Evaporated to dryness and dried under vacuum to give a yellowish red oily material (0.168 g, 61.5%), whose IR and NMR spectra were consistent with its formulation as CPMo(CO)5[P(OPh)3]4OTs. IR (CH2Cl2): vCO 2071 (s), 2010 (m, sh), 1984 (vs, br) cm⁻¹. ¹H NMR (CDCl3): δ 7.38 (m), 5.61 (s), 2.28 (s). ¹³C[¹H] NMR (CDCl3): δ 222.4 (d, Jpc = 40.8 Hz), 221.0 (d, Jpc = 31.1 Hz), 94.4 (s), 21.22 (s). The phenyl carbons are absent. The spectral properties were similar to those of CPMo(CO)5[P(OPh)3]BF₄.²,¹³

Reaction of mer,trans-Mn(CO)₅(PPh₃)₃(CHOH)⁺, CH₂CHO·SO₃⁻ with CH₂OH. To 20 mL of a 1:1 mixture of CH₂Cl₂ and CH₂OH at room temperature was added mer,trans-Mn(CO)₅(PPh₃)₃(CHOH)⁺·CH₂CHO·SO₃⁻ (0.20 g, 0.22 mmol) with stirring. The yellow solution was stirred for 3 h, at which time the solvent was removed under vacuum. The yellow residue was recrystallized from CH₂Cl₂/pentane to give yellow crystals of mer,trans-Mn(CO)₅(PPh₃)₃(CHOCH₃)⁺·CH₂CHO·SO₃⁻ with a yield of 0.16 g (50%). IR (CH₂Cl₂): vCO 2050 (w), 1965 (s, br) cm⁻¹. ¹H NMR (CDCl₃): δ 11.8 (s), 7.4 (m), 3.5 (a), 2.4 (a). ¹³C[¹H] NMR (CDCl₃): δ 238.2 (br s), 220.0 (t), 216.8 (t), 77.5 (s), 21.4 (a). The phenyl peaks are omitted. The spectral properties are comparable to those reported for mer,trans-Mn(CO)₅(PPh₃)₃(CHOCH₃)⁺·CF₃SO₃⁻.¹⁶⁶

Acknowledgment. Support of this work by the National Science Foundation (Grant RII-8610671) and the Commonwealth of Kentucky (EPSCoR Program) is gratefully acknowledged. Partial support of this work by the Department of Energy, Division of Chemical Sciences (Office of Basic Energy Sciences), is also gratefully acknowledged.

A. Z. Kreindlin, E. I. Fedin, P. V. Petrovskii, and M. I. Rybinskaya

Nesmeyanov Institute of Organoelement Chemistry, USSR Academy of Sciences, Moscow, USSR

R. M. Minyaev and R. Hoffmann*

Department of Chemistry, Cornell University, Ithaca, New York 14853

Received April 20, 1990

Summary: Starting from decamethylated metalloccenes, (Me₅C₅)M (M = Ru, Os), we generated a mixture of metallohydrodehydes, from which the aldehydes were separated and reduced to dicarbinols. These were used to obtain a mixture of dications, consisting primarily of the 1,2-isomers [C₅Me₅MC₅Me₅(CH₂)₂]⁺⁺ (M = Ru, Os), as well as their 1,1'-isomers, [(C₅Me₅CH₂)₂MC₅Me₅CH₂]⁺⁺ (M = Ru, Os). ¹H and ¹³C NMR spectra support the assigned structures. Molecular orbital calculations on the predominant 1,2-dication indicate substantial bending of the CH₂⁺⁺ groups out of the plane of the Cp ring, canting of the ring, and off-center slipping, deformations comparable to those occurring in the parent dication.

We have previously synthesized and studied stable Ru- and Os-containing monocations of the type [C₅Me₅MC₅Me₅CH₂]⁺⁺ (M = Ru, Os).¹² It was thus established experimentally that the donor-acceptor interaction between a primary α-carbocation center and an unshared electron pair on the metal in a metalloccene may be sufficient to form a true M−C σ bond (2.24 Å, M = Os; 2.27 Å, M = Ru; typical literature values for such σ bonds are ~2.22 Å).³

In these cations the CH₂ group is strongly bent toward the metal, moving out of the plane of the cyclopentadienyl ring by 41.8° (M = Os) and 40.3° (M = Ru) and essentially losing its carbocation character. At the same time the metalloccene structure of these cations is relatively little distorted (some detailed geometrical parameters will be presented below).


