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Reactions of Quinones and Quinoid Molecules with the Cp*Ru$^+$ Fragment. Electron Redistribution and Transposition Reactions

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The Cp*Ru$^+$ fragment, generated by protonation of $[Cp^*RuOMe]_2$ with CF_3SO_3H, reacts with benzoquinone in CH_2Cl_2 to yield $[Cp^*Ru(\eta^6\text{-}HOC_6H_4OH)](CF_3SO_3)$ (1), a hydroquinone complex. Attempts to isolate stable biradical species through reaction of Cp*Ru$^+$ with L (L = TCNQ, DMTCNQ, DETCNQ) yielded insoluble materials formulated as $\{(Cp^*Ru)_2L\}(CF_3SO_3)_2$ (2–4). Reactions with quinoid compounds, namely 3,3,6,6-tetramethoxy-1,4-cyclohexadiene (6) and 4,4-dimethoxycyclohexa-2,5-dien-1-one (5), yielded respectively $[Cp^*Ru(\eta^6\text{-}1,2,4\text{-}(OMe)_3C_6H_3)](CF_3SO_3)$ (9) and a mixture of compounds including $[Cp^*Ru(\eta^6\text{-}1,4\text{-}(OMe)_2C_6H_4)](CF_3SO_3)$ (8) and $[Cp^*Ru(\eta^6\text{-}p\text{-}MeOC_6H_4OH)](CF_3SO_3)$ (7). Authentic samples of 7 and 8 were prepared from reactions of Cp*Ru$^+$ with the respective arenes.

Introduction

It has long been known that coordination to a transition metal will modify the π system of unsaturated hydrocarbons. This results in a modification of bond lengths and chemical properties.[1]

Recently, several groups, including ours, have been interested in the coordination properties of the Cp*Ru$^+$ fragment.[2-9] This fragment shows an unusual affinity for η^6-arene coordination whatever the other function present on the arene, except terminal acetylene and cyano groups.[4c] This is true, for example, for phenol, phenate, benzoic acid, or benzoate[4b] and even for heterocycles such as thiophenes or pyridines.[4d,6]

We have shown recently that this affinity could be a driving force leading to the aromatization of C_6 compounds through dehydrogenation, dehydration, or even demethylation.[4f] Furthermore, cyclization reactions, for example of hexatriene into benzene, are also possible with this system.[4g]

This led us to try to find new pathways for aromatization reactions induced by the Cp*Ru$^+$ fragment. Reactions with quinones looked attractive, since these compounds possess a readily accessible aromatic biradical excited state. Either the observation of new reactions or the stabilization of a biradical structure were anticipated upon reaction with Cp*Ru$^+$. A recent example[2d] has demonstrated the possibility of obtaining dibenzo-*p*-quinodimethane complexes stabilized by Cp*Ru$^+$. We have extended this study to TCNQ and its alkyl derivatives, since the radical anions of these compounds are stable. It is noteworthy that the coordination chemistry of these molecules is not well developed[10] and that no π complexes of TCNQ or of its derivatives have been reported.

As a further extension of this work, we also considered the reactivity of Cp*Ru$^+$ with compounds having a quinoid structure to see whether aromatization is possible in this case.

Results and Discussion

Reaction of Cp*Ru$^+$ with 1,4-Benzoquinone. The reaction of $[Cp^*Ru(OMe)]_2$ with CF_3SO_3H in the presence of 1 equiv of 1,4-benzoquinone in CH_2Cl_2 at room temperature leads to a brown solution. After a reaction time of 2 h and recrystallization from $(CH_3)_2CO/Et_2O$, colorless crystals of $[Cp^*Ru(\eta^6\text{-}p\text{-}OHC_6H_4OH)](CF_3SO_3)$ (1) are recovered in a ca. 64% yield (see Scheme I, eq 1). Microanalytical and spectroscopic data are in agreement with the proposed formulation. For example, the hydroquinone ring is characterized by peaks at δ 5.83 (C–H) and 9.22 (O–H) in the ^{1}H NMR spectrum and by peaks at δ 75.8 (C–H) and 127.5 (C–O) in the ^{13}C NMR spectrum in agreement with its π coordination to ruthenium.

