Table I. Metal–Ring Distances in η^3-C_3R_3 Complexes

complex	M–C_3 centroid	M–C distances
$Ni(C_3Ph_3)Cl_2(py)\cdot(py)$[7b]	1.941 (5)	1.896 (8), 1.958 (8), 1.968 (8)
$Ni(C_3Ph_3)(\eta^5\text{-}C_5H_5)$[7c]	1.961 (4)	1.953 (6), 1.961 (6), 1.968 (6)
$Co(C_3Ph_3)(CO)_3$[7d]	2.01 (1)	2.008 (3), 1.995 (3), 2.024 (3)
$Mo(C_3Ph_3)(CO)_2(bpy)Br$[7e]	2.06	2.193 (18), 2.204 (26), 2.262 (22)
$W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2Me](PMe_3)Cl_2$	1.991	2.139 (5), 2.150 (6), 2.200 (6)

(2)–W–Cl(1) axis, the longer W–C(3) bond might be ascribed to steric interaction between Cl(2) and the *tert*-butyl group containing C(31). The tungsten atom lies 1.991 Å from the C_3 ring. The three ring substituents are displaced by –0.908 (C(11)), –0.632 (C(21)), and –0.752 Å (C(31)) from the C_3 ring, which translates into a bending back of C(11) by 36.7°, C(21) by 25.2°, and C(31) by 29.5° from the C_3 plane. The ring to substituent distances are C(1)–C(11) = 1.520 (8), C(2)–C(21) = 1.483 (9), and C(3)–C(31) = 1.525 (8) Å. Within the C_3 ring the distances are C(1)–C(2) = 1.466 (7), C(2)–C(3) = 1.416 (8), and C(3)–C(1) = 1.473 (8) Å; the shorter C(2)–C(3) bond is statistically just barely significant.

Several structures of molecules containing the C_3Ph_3 ring have been reported.[7] The metal–carbon distances in the C_3Ph_3 complexes in which the ring is symmetrically bound to the metal[7b–e] are listed in Table I. There appears to be a trend toward relatively short W–C distances in $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2Me](PMe_3)Cl_2$. This trend is supported by the fact that in $Ni(\eta^3\text{-}C_3Ph_3)(\eta^5\text{-}C_5H_5)$ the C_3 ring is *further* from the Ni than the C_5 ring by ~0.05 Å (1.779 vs. 1.726 Å) while in the W complex the C_3 ring is *closer* to the metal than the C_5 ring by ~0.05 Å (1.991 vs. 2.046 Å). Second, the phenyl rings in each η^3-C_3Ph_3 complex are bent out of the C_3 plane by ~20° while in the W complex the angles vary from ~25° (for the methyl substituent) to between ~30° and 37° (for the *tert*-butyl substituents). The structural evidence suggests that the tungsten complex contains a more tightly bound, less cyclopropenium-like, η^3-C_3 ring. The difference between the average C–C distance in the WC_3 system (1.45 Å) vs. in the C_3Ph_3 systems (1.42–1.43 Å), although barely significant, is consistent with this view.[8]

Of more impact than structural arguments is the fact that while the C_3 ring rotates readily in η^3-C_3R_3 complexes where ring rotation (or lack thereof) can be established,[8–10] in $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2Me](PMe_3)Cl_2$ the C_3 ring does not rotate readily.[11] It would not seem prohibitively difficult for solely steric reasons for the C_3 ring to rotate counterclockwise by 60° to produce an intermediate complex containing a plane of symmetry that passes through the PMe_3 ligand and C(2) and bisects the η^5-C_5H_5 ligand and the C(1)–C(3) bond. Therefore, we must conclude that the C_3 ring in $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2Me](PMe_3)Cl_2$ is significantly different from those in lower oxidation state η^3-C_3R_3 complexes. Although the data might support the argument that the complex contains W(VI) and a $C_3R_3^{3-}$ ligand, we prefer the less extreme point of view that it contains W(IV) and a $C_3R_3^-$ (i.e., η^3-cyclopropenyl) ligand.