Scheme I

Table I. Proton NMR Spectra of Mono- and Dications

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$, ppm</th>
<th>$J_{HH}$, Hz</th>
<th>$H_a$</th>
<th>$H_b$</th>
<th>$H_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_6$RuCCMe$_3$(CH$_2$OH)$_2$</td>
<td>4.70 (d, 2 H, 1.9); 5.12 (d, 2 H, 1.9)</td>
<td>1.96 (s, 6 H)</td>
<td>2.28 (s, 3 H)</td>
<td>2.07 (s, 15 H)</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_6$RuCCMe$_3$CH$_3$ &amp; 4.75 (s, 2 H)</td>
<td>1.63 (s, 6 H)</td>
<td>1.96 (s, 6 H)</td>
<td>1.86 (s, 15 H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_6$OsCCMe$_3$(CH$_2$OH)$_2$</td>
<td>4.59 (d, 2 H, 2.4); 5.19 (d, 2 H, 2.4)</td>
<td>1.75 (s, 6 H)</td>
<td>2.17 (s, 15 H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_6$OsCCMe$_3$CH$_3$ &amp; 4.40 (s, 2 H)</td>
<td>1.60 (s, 6 H)</td>
<td>1.85 (s, 6 H)</td>
<td>1.91 (s, 15 H)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Solutions of C$_2$H$_6$MCMe$_3$(CH$_2$OH)$_2$ in CD$_2$NO$_2$/CF$_3$SO$_2$H.

It should be noted that a related dication (V) was obtained by Pittman by treatment of the tertiary 1,1'-dicarbinol of ferrocene with superacid FSO$_3$H·SbF$_5$ at -60 °C. 

In the case of the permethylated derivatives, especially those of Ru and Os, one could expect greater stability. Thus, we undertook experiments to generate dications from carbinols IIIa,b by treatment with HBF$_4$·OEt$_2$. This was unsuccessful; the 1,2-dications (IVa, M = Ru; IVb, M = Os) were obtained only upon use of the superacid CF$_3$SO$_3$H in CH$_3$NO$_2$.

---


Table II. $^{13}$C NMR Spectra of Mono- and Dications

<table>
<thead>
<tr>
<th></th>
<th>CH$_2$</th>
<th>Me$_a$</th>
<th>Me$_b$</th>
<th>Me$_c$</th>
<th>C$_a$($C_8Mes$)</th>
<th>C$_b$($C_8Mes$)</th>
<th>C$_c$($C_8Mes$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_8$MesRuC$_8$Mes(CH$_2$)$_2$</td>
<td>88.38 (t, $^1J_{CH} = 171$ Hz)</td>
<td>9.43</td>
<td>10.10</td>
<td>10.45</td>
<td>111.32; 126.64</td>
<td>112.80</td>
<td>138.23</td>
</tr>
<tr>
<td>C$_8$MesRuC$_8$MesCH$_2$ &amp;</td>
<td>74.67 (t, $^1J_{CH} = 164$ Hz)</td>
<td>8.01</td>
<td>8.74</td>
<td>9.51</td>
<td>96.91; 106.56</td>
<td>97.22</td>
<td>107.20</td>
</tr>
<tr>
<td>C$_8$MesOsC$_8$Mes(CH$_2$)$_2$ &amp;</td>
<td>71.13 (t, $^1J_{CH} = 172$ Hz)</td>
<td>8.96</td>
<td>10.02</td>
<td>9.71</td>
<td>105.71; 115.09</td>
<td>107.57</td>
<td>134.50</td>
</tr>
<tr>
<td>C$_8$MesOsC$_8$MesCH$_2$ &amp;</td>
<td>55.36 (t, $^1J_{CH} = 166$ Hz)</td>
<td>7.64</td>
<td>8.47</td>
<td>9.02</td>
<td>90.60; 95.68</td>
<td>92.51</td>
<td>99.68</td>
</tr>
</tbody>
</table>

*Solutions of C$_8$MesMC$_8$Mes(CH$_2$OH)$_2$ in CH$_3$NO$_2$/CF$_3$SO$_3$H.  
*Solutions of C$_8$MesMC$_8$MesCH$_2$P$_2$F$_7$ in CH$_3$Cl$_2$.