The transformation of quinone into hydroquinone is further confirmed by an X-ray crystal structure determination. The structure consists of one Cp*Ru unit linked symmetrically to the six carbon atoms of hydroquinone. All the C–C distances within the Cp* ring are in the range expected for such compounds. The average carbon–carbon

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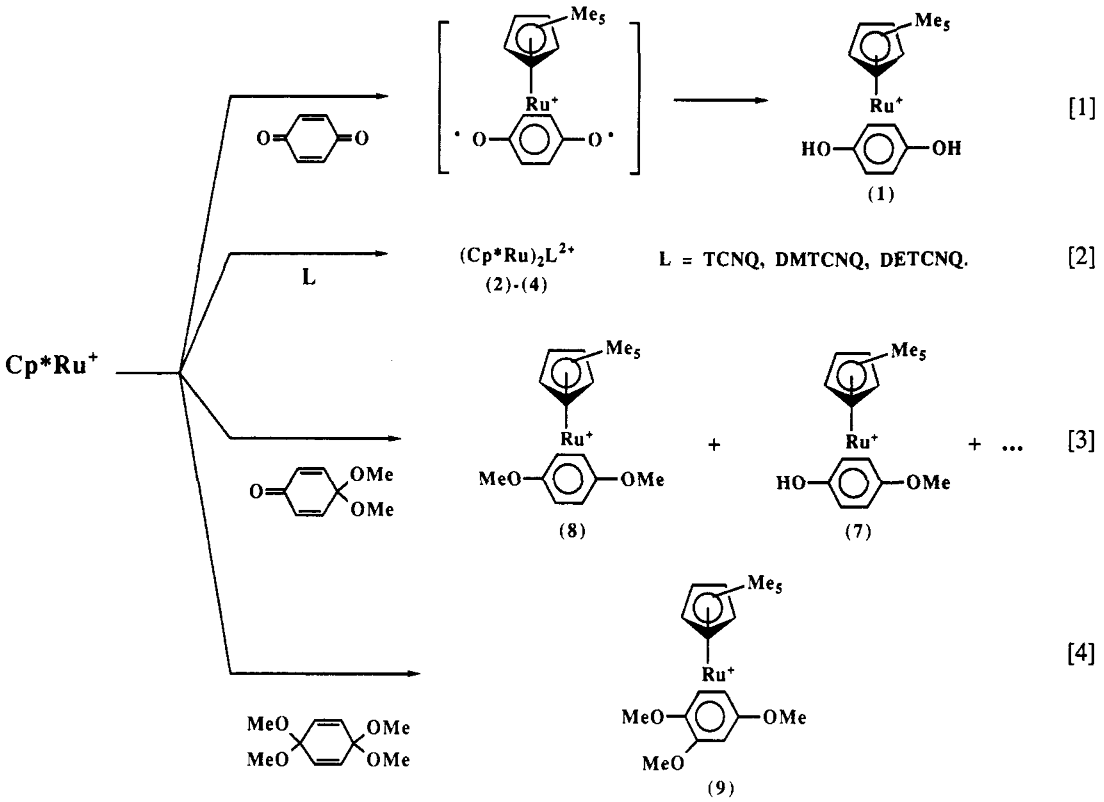
Scheme I. Reactions of Cp*Ru$^+$ with Quinones and Quinoid Molecules



bond length within the hydroquinone ring is 1.40 (2) Å, whereas the exocyclic carbon–oxygen distance of 1.367 (9) Å is typical for a single C–O bond. The hydrogen atom of the hydroxo group was located on the Fourier map and found to be engaged in a classical O–H···O$_1$(triflate) hydrogen bond (O–H = 1.161 (6) Å, O···O$_1$ = 2.59 (2) Å, H···O$_1$(triflate) = 1.460 (9) Å; O–H–O$_1$ = 166.0 (6)°).

In order to gain insight into the mechanism of quinone reduction, the reaction was carried out in the presence of the spin trap agent ^{t}BuNO. In a blank experiment carried out at room temperature, we observed that ^{t}BuNO reacts with quinone in CH_2Cl_2 solution to lead to the appearance of a stable complex ESR signal after 15 min. The intensity of the signal slowly grows until reaching saturation after 1 h. Under the same conditions, but in the presence of Cp*Ru$^+$, the appearance of the same ESR signal is instantaneous and is ca. 60 times more intense after 15 min than in the preceding case, suggesting that Cp*Ru$^+$ is a radical initiator.

The spectrum consists mainly of a triplet of multiplets (g = 2.0055). The triplet splitting is due to the interaction of the radical electron spin with one nitrogen nucleus, giving rise to the 1:1:1 intensity ratio a_N = 14.7 G. The radical electron also interacts with three different protons: a simulation led to the hyperfine coupling values a_H = 3.3, 0.9, and 0.5 G. The same spectrum was obtained in CD_2Cl_2 solution. If triflic acid is used instead of Cp*Ru$^+$ in this experiment, a very intense ESR spectrum (one single line) appears immediately at g = 2.0034 (ΔH_{pp} = 3 G) but is very different from the preceding one. Finally, in the absence of quinone, no ESR signal was detected.