Acknowledgment. This work was supported by N.S.F. Grant CHE 80-23448 (to M.R.C) and CHE 81-21282 (to R.R.S.). L.M. thanks the Halcon Corporation for a Fellowship during 1982–1983 and the Dow Chemical Co. for a Fellowship during 1983–1984.

Registry No. $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2Me](PMe_3)Cl_2$, 89890-11-9; $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2Me]Cl_2$, 89890-12-0.

Supplementary Material Available: Tables of observed and calculated structure factors, positional parameters, and anisotropic thermal parameters (23 pages). Ordering information is given on any current masthead page.

(7) (a) The list comprises $Ni(C_3Ph_3)Cl(py)_2\cdot(py)$,[7b] $Ni(C_3Ph_3)(\eta^5\text{-}C_5H_5)$,[7c] $Co(C_3Ph_3)(CO)_3$,[7d] $Mo(C_3Ph_3)(CO)_2(bpy)Br$,[7e] and $[M(C_3Ph_3)(PPh_3)_2]^+$ (M = Ni,[7f] Pd,[7f] Pt[7g]). In the latter cationic complexes the C_3Ph_3 ring is usually not symmetrically bound to the metal. (b) Tuggle, R. M.; Weaver, D. L. *Inorg. Chem.* **1971**, *10*, 2599; (c) *Ibid.* **1971**, *10*, 1504. (d) Chiang, T.; Kerber, R. C.; Kimball, S. D.; Lauher, J. W. *Ibid.* **1979**, *18*, 1687. (e) Drew, M. G. B.; Brisdon, B. J.; Day, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1310. (f) Mealli, C.; Midollini, S., Moneti, S.; Sacconi, L.; Silvestre, J.; Albright, T. A. *J. Am. Chem. Soc.* **1982**, *104*, 95. (g) McClure, M. D.; Weaver, D. L. *J. Organomet. Chem.* **1974**, *54*, C59.

(8) R. P. Hughes and A. L. Rheingold have informed us of two unpublished structures of the generic type $Mo(\eta^5\text{-}C_5H_5)(CO)_2(C_3R_3)$ in which the C_3 ring substitutents (R = Ph or *t*-Bu) are bent back from the metal by 37–44° but in which the C_3 ring is still further from the metal by ~0.05 Å. NMR evidence suggests that the phenyl substituents in $Mo(\eta^5\text{-}C_5H_5)(CO)_2[C_3(t\text{-}Bu)Ph_2]$ are equivalent on the NMR time scale, although they are not equivalent in the solid-state structure.

(9) Hughes, R. P.; Lambert, J. M. J.; Reisch, J. W.; Smith, W. L. *Organometallics* **1982**, *1*, 1403.

(10) The estimated barrier to ring rotation in hypothetical $Fe(\eta^3\text{-}C_3H_3)(CO)_3$ is 6–7 kcal mol^{-1}: Albright, T. A.; Hoffmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

(11) When a sample of $W(\eta^5\text{-}C_5H_5[C_3(CMe_3)_2Me](PMe_3)Cl_2$ is heated to 70 °C, a broad spectrum is obtained (reversibly) that is characteristic of a rapidly equilibrating mixture of $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2Me](PMe_3)Cl_2$, $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2Me]Cl_2$, and free PMe_3. We note that $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2Me](PMe_3)Cl_2$ reacts slowly at 25 °C with C_2Cl_6 to give $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2Me]Cl_2$ in high yield and that PEt_3 does not react with $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2Me]Cl_2$, presumably for steric reasons.

