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Transition Metal Stabilized *o*-Xylylenes. Reactivity of the Novel *o*-Xylylene Complex Ru(η^6-C_6Me_6)[η^4-$C_6Me_4(CH_2)_2$]

John W. Hull, Jr.,[1] Charles Mann, and Wayne L. Gladfelter*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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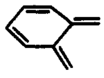
The title complex was prepared in 87% yield from the deprotonation of [Ru(C_6Me_6)$_2$](BF_4)$_2$ with excess potassium *tert*-butoxide in THF at −78 °C. Treatment of the mixed-sandwhich complex [Ru(1,2-$C_6H_4Me_2$)(C_6Me_6)](PF_6)$_2$ with excess potassium *tert*-butoxide resulted in preferential deprotonation of the hexamethylbenzene ligand, giving *o*-xylylene complex Ru(η^6-1,2-$C_6H_4Me_2$)[η^4-$C_6Me_4(CH_2)_2$]. Attempts to prepare *o*-xylylene complexes bearing no ring methyl groups by deprotonation of [Ru(*o*-xylene)$_2$]$^{2+}$ or [Ru(benzene)(*o*-xylene)]$^{2+}$ failed to give isolable complexes. The cyclohexadienyl complex [Ru(η^6-C_6Me_6)(η^5-$C_6Me_5CH_2$)]$^+$ was prepared as the PF_6^-, BPh_4^-, or $CF_3SO_3^-$ salt by monodeprotonating [Ru(C_6Me_6)$_2$](PF_6)$_2$ with 1 equiv of potassium *tert*-butoxide, by treating the title complex with 1 equiv of trifluoromethanesulfonic acid, or by stirring an equimolar mixture of [Ru(C_6Me_6)$_2$](BF_4)$_2$ and the title complex in acetonitrile. The exomethylene carbons of the coordinated *o*-xylylene were alkylated with excess CF_3SO_3Me to give [Ru(C_6Me_6)(1,2-$C_6Me_4Et_2$)]$^{2+}$ or were hydrogenated under catalytic conditions to give the single or doubly hydrogenated complexes Ru(η^4-$C_6HMe_5CH_2$)(η^6-C_6Me_6) and Ru(η^4-5,6-$C_6Me_6H_2$)(η^6-C_6Me_6). The singly hydrogenated product is a tautomer of the known 18-electron complex Ru(C_6Me_6)$_2$ but is much more stable toward oxidation. Treatment with Fe(CO)$_4$(NMe_3) gave a product bearing an Fe(CO)$_3$ group coordinated to the exomethylene diene system, along with an unexpected product characterized as a complex in which an iron acylate strap connects the two dissimilar hexamethylbenzene ligands. The coordinated *o*-xylylene ligand failed to undergo cycloaddition reactions when treated with dienophiles.

Introduction

Transition metals are often valuable in stabilizing organic molecules which cannot survive under normal laboratory conditions. *o*-Xylylene (1) is an example of this



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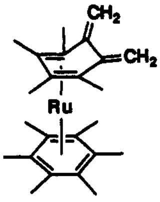

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type of reactive species. Coordination of this molecule to a transition metal yields a stable complex, and in most of the known monometal π-complexes of *o*-xylylene, the metal is believed to coordinate to the exocyclic diene.[2-5]

We have previously reported the double deprotonation of [Ru(C_6Me_6)$_2$]$^{2+}$ to give the novel *o*-xylylene complex Ru(η^6-C_6Me_6)[η^4-$C_6Me_4(CH_2)_2$] (2), where the metal was found to coordinate to the endocyclic diene system.[6] Astruc and co-workers have since prepared the iron analogue of 2, which is unstable above −20 °C.[7]

We report here our results of the study of the reactivity of 2 and our attempts to synthesize ruthenium stabilized *o*-xylylene complexes bearing less than four methyl groups.

