4 × 10 mL of hexane. The combined extracts were filtered through Celite; the insoluble residue was saved. Concentrating the filtrate to about 10 mL and chilling to 0 °C for several hours yielded 0.157 g of a yellow-orange solid. The ^1H NMR of the solid ($CDCl_3$) indicated the presence of **6**, $CpMo(CO)_2[P(OPh)_3]CH_3$,[16] and the metallacycle $CpMo(CO)_2[P(OPh)_2(o\text{-}OC_6H_4CH_2)]$[19] at about a 32:9:1 (Cp) integral ratio, respectively. The mixture was separated on a Florosil column, eluting with hexane, 1:10 CH_2Cl_2/hexane, and finally CH_2Cl_2. The latter fractions were evaporated to dryness, and the residue was dissolved in 10 mL of hexane. Chilling to −30 °C gave 0.120 g (63%) of yellow **6**. IR (hexane): ν_{CO} 1967 (m), 1890 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): trans δ 7.30 (m), 4.66 (d, J_{PH} = 1.1 Hz), 4.58 (d, J_{PH} = 3.8 Hz), 3.30 (s); cis δ 7.30 (m), 4.85 (s), CH_2 signal not distinct, 3.35 (s). The cis:trans ratio is 1:9, respectively [lit.[16] ^1H NMR ($CDCl_3$): trans δ 4.62 (d, J_{PH} = 1.2 Hz), 4.60 (d, J_{PH} = 3.6 Hz), 3.31 (s); cis δ 4.78 (s), 3.56 (s), CH_2 signal not distinct]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): trans δ 232.6 (d, J_{PC} = 34.6 Hz), 151.2 (d, J_{PC} = 7.3 Hz), 129.6 (s), 125.0 (s), 121.8 (d, J_{PC} = 4.4 Hz), 91.7 (s), 64.0 (d, J_{PC} = 13.2 Hz), 63.4 (s); cis δ 124.8 (s), 121.6 (d, J_{PC} = 4.7 Hz), 91.5 (s), 63.6 (d, J_{PC} = 31.4 Hz), other signals for this isomer not visible. After determination of the yield of **6**, the yields of the methyl complex and the metallacycle were calculated on the basis of the ^1H NMR ratio as 27% and 2%, respectively. The hexane-insoluble residue from above was dissolved in CH_2Cl_2, extracted with 2 × 20 mL of water, and then dried over $MgSO_4$. After filtration, the filtrate was evaporated to dryness and dried under vacuum to give a yellowish red oily material (0.158 g, 61%), whose IR and NMR spectra were consistent with its formulation as $CpMo(CO)_3[P(OPh)_3]^+OTs^-$. IR ($CH_2Cl_2$): ν_{CO} 2071 (s), 2010 (m, sh), 1984 (vs, br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.38 (m), 5.61 (s), 2.29 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 222.4 (d, J_{PC} = 40.8 Hz), 221.0 (d, J_{PC} = 3.1 Hz), 94.4 (s), 21.22 (s). The phenyl carbons are omitted. The spectral properties were similar to those of $CpMo(CO)_3[P(OPh)_3]^+BF_4^-$.[12]

Reaction of *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOH)^+$-$CH_3C_6H_4SO_3^-$ with CH_3OH. To 20 mL of a 1:1 mixture of CH_2Cl_2 and CH_3OH at room temperature was added *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOH)^+CH_3C_6H_4SO_3^-$ (0.20 g, 0.23 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 CH_2Cl_2/pentane to give yellow crystals of *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOCH_3)^+CH_3C_6H_4SO_3^-$ contaminated with a small amount of *trans*-$Mn(CO)_4(PPh_3)_2^+$-$CH_3C_6H_4SO_3^-$; the yield was 0.10 g (50%). IR (CH_2Cl_2): ν_{CO} 2050 (w), 1965 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 11.8 (s), 7.4 (m), 3.5 (s), 2.4 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 338.2 (br s), 220.0 (t), 216.8 (t), 77.5 (s), 21.4 (s). The phenyl peaks are omitted. The spectral properties are comparable to those reported for *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^-$.[13b]

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(19) The structure of this compound has been confirmed by X-ray crystallography; the details of its characterization will be reported elsewhere (D. H. Gibson, J. O. Franco, and J. F. Richardson, unpublished results).

