nm in pyridoxal enzyme–substrate complexes. Analogous dihydropyridine intermediates derived from vitamin B_6 analogues have been described by Maley and Bruice.[3]



1, Monoprotonated pyridoxal Schiff base (HL^-)

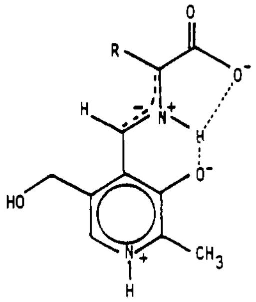


2, pyridoxamine Schiff base, monoprotonated form



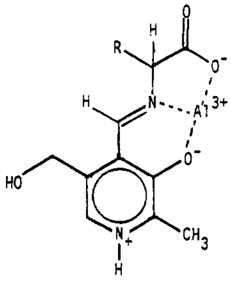
3, "Snell-Braunstein" intermediate

More recently NMR evidence for a deprotonated intermediate of the pyridoxal–alanine Schiff base, stabilized by complexation with Al(III), was reported by Abbott and Martell,[4] and the analogous monoprotonated Schiff base was suggested as a possible intermediate in vitamin B_6 catalyzed transamination in the absence of metal ions. Subsequently it was pointed out[5] that the diprotonated Schiff base is the more likely precursor of the carbanionic intermediate **4**.

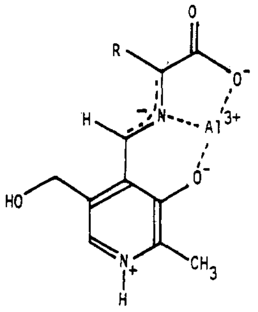


4, carbanion intermediate

In the present research, the kinetics of formation of the aldimine–Al(III) chelate **5** from pyridoxal and alanine, and also from pyridoxamine and pyruvate, has been followed by NMR. These systems are found to lead to the formation of an equilibrium mixture consisting primarily of the 1:1 Al(III):Schiff base (aldimine) chelate and a smaller amount of the 1:2 aldimine chelate. The presence of these Schiff base complexes in solution was found to be accompanied by the formation of the new species **6** having an NMR spectrum resembling that of the aldimine, but differing in having a more negative charge. It is apparently an aldimine-type deprotonated Al(III) chelate of the type described earlier.[4] This compound forms as transamination proceeds, finally approaching a steady concentration that seems to be a constant fraction of the parent Schiff base formed.



5, protonated Schiff base–Al(III) chelate



6, α-deprotonated intermediate (αDI)

It was found that, for a 1:1:1 ratio of pyridoxal, alanine, and Al(III) in D_2O at 10.0 °C and pD 5.0, the aldimine chelate concentration reaches a maximum and then levels off, as indicated by the NMR spectra in Figure 1. As the reaction progresses, the Al(III) complex of the α-deprotonated intermediate (αDI) appears somewhat more slowly than the aldimine chelate and the concentration increases and levels off, finally achieving a constant concentration of about 10% of that

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(1) Metzler, D. E.; Ikawa, M.; Snell, E. E. *J. Am. Chem. Soc.* **1954**, *76*, 648.
(2) Schirch, L. V.; Jenkins, W. T. *J. Biol. Chem.* **1964**, *239*, 3801.
(3) Maley, J. R.; Bruice, T. C. *J. Am. Chem. Soc.* **1968**, *90*, 2843.
(4) Abbott, E. H.; Martell, A. E. *J. Am. Chem. Soc.* **1973**, *95*, 5014.
(5) Martell, A. E. *Adv. Enzymol.* **1982**, *53*, 163.

0020-1669/84/1323-2734$01.50/0