Experimental Section

General Information. Literature procedures were used to prepare [RuCl$_2$(C_6H_6)]$_2$,[8] [RuCl$_2$(*o*-xylene)]$_2$,[8] [Ru(C_6Me_6)(*o*-xylene)](PF_6)$_2$,[9] and [Ru(C_6Me_6)$_2$]$^{2+}$ (BF_4^- or PF_6^- salt).[9] Trimethylaminetetracarbonyliron was prepared as previously reported,[10] purified by sublimation at room temperature and stored in a freezer under nitrogen without any apparent loss of purity. Tetrahydrofuran was distilled from benzophenone ketyl, methylene chloride was distilled over P_2O_5, and pentane, hexane, heptane, and toluene were distilled over calcium hydride or sodium metal. Potassium *tert*-butoxide was purchased from Aldrich, stored and weighed in a drybox, and used without further purification. Methyl trifluoromethanesulfonate was purchased from Aldrich and distilled over a small amount of P_2O_5 under nitrogen prior to use. All reactions were carried out under an atmosphere of nitrogen using normal Schlenk-line techniques unless otherwise noted. Elemental analyses were obtained from Galbraith Laboratories. NMR spectra were obtained with a Varian HFT-80 or a Nicolet NTCFT-1180 300-MHz spectrometer. The electron impact mass spectral data were obtained with the solids probe of an AEI-MS30 instrument.

Ru(η^6-C_6Me_6)[η^4-$C_6Me_4(CH_2)_2$] (2). [Ru(C_6Me_6)$_2$](BF_4)$_2$ (8.23 g, 13.7 mmol) was weighed into a 500-mL round-bottom double-neck flask equipped with a magnetic stir bar and a rubber septum. The flask was flushed with nitrogen, and 150 mL of dry THF was injected. A dropping funnel containing potassium *tert*-butoxide (6.16 g, 54.9 mmol) was fitted onto the flask under a stream of nitrogen, and 100 mL of THF was injected into the funnel to dissolve the butoxide. The reaction slurry was cooled to −78 °C, and the butoxide solution was added dropwise with efficient stirring over a 30–45-min period. The slurry became bright yellow as the addition of base proceeded. After addition was complete, the reaction was stirred at −78 °C for an additional 30 min, then warmed to room temperature and heated to near the boiling point of THF with a heating mantle for 15 min, and then cooled to room temperature. The solvent was removed under vacuum, leaving a bright yellow solid residue. The residue was extracted with portions of hot hexane and filtered under nitrogen, using a total of 400 mL of hexane for extraction and filtration.

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[1] Present address: Agricultural Chemicals Process Research, Dow Chemical U.S.A., 1710 Building, Midland, MI 48674.

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The filtrate was reduced in volume under vacuum to about 100 mL and cooled in a freezer to allow crystallization. The resulting orange microcrystalline product was collected on a glass frit in air and then placed under vacuum to remove traces of hexane. A second crop of crystals was obtained from the hexane filtrate and dried in a similar manner. The combined yield of 2 was 5.09 g (87%), and the overall yield of 2 in four steps from $RuCl_3 \cdot 3H_20$ was 60%. NMR and elemental analysis data were previously reported.[6]

$Ru(\eta^6\text{-}1,2\text{-}C_6H_4Me_2)[\eta^4\text{-}C_6Me_4(CH_2)_2]$ (5). $[Ru(1,2\text{-}C_6H_4Me_2)(C_6Me_6)](PF_6)_2$ (1.00 g, 1.52 mmol) and potassium *tert*-butoxide (0.68 g, 6.06 mmol) were weighed into a 50-mL round-bottom flask equipped with a magnetic stir bar, the flask was flushed with nitrogen, and 20 mL of dry THF was injected. The solution immediately turned yellow, and after the mixture was stirred at room temperature for about 15 min, the solvent was removed under vacuum, the yellow residue was extracted into pentane, and the solution was filtered through a Schlenk frit. The pentane was removed under vacuum, giving yellow solid *o*-xylylene complex. Attempts to recrystallize a high-purity sample of this complex from hydrocarbon solvents were unsuccessful; the solid precipitated as a powder rather than crystalline form. Attempts to purify the complex by sublimation at 0.03 mmHg vacuum with heating resulted in extensive decomposition. Proton NMR (C_6D_6): δ 5.10 (d, J = 1 Hz, 2 H), 4.71 (m, 2 H), 4.61 (d, J = 1 Hz, 2 H), 4.21 (m, 2 H), 1.78 (s, 6 H), 1.68 (s, 6 H), 1.59 (s, 6 H). IR (pentane): 1590 cm^{-1} (exo C=C). MS: *m/e* 368 (M^+). Anal. Calcd for $C_{20}H_{26}Ru$: C, 65.37; H, 7.13. Found: C, 63.97; H, 7.01.