$^1$H and $^{13}$C NMR spectra support the assigned spectra of these dications (see Tables I and II). Thus, the proton and carbon signals are significantly shifted to lower field, in comparison to the analogous monocation signals. Especially noteworthy are the $^{13}$C shifts. Thus, for the CH$_2$ group in the Ru case $\delta$($C_8Mes$) = 13.71 ppm and for the Os compound $\delta$($C_8Mes$) = 15.77 ppm. Analogous displacements are found for the hydrogen signals of the cyclopentadienyl rings. Also in agreement with the suggested 1,2-dication structure is the observation of the typical two doublets ($^2J_{CH} = 1.9$–2.4 Hz) characteristic of AB systems in $^1$H NMR spectra and a single $^{13}$C signal (triplet, $^2J_{CH} = 171$–172 Hz) for the CH$_2$ groups.

The relative instability of the 1,2-dications (both CH$_2$ centers in one ring) did not allow their isolation. Thus, we resorted to a theoretical calculation of their geometry, using the extended Hückel method. To define the geometry of these often unsymmetrical systems, it is useful to introduce the following three geometrical parameters: $\alpha$ = angle of bending of C–CH$_2$ out of the plane of the Cp ring; $\beta$ = angle of bending of M–center of Cp line from the 5-fold axis; $\gamma$ = displacement of the center of the Cp ring from the M–Cp perpendicular.

As structure VI indicates, these geometrical deformations are carried out in the following sequence: first $\alpha$ and $\beta$, then the "slipping off" $\gamma$.

Table III shows a comparison of the calculated deformation parameters of the [C$_8$H$_6$OsC$_8$H$_4$CH$_2$]$^+$ monocation with the experimental structure of the permethylated Cp species. The agreement is good. The calculated dication structure is for a C$_s$ species, a "disrotatory" displacement of both CH$_2$ groups toward the metal, and a greater displacement of the Cp ring off center. The calculated Os–CH$_2$ distance in the dication (2.33 Å) is not very different from the observed separation in the permethylated monocation. There is some correlation of the calculated charge densities (not shown here) with $^1$H and $^{13}$C chemical shifts, except at the CH$_2$ group. We calculate a small rotational barrier of 1 kcal/mol for the lower Cp ring in this molecule.

The detailed analysis of the NMR spectra of this species allows an assignment of a 1,1'-dication (CH$_2$ groups in different Cp rings) to a smaller component of the reaction mixture. A discussion of these isomers and their rotational barriers will be presented separately.

**Experimental Part**

The NMR spectra were taken on a Bruker WP-200SY spectrometer ($^1$H, 200.13 MHz; $^{13}$C, 50.31 MHz).

**Synthesis of IIa**. Oxidation of 1.9 g (5.1 mmol) of Ia and chromatographic separation of the mixture of the initial 1,2-monoaoldehde and a mixture of dialdehydes was accomplished according to ref 8. The mixture of dialdehydes so obtained was separated by preparative TLC on silica gel, twice eluted with benzene–ether (3:1) and after that benzene–ether (1:1). The practically pure 1,2-isomer was collected in a yield of 0.08 g (0.2 mmol, 4%) $^1$H NMR: $\delta$ 2.02 (s, 6 H, $\alpha$-Me), 1.77 (s, 3 H, $\beta$-Me), 1.66 (s, 13 H, $\gamma$-Me), 9.94 (s, 2 H, CHO).