Stable Simple Enols. 6. A Shift in the Threshold Mechanism of Correlated Rotation in 2,2-Dimesitylethenols from a One- to a Two-Ring Flip[1]

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Diaryl- and triarylvinyl systems Ar′ArC=C(Y)R and Ar′ArC=C(Y)Ar″ exist in a propeller conformation[2,3] and are the vinyl analogues of the molecular propellers Ar′ArXYR and Ar″Ar′ArXY.[3] Correlated rotation in molecular propellers is commonly analyzed in terms of flip mechanisms,[4,5] involving helicity reversal. For the Ar″Ar′ArX and Ar″Ar′ArXY systems the rotational mode of lowest activation energy (threshold mechanism) is the two-ring flip[4c,6] while for highly hindered Ar_2C=C(Y)Ar′ systems it is the three-ring flip.[3]

Only four[7] and three-ring[3] flips were so far reported for vinyl propellers. The threshold mechanism in these species should depend on the nature and the bulk of the double-bond substituents.[3b] Calculations[8] predict a propeller conformation for

(1) Part 5: Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.*, in press.

(2) (a) Kaftory, M.; Apeloig, Y.; Rappoport, Z. *J. Chem. Soc., Perkin Trans. 2*, in press. (b) Kaftory, M.; Biali, S. E.; Rappoport, Z., unpublished results.

(3) (a) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1981**, *103*, 7350; (b) *Ibid.* **1984**, *106*, 477.

(4) (a) Kurland, R. J.; Schuster, I. I.; Colter, A. K. *J. Am. Chem. Soc.* **1965**, *87*, 2279. (b) Gust, D.; Mislow, K. *Ibid.* **1973**, *95*, 1535. (c) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 27.

(5) A "flip" is a passage through a plane perpendicular to the reference plane with no edge interchange. The nonflipping rings pass through the reference plane with edge interchange.

(6) Wille, E. E.; Stephenson, D. S.; Capriel, P.; Binsch, G. *J. Am. Chem. Soc.* **1982**, *104*, 405.

(7) Willem, R.; Pepermans, H.; Hallenga, K.; Gielen, M.; Dams, R.; Geise, H. J. *J. Org. Chem.* **1983**, *48*, 1890.

(8) Stegemeyer, H.; Rapp, W. *Ber. Bunsenges. Phys. Chem.* **1971**, *75*, 1165.

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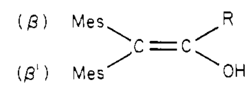
Table I. Coalescence Data for **1–3**

enol	process[a]	$\Delta\nu$, Hz[b]	T_c, K	$\Delta G_c^{\ddagger}$, kcal mol^{-1} [c]
1[d]	β' *o*-Me $\rightleftharpoons$ $\overline{\beta'\ o\text{-Me}}$	217	229	10.4
	β' Mes H $\rightleftharpoons$ $\overline{\beta'\ \text{Mes H}}$	66	215	10.3
	β *o*-Me $\rightleftharpoons$ $\overline{\beta\ o\text{-Me}}$	245	309	14.2
	β Mes H $\rightleftharpoons$ $\overline{\beta\ \text{Mes H}}$	78	293	14.2
2[d]	β or β' *o*-Me $\rightleftharpoons$ $\overline{\beta\ \text{or}\ \beta'\ o\text{-Me}}$[e]	204	270	12.5
	β or β' *o*-Me $\rightleftharpoons$ $\overline{\beta\ \text{or}\ \beta'\ o\text{-Me}}$[e]	210	270	12.5
	β or β' Mes H $\rightleftharpoons$ $\overline{\beta\ \text{or}\ \beta'\ \text{Mes H}}$	74	264	12.6
	β or β' Mes H $\rightleftharpoons$ $\overline{\beta\ \text{or}\ \beta'\ \text{Mes H}}$	84	264	12.7
3[f]	β or β' *o*-Me $\rightleftharpoons$ $\overline{\beta\ \text{or}\ \beta'\ o\text{-Me}}$	154	225	10.4
	β or β' *o*-Me $\rightleftharpoons$ $\overline{\beta\ \text{or}\ \beta'\ o\text{-Me}}$	185	225	10.4
	β and β' Mes H $\rightleftharpoons$ $\overline{\beta\ \text{and}\ \beta'\ \text{Mes H}}$[g]	76	219	10.5

[a] An overbar denotes an enantiomeric site. [b] At 300 MHz. [c] Determined from the exchange rate constant at T_c calculated by the Gutowsky–Holm approximation (Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228) and the Eyring equation. [d] In CD_3COCD_3. [e] Two *o*-Me groups at the β and β' ring are accidentally isochronous. [f] In $C_6D_5CD_3$. [g] The two pairs of protons at different rings are accidentally isochronous.