$[Ru(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_6Me_5CH_2)]^+$ (PF_6^-, BPh_4^-, or $CF_3SO_3^-$ Salt) (8). A. From $[Ru(C_6Me_6)_2]^{2+}$. A THF solution of potassium *tert*-butoxide (120 mg, 1.1 mmol) was added dropwise to a 5-mL THF slurry of $[Ru(C_6Me_6)_2](PF_6)_2$ (761 mg, 1.1 mmol) with vigorous stirring. After addition of base, the solution was stirred for 2 h at room temperature. The THF was evaporated under vacuum. The resulting orange solid was dissolved in CH_2Cl_2, and the solution was filtered under nitrogen and reduced in volume. Excess hexane was added to precipitate the bright orange PF_6^- salt of the cyclohexadienyl complex. This was collected on a frit, rinsed with diethyl ether, and dried in air to give 388 mg (61%) of product. This material is of good purity by proton NMR, but can be metathesized to the microcrystalline BPh_4^- salt by addition of excess $NaBPh_4$ to an acetonitrile solution of the PF_6^- salt and precipitation of the product by addition of diethyl ether. NMR and elemental analysis data for this complex were previously reported.[6]

B. From 2. An acetonitrile slurry of 2 (30 mg, 0.071 mmol) was treated with CF_3SO_3H (6.3 μL, 0.071 mmol), and the solution stirred until all of the solid *o*-xylylene complex was consumed over a period of a few minutes. The yellow solution was filtered, excess $NaBPh_4$ was added, and the solution volume was reduced on a rotary evaporator. Dropwise addition of diethyl ether to the concentrated solution resulted in the formation of orange microcrystalline product as the tetraphenylborate salt, which was collected on a frit and rinsed with absolute ethanol and then diethyl ether. Alternatively, this reaction could be carried out and monitored in an NMR tube. Thus, 2 (5.0 mg, 0.012 mmol) was placed into an NMR tube and 0.5 mL of acetonitrile-d_3 was added. Trifluoromethanesulfonic acid (1.0 μL, 0.012 mmol) was injected into the solution, and the NMR tube was shaken lightly for a few minutes until 2 was consumed, forming a clear orange solution. The NMR spectrum of this solution indicated clean, quantitative formation of the cyclohexadienyl complex as the triflate salt.

C. From 3 and 2. Complex 2 (5.0 mg, 0.012 mmol) and $[Ru(C_6Me_6)_2](BF_4)_2$ (7.2 mg, 0.012 mmol) were placed into an NMR tube, and 0.5 mL of acetonitrile-d_3 was added. After a few minutes of shaking, insoluble yellow 2 was completely consumed and the solution became clear orange. The proton NMR spectrum of this solution indicated quantitative formation of the cyclohexadienyl complex (as the BF_4^- salt). No singlet due to dication 3 remained in the NMR spectrum.