Synthesis, NMR Spectra, and Molecular Orbital Calculations of Ruthenium and Osmium Dications of the Type $[C_5Me_5MC_5Me_3(CH_2)_2]^{2+}$

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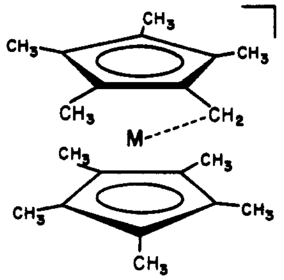
Summary: Starting from decamethylated metallocenes, $(Me_5C_5)_2M$ (M = Ru, Os), we generated a mixture of aldehydes, from which the dialdehydes were separated and reduced to dicarbinols. These were used to obtain a mixture of dications, consisting primarily of the 1,2-isomers $[C_5Me_5MC_5Me_3(CH_2)_3]^{2+}$ (M = Ru, Os), as well as their 1,1′-isomers, $[(C_5Me_4CH_2)M(C_5Me_4CH_2)]^{2+}$ (M = Ru, Os). ^1H and ^{13}C NMR spectra support the assigned structures. Molecular orbital calculations on the predominant 1,2-dication indicate substantial bending of the CH_2^+ 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 $[C_5Me_5MC_5Me_4CH_2]^+$ (M = Ru, Os).[1,2] 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 metallocene may be sufficiently strong 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 CH_2 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 metallocene structure of these cations is relatively little distorted (some detailed geometrical parameters will be presented below).

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(1) Rybinskaya, M. I.; Kreindlin, A. Z.; Fadeeva, S. S. *J. Organomet. Chem.* **1988**, *358*, 363.

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(3) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679.

0276-7333/91/2310-1206$02.50/0

Scheme I

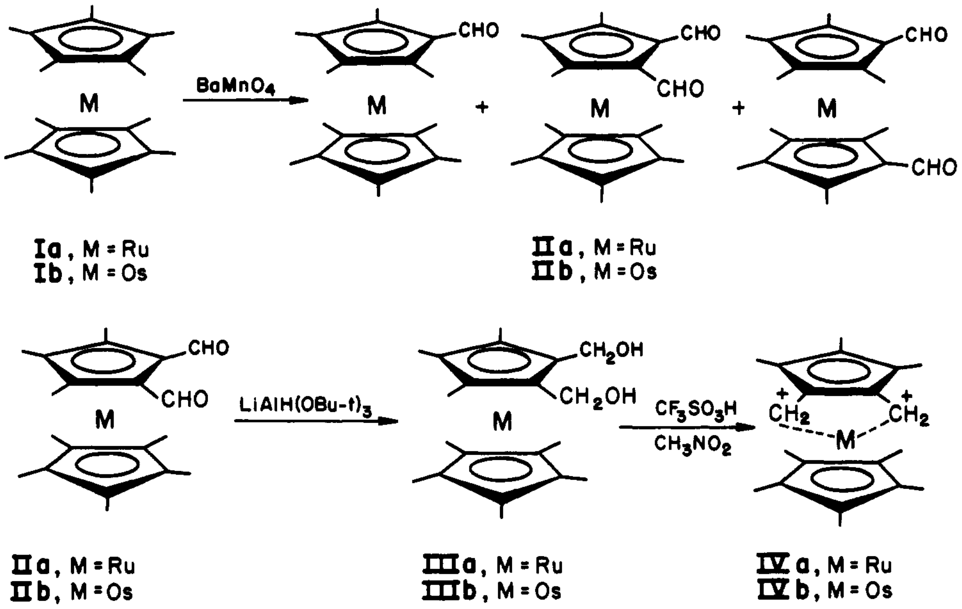
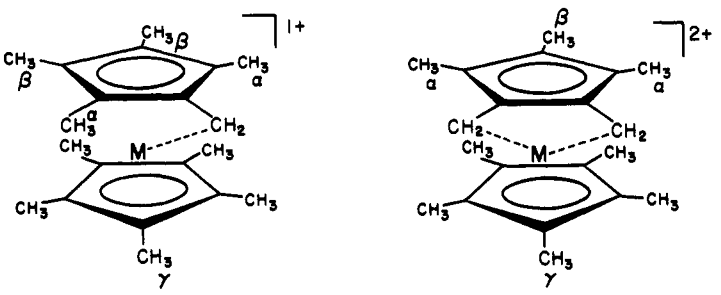