$Ph_2C{=}CH_2$ and a one-ring flip as the threshold mechanism with transition-state energy 2.6 kcal mol^{-1} lower than that of the two-ring flip. We report here the first examples of one- and two-ring flips and a substituent-dependent shift in the threshold mechanism in the series of 1,1-diarylvinyl propellers.

2,2-Dimesitylethenol (**1**)[9] and its 1-methyl and 1-*tert*-butyl analogues (**2**)[10] and (**3**)[11] are stable simple enols[12] belonging to



1, R = H
2, R = Me
3, R = *t*-Bu

Mes = 2,4,6-$Me_3C_6H_2$

the 1,1-diarylvinyl two-blade propellers. The 300-MHz ^{1}H NMR spectrum of **1** in CD_3COCD_3 at 200 K shows six methyl and three aromatic proton signals indicating restricted rotation around the C(sp^2)–C(aryl) bonds and is therefore consistent with a frozen propeller conformation. Assignment of the *o*-Me signals to the β or the β' ring was based on inspection of space-filling models. On raising the temperature the two pairs of *o*-Me groups and the two pairs of aromatic protons coalesce. Different barriers were found for the exchange of diastereotopic groups in the two rings. $\Delta G_c^{\ddagger} = 10.4 \pm 0.05$ and 14.2 kcal mol^{-1} for the β' and the β ring, respectively (Table I).

The dynamic NMR behavior of **2** and **3** is different. The 300-MHz ^{1}H NMR of **2** in CD_3COCD_3 at 200 K shows five Me singlets at δ 1.72–2.43 (an *o*-Me and the vinylic Me are isochronous, cf. Table I), an OH singlet at δ 7.68, and four Mes H singlets at δ 6.65–6.97. For **3** in $C_6D_5CD_3$ at 185 K one broad *t*-Bu singlet at δ 1.21, six Me singlets at δ 1.92–2.54, an OH singlet at δ 4.87, and two Mes H singlets at δ 6.49 and 6.74 (cf. Table I) were observed (Figure 1). The pairs of protons that are involved in a mutual exchange process were identified by the saturation transfer method.[3,13] Upon raising the temperature several coalescence processes were observed for both **2** and **3** (Table I), but

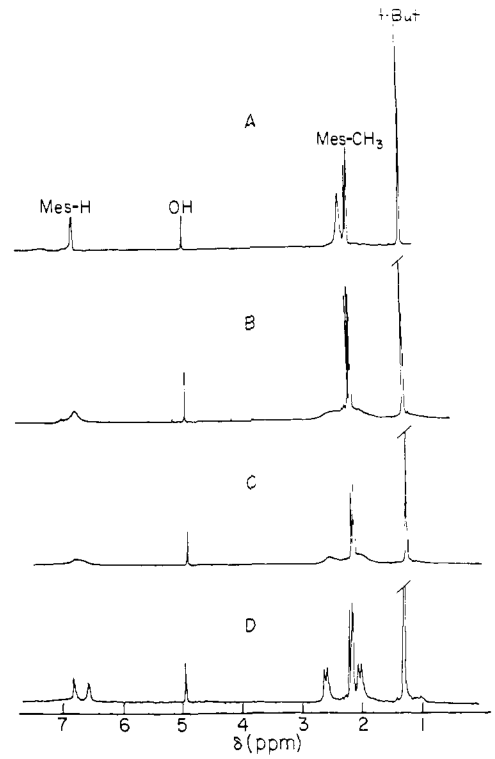


Figure 1. 300-MHz ^{1}H NMR of **3** in $C_6D_5CD_3$: (A) at 265 K, (B) at 225 K, (C) at 219 K, (D) at 191 K. The multiplet centered at δ 2.19 is due to unlabeled methyl group of the toluene.