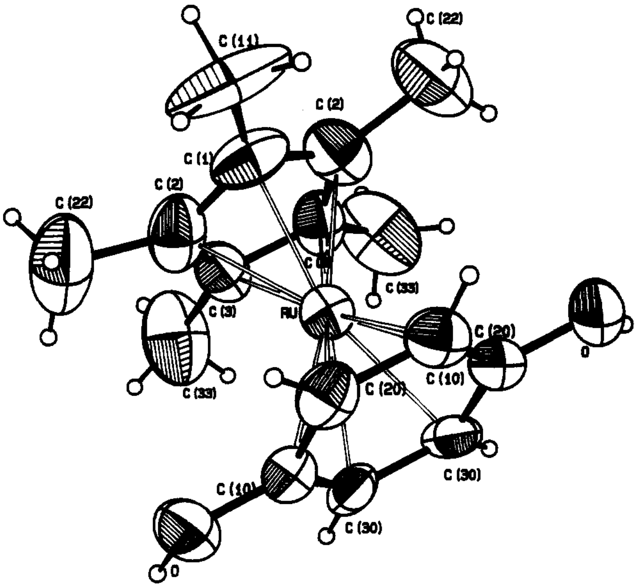


Figure 1. ORTEP view of the cation [Cp*Ru(η^6-p-HOC_6H_4OH)]$^+$. Selected bond lengths (Å) and angles (deg): C(10)–C(20), 1.38 (1); C(10)–C(30), 1.42 (1); C(20)–C(20), 1.42 (2); C(10)–O, 1.367 (9); O–H, 1.161 (6); Cp*(centroid)–Ru, 1.790 (1); hydroquinone(centroid)–Ru, 1.714 (1); C(10)–O–H, 114.2 (6); C(10)–C(20)–C(20), 120.2 (4); C(10)–C(30)–C(30), 119.4 (4); O–C(10)–C(20), 117.6 (7); O–C(10)–C(30), 121.9 (7); C(20)–C(10)–C(30), 120.5 (7).

Two mechanisms can explain the formation of a quinone radical in the presence of Cp*Ru$^+$. The first would be a one- or two-electron reduction of quinone with concomitant oxidation of ruthenium. However, Cp*Ru$^+$ is not oxidized in CH_2Cl_2 between 0.300 and 1.00 V, whereas quinone is reduced at −0.431 V, which prevents any electron-transfer reaction between the two species. Furthermore, the oxidation of Cp*Ru$^+$ should lead to ruthenium(III) species which are normally observable by ESR spectroscopy.[11] We did not observe any evidence for such compounds. The second mechanism would involve a π coordination of quinone, implying a rearrangement of its π-orbital system. This would lead to an intermediate biradical species. This biradical can most probably also be produced by photo-

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[11] For example: Medhi, O. K.; Agarwala, U. *Inorg. Chem.* **1980**, *19*, 1381.

lysis, which explains the similarity of ESR spectra in the presence or absence of ruthenium.

The coordinated biradical would then be able to abstract $H^\bullet$ from molecules present in solution. We have been unable to characterize the hydrogen-donor species and the transformed product. However, since methanol resulting from the protonation of $[Cp^*Ru(OMe)]_2$ is always present in the reaction mixture, this could be the source of hydrogen.

Reaction of Cp^*Ru^+ with Tetracyanoquinodimethane and Derivatives. The preceding result prompted us to try to obtain stable radical species using quinone derivatives such as tetracyanoquinodimethane (TCNQ) and its dimethyl (DMTCNQ) and diethyl (DETCNQ) derivatives. The reactions of Cp^*Ru^+ with these compounds in CH_2Cl_2 lead rapidly at room temperature to the precipitation of greenish insoluble materials that are analyzed as $[(Cp^*Ru)_2L](CF_3SO_3)_2$ (L = TCNQ (**2**), DMTCNQ (**3**), DETCNQ (**4**)) in high yield (~60%); see Scheme I, eq 2). The microanalyses were reproducible. The infrared spectra of the green materials in KBr disks show the presence of TCNQ and Cp* ligands (e.g. for L = TCNQ: $\nu_{CN} = 2180, 2134\ cm^{-1}$; $\nu_{CN} = 2222\ cm^{-1}$ for free TCNQ) as well as CF_3SO_3 anion. The compound was found to be diamagnetic by magnetic susceptibility measurements at room temperature. However, the ESR spectrum at room temperature shows a single band at $g = 2.003$ ($\Delta H_{pp} = 10$ G) attributable to $TCNQ^{\bullet-}$.