Table I. Proton NMR Spectra of Mono- and Dications



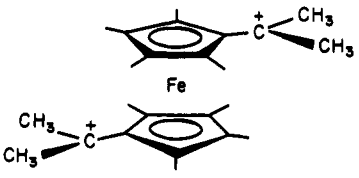
	δ, ppm			
	CH_2^+ ($^2J_{HH}$, Hz)	H_α	H_β	H_γ
$C_5Me_5RuC_5Me_3(CH_2^+)_2$[a]	4.70 (d, 2 H, 1.9); 5.12 (d, 2 H, 1.9)	1.96 (s, 6 H)	2.28 (s, 3 H)	2.07 (s, 15 H)
$C_5Me_5RuC_5Me_4CH_2^+$[b]	4.75 (s, 2 H)	1.63 (s, 6 H)	1.96 (s, 6 H)	1.86 (s, 15 H)
$C_5Me_5OsC_5Me_3(CH_2^+)_2$[a]	4.59 (d, 2 H, 2.4); 5.19 (d, 2 H, 2.4)	1.75 (s, 6 H)	2.17 (s, 18 H)[c]	
$C_5Me_5OsC_5Me_4CH_2^+$[b]	4.40 (s, 2 H)	1.60 (s, 6 H)	1.85 (s, 6 H)	1.91 (s, 15 H)

[a] Solutions of $C_5Me_5MC_5Me_3(CH_2OH)_2$ in CD_3NO_2/CF_3SO_3H. [b] Solutions of $C_5Me_5MC_5Me_4CH_2^+PF_6^-$ in CD_2Cl_2. [c] In this case the positions of H_α and H_γ signals coincide.

The successful synthesis of the permethylated monocations as well as theoretical considerations have prompted us to use permethylated dicarbinols of the type $C_5Me_5MC_5Me_3(CH_2OH)_2$ (M = Ru, Os) in the preparation of the corresponding dications.

We obtained the carbinols by reduction of the dialdehydes isolated upon oxidation of decamethylmetallocenes (Ia, M = Ru; Ib, M = Os; see Scheme I) by $BaMnO_4$, as described earlier.[4] It should be noted that even with a 10-fold excess of $BaMnO_4$, the primary products of oxidation are the monoaldehydes. The dialdehydes, in the mixture of which the 1,2-isomers dominate, are formed in low yield. The essentially pure 1,2-dialdehydes $C_5Me_5MC_5Me_3(CHO)_2$ (IIa, M = Ru; IIb, M = Os) were obtained after chromatography on silica gel[9] and were reduced by $LiAl(t\text{-}OBu)_3H$ to the corresponding 1,2-dicarbinols IIIa,b. These carbinols were utilized to obtain the 1,2-dications $[C_5Me_5MC_5Me_3(CH_2)_2]^{2+}$ (IVa, M = Ru; IVb, M = Os).