**Synthesis of IIIa**. Reduction of 0.2 g (0.5 mmol) of IIa by LiAlH$_4$ in t-BuOH, analogous to the reduction of the monoaoldehde, leads to 0.19 g (0.47 mmol, 95%) of IIIa. $^1$H NMR for IIIa: $\delta$ 1.62 (s, 15 H, $\gamma$-Me), 1.64 (s, 3 H, $\beta$-Me), 1.77 (s, 6 H, $\alpha$-Me), 3.83 and 4.03 (AB $q$, 4 H, $^2J_{CH} = 1.3$ Hz, 2 CH$_2$). In the spectra there are also signals of IIIa with an intramolecular hydrogen bond, whose $R_f$ values are smaller. Traces of the 1,3-isomers are also formed.

---


(9) It is significantly more difficult to obtain the 1,1'-dialdehydes, whose $R_f$ values are smaller. Traces of the 1,3-isomers are also formed.
The mixture of dialdehydes were carried out as in ref 4. The signals that partially overlap the signals of IIIa with a free hydrogen bond.

Synthesis of IIb. Oxidation of 2.3 g (5.0 mmol) of Ib and chromatographic separation of the reactant Ib monoaldehyde and the mixture of dialdehydes were carried out as in ref 4. The mixture of dialdehyde was separated analogously to the mixture of the Ru analogues; yield of IIb 0.1 g (0.21 mmol, 4%). $^{1}H$ NMR: $\delta$ 2.07 (s, 6 H, $\alpha$-Me), 1.82 (s, 3 H, $\beta$-Me), 1.76 (s, 15 H, $\gamma$-Me), 9.94 (s, 2 H, CHO). Anal. Found: C, 49.27; H, 6.83; Os, 39.99. Calcd for $\text{C}_{92}\text{H}_{85}\text{Os}$: C, 48.76; H, 6.14; Os, 39.80.

Synthesis of IIb. The reduction of 0.24 g (0.5 mmol) of Ib by the action of LiAlH$_4$(t-Bu$_3$I) analogously to the reduction of the monoaldehde,* leads to 0.22 g (0.45 mmol, 90%) of IIIb. $^{1}H$ NMR: $\delta$ 1.79 (s, 6 H, $\alpha$-Me), 1.71 (s, 3 H, $\beta$-Me), 1.78 (s, 15 H, $\gamma$-Me), 4.02 and 4.04 (AB q, $^{3}J_{HH} \geq 7$ Hz, 4 H, 2 CH$_2$). Anal. Found: C, 48.32; H, 6.16; Os, 38.28. Calcd for $\text{C}_{92}\text{H}_{85}\text{Os}$: C, 48.76; H, 6.14; Os, 39.80.

Synthesis of Dications and Recording of $^1$H and $^{13}$C NMR Spectra. To a solution of IIa (or IIb) in CD$_2$NO$_2$ or CH$_3$NO$_2$ under an Ar atmosphere was added a small excess of CF$_3$SO$_2$H. This was transferred in an ampule to the NMR spectrometer. The results are given in Tables I and II.

Acknowledgment. We are grateful to the National Science Foundation for its support of this research through Grant CHE8912070.

Heteroaromatic Nitrogen Ligand Studies with the ($\eta^5$-Pentamethycyclopentadienyl)ruthenium Cation: $\eta^1$(N) and $\eta^6$(\pi) Bonding Modes and Factors That Influence a Nitrogen to \pi Rearrangement

Richard H. Fish,* Raymond H. Fong, Anh Tran, and Eduardo Baralt
Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720
Received August 20, 1990