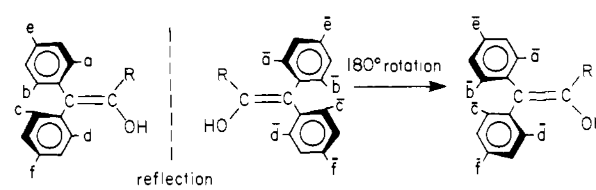
Table II. Enantiomerization Pathways for **1–3**

ring-flip route	flipping[a] rings	site exchanged[b]
zero ring	[none]	(a$\bar{a}$)(b$\bar{b}$)(c$\bar{c}$)(d$\bar{d}$)(e$\bar{e}$)(f$\bar{f}$)
one ring	[β]	(a$\bar{b}$)($\bar{b}$a)(c$\bar{c}$)(d$\bar{d}$)(e$\bar{e}$)(f$\bar{f}$)
	[β']	(a$\bar{a}$)(b$\bar{b}$)(c$\bar{d}$)(d$\bar{c}$)(e$\bar{e}$)(f$\bar{f}$)
two ring	[β,β']	(a$\bar{b}$)(b$\bar{a}$)(c$\bar{d}$)(d$\bar{c}$)(e$\bar{e}$)(f$\bar{f}$)

[a] Greek letters in brackets indicate the flipping ring(s). [b] Letters in each bracket indicate the site exchanging groups.

in each case only a single barrier was found: $\Delta G_c^{\ddagger} = 12.6 \pm 0.08$ kcal mol^{-1} for **2** and 10.4 ± 0.03 kcal mol^{-1} for **3**.

Analysis of the coalescence processes is aided by drawing the two enantiomeric propellers as mirror images.[14] We label the methyl groups positions in **1a–3a** by the letters a–f and groups



1a, R = H
2a, R = Me
3a, R = *t*-Bu

1b, R = H
2b, R = Me
3b, R = *t*-Bu

in enantiomeric sites in **1b–3b** by the same letters with an overbar (i.e., $\bar{a}$–$\bar{f}$). The four different routes that lead to *enantiomerization* (e.g., **1a** $\rightleftharpoons$ **1b**) are analyzed in Table II, following Mislow's analysis for the Ar_3CY system.[4b] An (a$\bar{b}$) (b$\bar{a}$) designation represents exchange of the a and b methyl groups and therefore a coalescence process between them.

We conclude that the threshold rotational mechanism for **1** is the [β']-ring flip which exchanges the two pairs of diastereotopic groups on the β' ring and has $\Delta G_c^{\ddagger} = 10.4$ kcal mol^{-1}.[15] In this

(9) Fuson, R. C.; Rowland, S. P. *J. Am. Chem. Soc.* **1943**, *65*, 992.
(10) Fuson, R. C.; Armstrong, L. J.; Chadwick, J. W.; Rowland, S P.; Shenk, W. J.; Soper, Q. F. *J. Am. Chem. Soc.* **1945**, *67*, 386.
(11) Prepared in a low yield (with satisfactory analytical data) by reacting dimesityl ketene with *t*-BuLi.
(12) For reviews, see: Hart, H. *Chem. Rev.* **1979**, *79*, 515. Hart, H.; Sasaoka, M. *J. Chem. Educ.* **1980**, *57*, 685.
(13) Forsén, S.; Hoffman, R. A. *J. Chem. Phys.* **1963**, *39*, 2892; **1964**, *40*, 1189; *Acta Chem. Scand.* **1963**, *17*, 1787.

(14) See reference 3b for drawing convention.

process, the β ring passes through the double bond plane at the transition state and edge interchange, but no interchange of pairs of diastereotopic groups takes place. The second process having $\Delta G_c^{\ddagger} = 14.2$ kcal mol^{-1} interchanges these groups, and it could be either a [β]- or a [β,β']-ring flip.