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 $FSO_3H\text{-}SbF_5$ at −60 °C.[5]



V

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 $HBF_4\cdot OEt_2$. This was unsuccessful; the 1,2-dications (IVa, M = Ru; IVb, M = Os) were obtained only upon use of the superacid CF_3SO_3H in CH_3NO_2.

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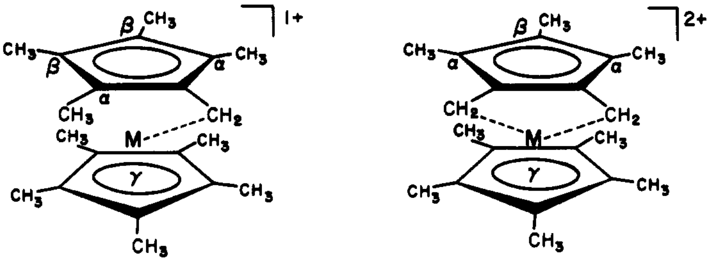
(4) Kreindlin, A. Z.; Petrovskii, P. V.; Rybinskaya, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 1620.

(5) Pittman, C. U. *Tetrahedron Lett.* **1967**, 3619.

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



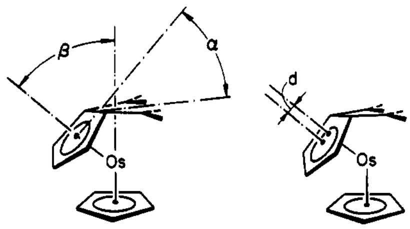
	δ, ppm						
	CH_2	Me_α	Me_β	Me_γ	$C_{\alpha,\beta}(C_5Me_{3(4)})$	$C_\gamma(C_5Me_5)$	$C_1(C_5Me_{3(4)})$
$C_5Me_5RuC_5Me_3(CH_2^+)_2$[a]	88.38 (t, $^1J_{CH}$ = 171 Hz)	9.43	10.10	10.45	111.32; 126.64	112.80	138.23
		(q, $^1J_{CH}$ = 131 Hz)					
$C_5Me_5RuC_5Me_4CH_2^+$[b]	74.67 (t, $^1J_{CH}$ = 164 Hz)	8.01	8.74	9.51	96.91; 105.36	97.22	107.20
		(q, $^1J_{CH}$ = 129 Hz)					
$C_5Me_5OsC_5Me_2(CH_2^+)_2$[a]	71.13 (t, $^1J_{CH}$ = 172 Hz)	8.96	10.02	9.71	105.71; 115.09	107.57	134.50
		(q, $^1J_{CH}$ = 131 Hz)					
$C_5Me_5OsC_5Me_4CH_2^+$[b]	55.36 (t, $^1J_{CH}$ = 166 Hz)	7.64	8.47	9.02	90.60; 95.68	92.51	99.68
		(q, $^1J_{CH}$ = 130 Hz)					

[a] Solutions of $C_5Me_5MC_5Me_3(CH_2OH)_2$ in CH_3NO_2/CF_3SO_3H. [b] Solutions of $C_5Me_5MC_5Me_4CH_2^+PF_6^-$ in CH_2Cl_2.

^1H 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 $\delta_{(CH_2^+)_2} - \delta_{CH_2^+} = 13.71$ ppm and for the Os compound $\delta_{(CH_2^+)_2} - \delta_{CH_2^+} = 15.77$ 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 ($^2J_{HH}$ = 1.9–2.4 Hz) characteristic of AB systems in ^1H NMR spectra and a single ^{13}C signal (triplet, $^1J_{CH}$ = 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.[6] To define the geometry of these often unsymmetrical systems, it is useful to introduce the following three geometrical parameters: α = angle of bending of C–CH_2 out of the plane of the Cp ring; β = angle of bending of M–center of Cp line from the 5-fold axis; d = 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 α and β, then the "slipping off" d.