Summary: The reactions of the ($\eta^5$-pentamethycyclopentadienyl)ruthenium tris(acetonitrile) cationic complex [Cp*Ru(\text{CH}_3\text{CN})$_3$]$_2$(OTf)$_2$ with pyridine (1), 2-methylpyridine (2), and quinoline (3) were studied to ascertain bonding modes as a function of heteroaromatic nitrogen ligand structure. Ligand 1 bonds $\eta^1$(N) and forms mono- or tris(pyridine) complexes with [Cp*Ru(\text{CH}_3\text{CN})$_3$]$^{++}$ depending on ligand concentration. Ligand 2 only forms an $\eta^6$ complex with [Cp*Ru(\text{CH}_3\text{CN})$_3$]$^{++}$, while ligand 3 also forms an $\eta^6$ complex, but with the benzo ring not the nitrogen ring. In the presence of excess pyridine, the complexed CH$_3$CN ligands are fully displaced to form [Cp*Ru($\eta^1$(N)-pyridine)$_3$]$^{++}$, while in the presence of excess 2 or 3 only the [Cp*Ru($\eta^1$(N)-ligand)(\text{CH}_3\text{CN})$_3$]$^{++}$ complexes are formed. The latter [Cp*Ru($\eta^1$(N)-ligand)(\text{CH}_3\text{CN})$_3$]$^{++}$ complexes with ligands 2 and 3 were not isolated; rather, they undergo a rapid nitrogen (N) to \pi rearrangement to the corresponding $\eta^6$ complexes, [Cp*Ru($\eta^6$-2-methylpyridine or quinoline)]$_2^{++}$. The isolation of [Cp*Ru($\eta^1$(N)-pyridine)(\text{CH}_3\text{CN})$_3$]$^{++}$ and its conversion to [Cp*Ru($\eta^6$(\pi)-pyridine)]$_2^{++}$ clearly demonstrates the pathway to the $\eta^6$ complexes. Ligand-exchange reactions of [Cp*Ru($\eta^6$(\pi)-pyridine)]$_2^{++}$ with CD$_2$CN and pyridine-$d_5$ show facile replacement of the $\eta^6$-bonded pyridine, while the former result with CD$_2$CN ligand exchange proves that the N to \pi rearrangement is not reversible. Factors such as ligand steric effects and the propensity of the Cp*Ru$^{++}$ group to act as an arenophile will also be discussed.

In the course of our bonding studies of mono- and polynuclear heteroaromatic nitrogen ligands with the ($\eta^5$-pentamethycyclopentadienyl)rhodium dication (Cp*Rh$^{2+}$)$^{1a}$ and the ($\eta^6$-cyclopentadienyl)ruthenium cation (Cp*Ru$^{3+}$)$^{1b}$ Chaudret and co-workers recently published some results on the bonding mode of pyridine, several methyl-substituted pyridine ligands, and quinoline with the ($\eta^5$-pentamethycyclopentadienyl)ruthenium cation (Cp*Ru$^{3+}$)$^{2}$.

Since our bonding results with [Cp*Rh(\text{CH}_3\text{CN})$_3$]$^{2+}$ and [Cp*Ru(\text{CH}_3\text{CN})$_3$]$^{2+}$ as starting complexes were dramatically different for similar mono- and polynuclear heteroaromatic nitrogen ligands, i.e., $\eta^1$(N)- not $\eta^6$-bonding$^{1a,b}$ we decided to examine the reactions of [Cp*Ru(\text{CH}_3\text{CN})$_3$](OTf)$_2$, a conveniently prepared starting material$^{2}$ with pyridine (1), 2-methylpyridine (2), and quinoline (3) to ascertain bonding modes as a function of heteroaromatic nitrogen ligand structure. We also wanted to determine whether any $\eta^6$ complexes that formed with 1-3 and [Cp*Ru(\text{CH}_3\text{CN})$_3$]$^{2+}$ emanated from our recently reported N to \pi rearrangement that appears to be general for complexes that have a [Cp*Ru($\eta^1$(N)-ligand)(\text{CH}_3\text{CN})$_3$]$^{2+}$ structure.$^{1b,4}$

Results and Discussion

The reaction of excess pyridine (1) and [Cp*Ru(\text{CH}_3\text{CN})$_3$](OTf)$_2$ in CH$_2$Cl$_2$ at ambient temperature provided only [Cp*Ru($\eta^1$(N)-pyridine)$_3$]$^{4+}$ (4) in 87% yield; no corresponding $\eta^6$ complex was observed. The 500-MHz $^1$H NMR spectrum (CD$_2$Cl$_2$) of 4 provided clear evidence for the $\eta^1$(N)-bonding mode with signals at 8.3, 7.73, and 7.34 ppm that were shifted downfield from free pyridine,$^{1b,4}$ while the $^1$H resonance was found at 1.29 ppm. A similar product was also observed when (CH$_3$)$_2$CO was substituted for CH$_2$Cl$_2$ as the solvent. This latter result is in contrast

---

(4) Fish, R. H.; Kim, H.-S.; Fong, R. H. Organometallics 1991, 10, 770.