Although the identity of the barriers calculated for both rings of **2** and **3** can be accounted for by successive ([β], [β']) one-ring flips, the two one-ring flips are expected to have different $\Delta G_c^{\ddagger}$'s since the β- and β'-mesityl rings are in diastereomeric environments. Moreover, the substantial change in the environment of the β ring in **2** and **3** changes the barrier, but still a single barrier is obtained for both rings in each substrate. Consequently, the two-ring flip is the threshold mechanism for both **2** and **3**.[16]

The shift in the rotational mechanism from a one-ring flip in **1** to a two-ring flip in **2** and **3** is rationalized by steric effects. The alkyl group should increase the $\Delta G_c^{\ddagger}$ of the [β']-ring flip by hindering the passage of the β ring through the double-bond plane. Concurrently, the $\Delta G_c^{\ddagger}$ value for the two-ring flip is lowered by increasing the torsional angle of the β ring and thus raising the ground-state energy, therefore shifting the threshold mechanism. The higher barrier for **2** compared with **3** is consistent with this explanation.

Acknowledgment. The assistance of Drs. D. Kost and E. Aharon-Shalom and the support by a grant from the United States-Israel Binational Science Foundation (BSF), Jerusalem, Israel, are gratefully acknowledged.

Registry No. 1, 54288-04-9; **2**, 89959-15-9; **3**, 89959-16-0; *t*-BuLi, 594-19-4; dimesitylketene, 87871-33-8.

(15) The zero-ring flip route does not exchange diastereotopic groups (cf. Table II) and hence cannot be monitored by NMR. It can be safely excluded as the threshold mechanism since its transition state, where the two rings pass through the reference plane, is so overcrowded that its $\Delta G^{\ddagger}$ should be much higher than that for the one-ring flip. Moreover, this route and the set of "nonflip" rotational mechanisms (i.e., rotation of one or two rings by π radians while the nonrotating rings remain fixed) were excluded in the closely related trimesitylvinyl system substituted with a prochiral group.[3b]

(16) The different solvent used with **2** and **3** should have negligible effect on $\Delta G_c^{\ddagger}$.[3b]

Hydrogen Oxide Bridged Dimers of Metal Ions in Solution

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It was recently postulated that some metal ions may exist in aqueous solution as dinuclear species bridged by hydrogen oxide ligands.[1,2] Such species were discovered in the *crystalline state* and are formed by a strong and symmetric hydrogen bond between an aqua ligand of one metal atom and a hydroxo ligand of another metal atom. The O···O separation in the H_3O_2 ligand is 2.44–2.52 Å. If species such as $[M(H_3O_2)M]^{(2n-1)+}$ do indeed exist in equilibrium with the hydrolyzed mononuclear species M_{aq}^{n+} and $MOH^{(n-1)+}$, the current view on hydrolysis of metal ions in solution[3] may have to be modified. However, to date such hydrogen oxide

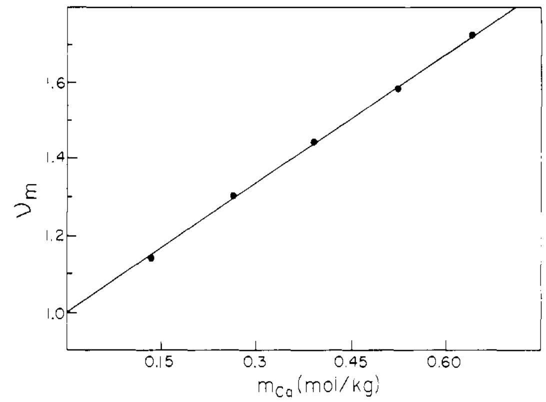

Figure 1. The dependence of ν_m, the apparent number of calcium ions per formula weight of $Ca(NO_3)_2 \cdot 4H_2O$, on the molality *m*, in a saturated solution of barium nitrate at 25 °C.

bridged species were only reported in crystals.[1,2]

Recently, the existence of dinuclear H_3O_2-bridged species was reported in crystals of the iodide salt of *cis*-bis(bipyridine)hydroxoaquachromium(III).[2] This salt was prepared by neutralizing the solution of $[Cr(bpy)_2(H_2O)_2](NO_3)_3 \cdot {}^1/_2H_2O$[4] with 1 equiv of NaOH and crystallization by the addition of KI. The two chromium atoms of the tetrapositive ion $[(bpy)_2Cr(H_3O_2)_2Cr(bpy)_2]^{4+}$ are bridged by *two* μ-H_3O_2 ligands. We now report the first evidence for dinuclear species of this type in *aqueous solution.*