These results are consistent with the coordination of TCNQ but are unconclusive on the mode of coordination (through CN groups or aromatic ring). The presence of the ESR signal could arise from either some small charge transfer within the complex (in such a case, the Ru^{III} signal could be unobservable because of the small amount of such a species) or traces of free $TCNQ^{\bullet-}$ which could not be eliminated from the precipitated solid.

Unfortunately, any attempt at direct crystallization or recrystallization failed since the compounds are insoluble in methanol, acetone, dichloromethane, and THF and decompose in nitromethane or acetonitrile. In these last two solvents an orange solution containing TCNQ was obtained, indicating a reversible reduction if any. In summary we propose for these compounds of stoichiometry $[(Cp^*Ru)_2L](CF_3SO_3)_2$ either a triple-decker formulation as in $[CpRuCp^*RuCp^*](PF_6)$[8a] and $[Cp^*Ru(\eta^5{:}\eta^5\text{-}C_5Me_4OH)RuCp^*](CF_3SO_3)$[12] or a polymeric compound containing TCNQ units linked to several Cp*Ru units through the cyano groups.

In both cases the magnetic properties could result from charge transfer between the metal and the ligand, even though no ESR signal of the metal was observed.

Reactions with Other Quinone Type Species. We have shown in a previous report that Cp^*Ru^+ was able to aromatize C_6 hydrocarbons through activation of C–H and/or C–O and/or C–C bonds.[4f] In the latter process the presence of ethane in the reaction gases suggested a radical pathway for the elemental carbon–carbon bond–cleavage step. This result, together with the observations reported in this paper, led us to study other similar compounds containing *gem*-dialkoxy groups to see whether aromatization is possible and what mechanism this would involve. We studied first 4,4,-dimethoxycyclohexa-2,5-dien-1-one (**5**) and 3,3,6,6-tetramethoxy-1,4-cyclohexadiene (**6**).

The reaction of Cp^*Ru^+ with **5** yields a complex mixture as revealed by ^1H NMR spectroscopy (see Scheme I, eq 3). Thus, several peaks attributed to Cp* are observed near δ 2, whereas complex features are observed near δ 6 for π-coordinated aromatic derivatives. We checked that the major component of this mixture (ca. 30% spectroscopic yield) is $[Cp^*Ru(\eta^6\text{-}p\text{-}MeOC_6H_4OH)](CF_3SO_3)$ (**7**) by preparing an authentic sample from Cp^*Ru^+ and *p*-hydroxyanisole (see eq 5). The complex shows the Cp* peak at δ 2.11, the methoxy group at δ 3.93, and an AA′BB′ pattern for the aromatic protons centered at δ 5.90 and 6.05 ($J_{app} = 6.6$ Hz) in the ^1H NMR spectrum.

$$Cp^*Ru^+ + CH_3OC_6H_4OH \rightarrow \underset{\text{cation of } \mathbf{7}}{[Cp^*Ru(\eta^6\text{-}p\text{-}MeOC_6H_4OH)]^+} \quad (5)$$

$[Cp^*Ru(\eta^6\text{-}C_6H_4(p\text{-}OMe)_2)](CF_3SO_3)$ (**8**) was also detected in the mixture (ca 20% spectroscopic yield) by comparison with an authentic sample prepared from Cp^*Ru^+ and 1,4-dimethoxybenzene (see eq 6). This complex shows the Cp* peak at δ 2.13, the methoxy groups at δ 3.95, and the aromatic signal at δ 6.12. The other components of the mixture were not identified but since two other peaks are visible in the methoxy region, it is possible that a migration reaction has occurred.

$$Cp^*Ru^+ + C_6H_4(OMe)_2 \rightarrow \underset{\text{cation of } \mathbf{8}}{[Cp^*Ru(\eta^6\text{-}C_6H_4(p\text{-}OMe)_2)]^+} \quad (6)$$