VI

Table III shows a comparison of the calculated deformation parameters of the $[C_5H_5OsC_5H_4CH_2]^+$ monocation with the experimental structure of the permethylated Cp species.[7] 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 ^1H 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.

Table III. Comparison of Monocation Structures, Calculated and Experimental, and a Calculated 1,2-Dication Geometry

	calcd $[C_5H_5OsC_5H_4CH_2]^+$	obsd $[C_5Me_5OsC_5Me_4CH_2]^+$	calcd $[C_5H_5OsC_5Me_3(CH_2)_4]^{2+}$
α, deg	40	41.8	35
β, deg	12	6.9	18
d, Å	0.2	0.2	0.36

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 (^1H, 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 Ia monoaldehyde 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%) ^1H NMR: δ 2.02 (s, 6 H, α-Me), 1.77 (s, 3 H, β-Me), 1.66 (s, 15 H, γ-Me), 9.94 (s, 2 H, CHO).

Synthesis of IIIa. Reduction of 0.2 g (0.5 mmol) of IIa by $LiAlH(t\text{-}OBu)_3$, analogous to the reduction of the monoaldehyde,[8] leads to 0.19 g (0.47 mmol, 95%) of IIIa. ^1H NMR for IIIa: δ 1.62 (s, 15 H, γ-Me), 1.64 (s, 3 H, β-Me), 1.77 (s, 6 H, α-Me), 3.83 and 4.03 (AB q, 4 H, $^2J_{HH}$ = 1.3 Hz, 2 CH_2). In the spectra there are also signals of IIIa with an intramolecular hydrogen bond,

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(6) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179; **1962**, *37*, 2872. The parameters we used are taken from: Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

(7) Rybinskaya, M. I.; Kreindlin, A. Z.; Struchkov, Yu. T.; Yanovsky, A. I. *J. Organomet. Chem.* **1989**, *359*, 233.

(8) Kreindlin, A. Z.; Petrovskii, P. V.; Rybinskaya, M. I.; Yanovsky, A. I.; Struchkov, Yu. T. *J. Organomet. Chem.* **1987**, *319*, 229.

(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.

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 dialdehydes was separated analogously to the mixture of the Ru analogues; yield of IIb 0.1 g (0.21 mmol, 4%). ^{1}H NMR: δ 2.07 (s, 6 H, α-Me), 1.82 (s, 3 H, β-Me), 1.76 (s, 15 H, γ-Me), 9.94 (s, 2 H, CHO). Anal. Found: C, 49.27; H, 5.23; Os, 38.99. Calcd for $C_{20}H_{26}O_2Os$: C, 49.16; H, 5.36; Os, 38.92.

Synthesis of IIIb. The reduction of 0.24 g (0.5 mmol) of IIb by the action of LiAlH(t-OBu)$_3$, analogous to the reduction of the monoaldehyde,[4] leads to 0.22 g (0.45 mmol, 90%) of IIIb. ^{1}H NMR: δ 1.79 (s, 6 H, α-Me), 1.71 (s, 3 H, β-Me), 1.78 (s, 15 H, γ-Me), 4.02 and 4.04 (AB q, $^2J_{HH} \leq 7$ Hz, 4 H, 2 CH$_2$). Anal. Found: C, 48.32; H, 6.16; Os, 38.28. Calcd for $C_{20}H_{30}O_2Os$: C, 48.75; H, 6.14; Os, 38.60.

Synthesis of Dications and Recording of ^{1}H and ^{13}C NMR Spectra. To a solution of IIIa (or IIIb) in CD_3NO_2 or CH_3NO_2 under an Ar atmosphere was added a small excess of CF_3SO_3H. This was transferred in an ampule to the NMR spectrometer. The results are given in Tables I and II.