Deprotonation of a $[Cr(bpy)_2(H_2O)_2]^{3+}$ ion by 1 equiv of OH^- was expected to yield a hydroxoaqua ion[4] $[Cr(bpy)_2H_2O(OH)]^{2+}$. It is now claimed that the main product of this reaction, in concentrated solution, is the dinuclear bis(μ-H_3O_2) bridged ion rather than the mononuclear hydroxoaqua ion (reaction 1).

$$[Cr(bpy)_2(H_2O)_2]^{3+} + OH^- \rightleftharpoons {}^1/_2[(bpy)_2Cr(H_3O_2)_2Cr(bpy)_2]^{4+} + H_2O \quad (1)$$

$${}^1/_2[(bpy)_2Cr(H_3O_2)_2Cr(bpy)_2]^{4+} + OH^- \rightleftharpoons [Cr(bpy)_2(OH)_2]^+ + H_2O \quad (2)$$

If more than one OH^- per chromium atom is used, the dihydroxo ion is formed by reaction 2. Evidence for dimerization of the hydroxoaqua ion is based on the *decrease* of the number of chromium particles in reaction 1[5] and its increase in reaction 2. The number, ν, of discrete chromium particles per diaqua ion should decrease from $\nu = 1$ to $\nu = {}^1/_2$ as the diaqua ion is titrated with 1 mol of OH^- and then rise again to $\nu = 1$ as a second mole of OH^- is added. ν may be determined by measuring a colligative property of the solution. A most suitable method for ionic solutes is three-phase vapor tensiometry, TPVT.[6,7] The three-phase solvent system consists of a saturated solution of an electrolyte in water, in equilibrium with the crystalline phase of that electrolyte and with water vapor. An isobaric temperature difference $(\Delta T)_p$ is established when the pure solvent is equilibrated with a solution of a foreign solute in the same solvent, at constant pressure. The *apparent number*, ν_m, of free particles per formula of solute depends on the molality of the solute (*m*), the three-phase ebulioscopic constant K_e, and $(\Delta T)_p$[8]

$$\nu_m = (\Delta T)_p / K_e m \quad (3)$$

The apparent particle number ν_m depends linearly on *m*.

$$\nu_m = \nu + Nm \quad (4)$$

ν, the true number of free particles per formula of solute, is

(1) (a) Bino, A.; Gibson, D. *J. Am. Chem. Soc.* **1981**, *103*, 6741–6742; (b) *Ibid.* **1982**, *104*, 4383–4388; (c) *Inorg. Chem.* **1984**, *24*, 109–115.

(2) Ardon, M.; Bino, A. *J. Am. Chem. Soc.* **1983**, *105*, 7747–7748.

(3) Burgess, J.; "Metal Ions in Aqueous Solutions"; Wiley: New York, 1978; pp 259–309.

(4) (a) Inskeep, R. J.; Bjerrum, J. *Acta Chem. Scand.* **1961**, *15*, 62–68. (b) Inskeep, J. R.; Benson, M. *J. Inorg. Nucl. Chem.* **1961**, *20*, 290–294.

(5) The possibility that the dinuclear bis(μ-hydroxo) ion $[(dpy)_2Cr(OH)_2Cr(dpy)_2]^{4+}$ was formed in solution under the experimental condition used in this work (several hours at 25 °C) was checked and ruled out.

(6) (a) Magyar, B. *Helv. Chim. Acta* **1965**, *48*, 1259. (b) *Ibid.* **1968**, *51*, 194–204; (c) *Structure Bond.* (*Berlin*) **1973**, *14*, 111–140.

(7) Magyar, B.; Schwarzenbach, G. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 943–955.

(8) In practice, the steady-state temperature difference $(\Delta T)_s$, which is proportional to $(\Delta T)_p$, is measured.[7]

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