In order to gain some evidence for this hypothesis, Cp^*Ru^+ was reacted with **6**. In contrast to the preceding reaction, this one was selective and produced $[Cp^*Ru(\eta^6\text{-}1,2,4\text{-}(CH_3O)_3C_6H_3)](CF_3SO_3)$ (**9**) (see Scheme I, eq 4). The complex shows in its ^1H NMR spectrum the Cp* ligand at δ 2.10, three methoxo signals at δ 3.97, 4.00, and 4.06, and an ABC pattern for the aromatic protons corresponding to the protons in the 3-, 5-, and 6-positions on the arene ring (δ(H_3) 6.43, δ(H_6) 6.32, δ(H_5) 5.90; $J_{H_3H_6}$ not observed, $J_{H_3H_5} = 1.7$ Hz, $J_{H_5H_6} = 6.4$ Hz). The ^{13}C NMR spectrum confirms our proposal, showing peaks at δ 9.8 ($C_5\mathit{Me}_5$), 94.6 (C_5Me_5), 57.1, 57.3, and 57.4 for the three methoxo groups, 72.3, 70.9, and 65.3 for C_3, C_6, and C_5, and 121.3, 122.7, and 128.9 for C_1, C_2, and C_4.

This reaction was performed in an ESR tube in the presence of ^tBuNO as a spin trap, but no radical formation was detected.

Under the same conditions, a blank experiment carried out with **6** and triflic acid instead of Cp^*Ru^+ did not lead to 1,2,4-trimethoxybenzene.

The reaction, however, probably involves an acid type mechanism (see Scheme II). Cp^*Ru^+ may abstract a methoxo group from **6**. The carbocation would then rearrange through migration of a methoxo group to the 1-, 2-, 4-, or 5-position and expulsion of H^+, which would in turn protonate $[Cp^*RuOMe]_2$, liberating Cp^*Ru^+, which would react with the arene moiety to give **9**. It seems, therefore, that no radical needs to be involved in this transposition reaction.

The complexity of the reaction of **5** with Cp^*Ru^+ probably results from the ability of the system to undergo different initial pathways (generation of a carbocation or of a radical) and from this possible transposition.

Conclusion

This study reveals two new aspects of the rich reactivity of Cp^*Ru^+. The first is the capability to modify the π system of quinone to produce hydroquinone (the spin trap experiment, although not conclusive, is in agreement with a biradical intermediate). We failed to fully elucidate the structures of the well-defined products resulting from the reactions of TCNQ and its derivatives with Cp^*Ru^+. Although π coordination for TCNQ (model for the quinone

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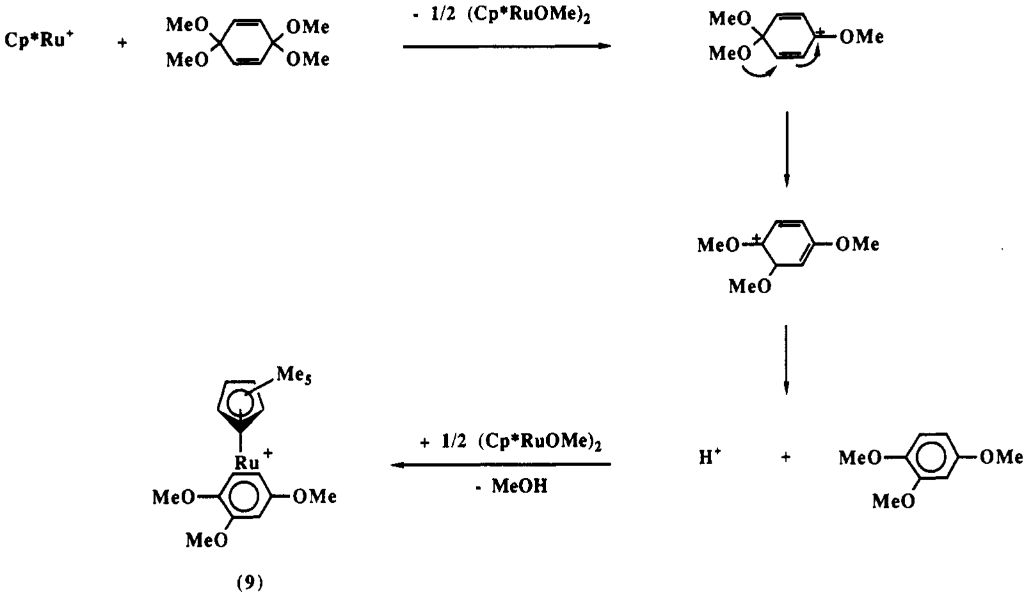
[12] Chaudret, B.; Dahan, F.; He, X.-D. *J. Chem. Soc., Chem. Commun.* **1990**, 1111.

Scheme II. Proposed Mechanism for the Transposition Reaction



reaction) in a "triple-decker" compound is possible, it still remains to be proven.