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Heteroaromatic Nitrogen Ligand Studies with the (η^5-Pentamethylcyclopentadienyl)ruthenium Cation: η^1(N) and η^6(π) Bonding Modes and Factors That Influence a Nitrogen to π Rearrangement

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Summary: The reactions of the (η^5-pentamethylcyclopentadienyl)ruthenium tris(acetonitrile) cationic complex $[Cp^*Ru(CH_3CN)_3](OTf)$ 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 η^1(N) and forms mono- or tris(pyridine) complexes with $[Cp^*Ru(CH_3CN)_3]^+$ depending on ligand concentration. Ligand **2** only forms an η^6 complex with $[Cp^*Ru(CH_3CN)_3]^+$, while ligand **3** also forms an η^6 complex, but with the benzo ring not the nitrogen ring. In the presence of excess pyridine, the complexed CH_3CN ligands are fully displaced to form $[Cp^*Ru(\eta^1(N)\text{-pyridine})_3]^+$, while in the presence of excess **2** or **3** only the $[Cp^*Ru(\eta^1(N)\text{-ligand})(CH_3CN)_2]^+$ complexes are formed. The latter $[Cp^*Ru(\eta^1(N)\text{-ligand})(CH_3CN)_2]^+$ complexes with ligands **2** and **3** were not isolated; rather, they undergo a rapid nitrogen (N) to π rearrangement to the corresponding η^6 complexes, $[Cp^*Ru(\eta^6\text{-2-methylpyridine or quinoline})]^+$. The isolation of $[Cp^*Ru(\eta^1(N)\text{-pyridine})(CH_3CN)_2]^+$ and its conversion to $[Cp^*Ru(\eta^6\text{-pyridine})]^+$ clearly demonstrates the pathway to the η^6 complexes. Ligand-exchange reactions of $[Cp^*Ru(\eta^6\text{-pyridine})]^+$ with CD_3CN and pyridine-d_5 show facile replacement of the η^6-bonded pyridine, while the former result with CD_3CN ligand exchange proves that the N to π 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 (η^5-pentamethylcyclopentadienyl)rhodium dication (Cp^*Rh^{2+})[1a] and the (η^5-cyclopentadienyl)ruthenium cation ($CpRu^+$),[1b] Chaudret and co-workers recently published some results on the bonding mode of pyridine, several methyl-substituted pyridine ligands, and quinoline with the (η^5-pentamethylcyclopentadienyl)ruthenium cation (Cp^*Ru^+).[2] In all cases, they isolated η^6(π)-bonded Cp^*Ru^+ complexes, while observing a pronounced solvent effect in acetone that provided a pyridine N-bonded complex (py_6Ru^{2+}), with a concomitant loss of Cp*.

Since our bonding results with $[Cp^*Rh(CH_3CN)_3]^{2+}$ and $[CpRu(CH_3CN)_3]^+$ as starting complexes were dramatically different for similar mono- and polynuclear heteroaromatic nitrogen ligands, i.e., η^1(N)- not η^6-bonding,[1a,b] we decided to examine the reactions of $[Cp^*Ru(CH_3CN)_3](OTf)$, a conveniently prepared starting material,[3] 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 η^6 complexes that formed with **1**–**3** and $[Cp^*Ru(CH_3CN)_3]^+$ emanated from our recently reported N to π rearrangement that appears to be general for complexes that have a $[CpRu(\eta^1(N)\text{-ligand})(CH_3CN)_2]^+$ structure.[1b,4]

Results and Discussion

The reaction of excess pyridine (**1**) and $[Cp^*Ru(CH_3CN)_3](OTf)$ in CH_2Cl_2 at ambient temperature provided only $[Cp^*Ru(\eta^1(N)\text{-pyridine})_3]^+$ (**4**) in 87% yield; no corresponding η^6 complex was observed. The 500-MHz ^{1}H NMR spectrum (CD_2Cl_2) of **4** provided clear evidence for the η^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 Cp* resonance was found at 1.29 ppm. A similar product was also observed when $(CH_3)_2CO$ was substituted for CH_2Cl_2 as the solvent. This latter result is in contrast

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