The second aspect involves a new transposition reaction which again gives evidence for the high Lewis acidity of the Cp*Ru$^+$ fragment.

These properties together with those previously reported, i.e. strong affinity for arenes, high Lewis acidity, hydrogen-transfer catalyst, electron-releasing effect in π complexes, radical generator, will make the Cp*Ru$^+$ fragment a powerful tool in organic and materials chemistry. We are presently exploring these possibilities.

Finally, we should note that a precedent exists for hydrogenation of aromatic hydrocarbons upon coordination to a CpFe$^+$ moiety. Here, the formation of radicals in a position α to the aromatic cycle could also explain this hydrogenation. However, a clear description of the mechanism was found to be difficult at that time, since these reactions occurred at high temperature (80–160 °C) in the presence of $AlCl_3$.[13]

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere by using Schlenk-line techniques. Solvents were degassed before use. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer. IR and ESR spectra were recorded on an Perkin-Elmer FT 1725X and a Bruker ER 200TT instrument, respectively. The ESR simulating program was provided by A. Mari.

Elemental analyses were performed in the "Laboratoire de Chimie de Coordination du CNRS à Toulouse".

The brown solution of Cp*Ru$^+$ in dichloromethane was used in situ for all the following syntheses. It was obtained after reaction of CF_3SO_3H with [Cp*Ru(OMe)]$_2$, prepared from (Cp*RuCl$_2$)$_n$ according to a published method.[4b]

Reaction of Cp*Ru$^+$ with 1,4-Benzoquinone. CF_3SO_3H (0.98 mmol, 87 μL) was added to a stirred dichloromethane solution (10 mL) of [Cp*RuOMe]$_2$ (from 0.98 mmol (300 mg) of [Cp*RuCl$_2$]$_n$). After 10 min of stirring, 1,4-benzoquinone (0.98 mmol, 106 mg) was added. After a reaction time of 2 h, diethyl ether was then added, the precipitate was filtered and washed with ether (3 × 5 mL). [Cp*Ru(η^6-*p*-HOC_6H_4OH)](CF_3SO_3) (1) was obtained as white microcrystals upon recrystallization from $(CH_3)_2CO/Et_2O$ (yield 64%). Anal. Calcd for $C_{17}H_{21}O_5F_3SRu$: C, 41.21; H, 4.24. Found: C, 42.10; H, 4.61. Crystals suitable for X-ray analysis were obtained in this way. ^1H NMR (($CD_3)_2CO$): δ 2.08 (s, 15 H, C_5Me_5), 5.83 (s, 4 H, C_6H_4), 9.22 (br, 2 H, OH). ^{13}C NMR (($CD_3)_2CO$): δ 9.5 (q, J_{C-H} = 128 Hz, $C_5(CH_3)_5$), 75.8 (d, J_{C-H} = 177 Hz, C_6H_4), 95.0 (s, C_5Me_5), 127.5 (s, *C*–OH).

X-ray Structural Determination of [Cp*Ru(η^6-*p*-HOC_6H_4OH)](CF_3SO_3) (1): $C_{17}H_{21}F_3O_5RuS$, M_r = 495.47, yellowish prismatic crystals, orthorhombic, space group *Pbcm*, a = 7.490 (1) Å, b = 26.748 (6) Å, c = 9.932 (2) Å, V = 1993.3 (4) Å^3, D_{calc} = 1.65 g cm^{-3}, Z = 4, μ(Mo Kα) = 9.23 cm^{-1}. X-ray diffraction data were collected on an Enraf-Nonius CAD4-Micro VAX-II diffractometer system using the ω-2θ scan technique with graphite-monochromated Mo Kα radiation. A total of 2248 independent reflections were measured (to 2θ = 52°), of which 1244 were judged to be "observed" ($I > 3\sigma(I)$). The structure was solved by a combination of Patterson and direct methods, and full-matrix least-squares refinement (all non-H atoms anisotropic) reached R = 0.068 (R_w = 0.099) with a goodness-of-fit value of 1.973. Hydrogen atoms, except those for one methyl group of Cp*, were located on a difference Fourier map but were simply included in structure factor calculations. A possible disorder (not resolved) in the triflate anion, in view of the high values of thermal parameters of the atoms C, S, O_1, O_2, F_1, and F_2 is probably responsible for the relatively high values of the conventional R factors.

Reaction of Cp*Ru$^+$ with TCNQ. CF_3SO_3H (0.98 mmol, 87 μL) was added to a stirred dichloromethane solution (10 mL) of [Cp*RuOMe]$_2$ (from 0.98 mmol (300 mg) of (Cp*RuCl$_2$)$_n$). After 10 min of stirring, TCNQ (0.98 mmol, 200 mg) was added. After a reaction time of 2 h, the green precipitate was filtered and washed with dichloromethane (3 × 5 mL) to give [(Cp*Ru)$_2$TCNQ](CF_3SO_3)$_2$ (2; yield 60%). Anal. Calcd for $C_{34}H_{34}N_4F_6S_2O_6Ru_2$: C, 41.89; H, 3.52; N, 5.75. Found: C, 40.86; H, 3.45; N, 6.15.

Reaction of Cp*Ru$^+$ with DMTCNQ. The same procedure as above was used with DMTCNQ (0.98 mmol, 227 mg). [(Cp*Ru)$_2$(DMTCNQ)](CF_3SO_3)$_2$ (3) was obtained as a green powder (yield 63%). Anal. Calcd for $C_{36}H_{38}N_4F_6S_2O_6Ru_2$: C, 43.11; H, 3.82; N, 5.59. Found: C, 42.85; H, 3.60; N, 5.95.

Reaction of Cp*Ru$^+$ with DETCNQ. The same procedure as above was used with DETCNQ (0.98 mmol, 255 mg). [(Cp*Ru)$_2$DETCNQ](CF_3SO_3)$_2$ (4) was obtained as a green powder (yield 64%). Anal. Calcd for $C_{38}H_{42}N_4F_6S_2O_6Ru_2$: C, 44.27; H, 4.11; N, 5.43. Found: C, 44.62; H, 3.75; N, 5.62.

Reaction of Cp*Ru$^+$ with 4,4-Dimethoxycyclohexa-2,5-dien-1-one (5). CF_3SO_3H (0.65 mmol, 57 μL) was added to a stirred dichloromethane solution (10 mL) of [Cp*RuOMe]$_2$ (from 0.65 mmol (200 mg) of (Cp*RuCl$_2$)$_n$). After 10 min of stirring,

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5 (0.64 mmol, 90 μL) was added. After a reaction time of 2 h (the same results were obtained after stirring overnight), the brown-green solution was evaporated to dryness and the residue washed several times with diethyl ether until the filtrate was colorless. We were unable to obtain a pure complex after several attempts at recrystallization. A mixture of different species was always obtained, from which the two complexes [Cp*Ru(η^6-*p*-MeOC$_6$H$_4$OH)](CF$_3$SO$_3$) (7) and [Cp*Ru(η^6-*p*-MeOC$_6$H$_4$OMe)](CF$_3$SO$_3$) (8) were identified by comparison to an authentic sample (see below).

Reaction of Cp*Ru$^+$ with 4-Methoxyphenol. CF$_3$SO$_3$H (0.28 mmol, 25 μL) was added to a stirred dichloromethane solution (10 mL) of [Cp*RuOMe]$_2$ (from 0.28 mmol (86 mg) of (Cp*RuCl$_2$)$_n$). After 10 min of stirring, MeOC$_6$H$_4$OH (0.28 mmol, 35 mg) was added. After it was stirred overnight, the mixture was evaporated to dryness. The residue was washed several times with diethyl ether until the filtrate was colorless. The precipitate was recrystallized from CH$_2$Cl$_2$/Et$_2$O, affording [Cp*Ru(η^6-*p*-MeOC$_6$H$_4$OH)] (CF$_3$SO$_3$) (7) as greenish crystals (yield ca. 80%). Anal. Calcd for C$_{18}$H$_{23}$O$_5$F$_3$SRu: C, 42.44; H, 4.52. Found: C, 42.05; H, 4.65. ^{1}H NMR ((CD$_3$)$_2$CO): δ 2.11 (s, 15 H, C$_5$(CH$_3$)$_5$), 3.93 (s, 3 H, OCH$_3$), 5.90 and 6.05 (AA′BB′, 4 H, J_{app} = 6.6 Hz, C$_6$H$_4$). ^{13}C NMR ((CD$_3$)$_2$CO): δ 9.7 (q, $J_{\text{C-H}}$ = 128 Hz, C$_5$(*C*H$_3$)$_5$), 56.7 (q, $J_{\text{C-H}}$ = 146 Hz, OCH$_3$), 74.4 (d, $J_{\text{C-H}}$ = 177 Hz, C$_6$H$_4$), 75.6 (d, $J_{\text{C-H}}$ = 176 Hz, C$_6$H$_4$), 128.2 (s, C$_6$H$_4$), 130.0 (s, C$_6$H$_4$), 95.3 (s, *C*$_5$(CH$_3$)$_5$).

Reaction of Cp*Ru$^+$ with 1,4-Dimethoxybenzene. The same procedure as above was used with CF$_3$SO$_3$H (0.49 mmol, 45 μL), (Cp*RuCl$_2$)$_n$ (0.49 mmol, 150 mg) and C$_6$H$_4$(OMe)$_2$ (0.48 mmol, 66 mg). [Cp*Ru(C$_6$H$_4$(OMe)$_2$)](CF$_3$SO$_3$) (8) was obtained as a gray powder (yield ca. 80%). Anal. Calcd for C$_{19}$H$_{25}$O$_5$F$_3$SRu: C, 43.59; H, 4.78. Found: C, 43.51; H, 4.78. ^{1}H NMR ((CD$_3$)$_2$CO): δ 2.13 (s, 15 H, C$_5$(CH$_3$)$_5$), 3.95 (s, 6 H, OCH$_3$), 6.12 (s, 4 H, C$_6$H$_4$).

Reaction of Cp*Ru$^+$ with 3,3,6,6-Tetramethoxy-1,4-cyclohexadiene (6). The same procedure as above was used with CF$_3$SO$_3$H (0.65 mmol, 57 μL), (Cp*RuCl$_2$)$_n$ (0.65 mmol, 200 mg), and 6 (0.64 mmol, 127 mg). [Cp*Ru(η^6-1,2,4-(MeO)$_3$C$_6$H$_3$)]-(CF$_3$SO$_3$) (9) was obtained as a gray powder (yield ca. 60%). Anal. Calcd for C$_{20}$H$_{27}$O$_6$F$_3$SRu: C, 43.40; H, 4.88. Found: C, 43.08; H, 4.83. ^{1}H NMR ((CD$_3$)$_2$CO): δ 2.10 (s, 15 H, C$_5$(CH$_3$)$_5$), 3.97 (s, 3 H, OCH$_3$), 4.00 (s, 3 H, OCH$_3$), 4.06 (s, 3 H, OCH$_3$), 5.90 (dd, 1 H, $J_{\text{H}_3\text{-H}_5}$ = 1.7 Hz, $J_{\text{H}_5\text{-H}_6}$ = 6.4 Hz, H$_5$), 6.32 (d, 1 H, $J_{\text{H}_5\text{-H}_6}$ = 6.4 Hz, H$_6$), 6.43 (d, 1 H, $J_{\text{H}_3\text{-H}_5}$ = 1.7 Hz, H$_3$). ^{13}C NMR ((CD$_3$)$_2$CO): δ 9.8 (q, $J_{\text{C-H}}$ = 128 Hz, C$_5$(*C*H$_3$)$_5$), 57.1 (q, $J_{\text{C-H}}$ = 147 Hz, OCH$_3$), 57.3 (q, $J_{\text{C-H}}$ = 147 Hz, OCH$_3$), 57.4 (s, $J_{\text{C-H}}$ = 147 Hz, OCH$_3$), 65.3 (d, $J_{\text{C-H}}$ = 179 Hz, C$_5$), 70.9 (d, $J_{\text{C-H}}$ = 179 Hz, C$_6$), 72.3 (d, $J_{\text{C-H}}$ = 174 Hz, C$_3$), 121.3 (s, C$_{1\text{ or }2\text{ or }4}$), 122.7 (s, C$_{2\text{ or }1\text{ or }4}$), 128.9 (s, C$_{4\text{ or }2\text{ or }1}$).

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Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, bond lengths and angles, root-mean-square amplitudes of thermal vibration, and torsion angles (11 pages). Ordering information is given on any current masthead page.

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Theoretical Study of Ligand Substitution Reactions in Pentacoordinated Silicon Species

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Ab initio MO calculations have been carried out to study the reactions of pentacoordinated silicon species SiH$_3$F$_2^-$ and SiH$_2$F$_3^-$ with H$^-$ and F$^-$. The possibility of ligand displacements taking place via hexacoordinated intermediates has been discussed by locating the transition state on the potential energy surface. The difference in mechanisms between the reaction of silicon species and the biomolecular nucleophilic substitution reaction of carbon compounds has been clarified by applying the orbital interaction scheme.

Introduction

The chemistry of penta- and hexacoordinated silicon species is developing rapidly.[1-9] For instance, pentacoordinated species have been suggested to be the intermediates in nucleophilic displacements at silicon centers.[10-12] Hexacoordinated silicon species are now also assumed to intervene in the reactions of organosilicon

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