$[Ru(C_6Me_6)(1,2\text{-}C_6Me_4Et_2)]^{2+}$ (PF_6^- or $CF_3SO_3^-$ Salt) (9). Complex 2 (5.0 mg, 0.012 mmol) was placed into an NMR tube, and 0.5 mL of pure distilled CF_3SO_3Me was added. After a few minutes of agitation, insoluble 2 was completely consumed. The NMR tube was placed into a Schlenk tube and evacuated, removing the excess methyl triflate and leaving pure diethylated complex in essentially quantitative yield as a white solid (as its triflate salt) as shown by the proton NMR spectrum in CD_3CN. Alternatively, a benzene solution of 2 was treated with an excess of methyl triflate under nitrogen and allowed to stir at room temperature overnight. The solution color initially turned red and then gradually turned colorless as a white precipitate formed. The solid diethylated complex was collected on a frit as the $CF_3SO_3^-$ salt and was crystallized from CH_3CN/Et_2O. Metathesis to the PF_6^- salt was carried out by dissolving the triflate salt into water, filtering the solution, and additing excess of NH_4PF_6 to the filtrate precipitate the white PF_6- salt, which was recrystallized from CH_3CN/EtOH. NMR and elemental analysis data for the bis(triflate) salt were previously reported.[6]

$Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6HMe_5CH_2)$ (10). Complex 2 (30.0 mg, 0.071 mmol) was placed into a Kontes reaction tube equipped with a magnetic stir bar and then 3 mL of dry heptane was added. The tube was degassed by the freeze–pump–thaw method and then placed under 26 psig of hydrogen pressure and heated to 150 °C in an oil bath with stirring for 3.5 h. After cooling of the solution to room temperature and venting the pressure, the solution was filtered in air and evacuated to give a light yellow residue of crude monohydrogenated complex 10 (19.7 mg, 65%). This solid was recrystallized from cold hexane, collecting the crystals in air. Proton NMR (C_6D_6): δ 4.75 (m, 1 H), 4.58 (m, 1 H), 1.77 (s, 18 H), 1.73 (s, 3 H), 1.65 (s, 3 H), 1.40 (s, 3 H), 1.19 (d, J = 6.6 Hz, 3 H), 1.19 (slightly broadened singlet, 3 H). MS: *m/e* 425 (M^+). IR (hexane): 1598 cm^{-1} (s, exo C=C). Anal. Calcd for $C_{24}H_{36}Ru$: C, 67.73; H, 8.53. Found: C, 67.90; H, 8.78.

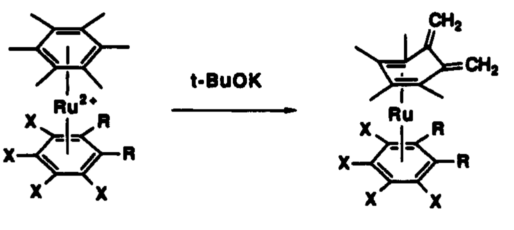
$Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}5,6\text{-}C_6Me_6H_2)$ (11). Complex 2 (50.0 mg, 0.118 mmol) and about 7 mg of 5% palladium on activated carbon were placed into a Kontes reaction tube, 5 mL of dry toluene was added, and the tube was degassed by the freeze–pump–thaw method. The tube was placed under 50 psig of hydrogen pressure and heated to 130 °C with stirring for 5 h. After the tube was cooled to room temperature and the pressure was vented, the solution was filtered in air and evacuated to obtain 27.2 mg (54%) of the hydrogenated product 11 as a white microcrystalline solid. The solid was purified by recrystallization from a cold concentrated hexane solution. Proton NMR (C_6D_6): δ 1.83 (s, 18 H), 1.70 (s, 6 H), 1.69 (m, 2 H), 1.21 (s, 6 H), 0.87 (apparent d of d, 6 H). MS: *m/e* 428 (M^+). Anal. Calcd for $C_{24}H_{38}Ru$: C, 67.41; H, 8.96. Found: C, 67.25; H, 8.62.

$Ru(\eta^6\text{-}C_6Me_6)[\eta^4,\eta^4\text{-}C_6Me_4(CH_2)_2]Fe(CO)_3$ (12). Freshly sublimed (trimethylamine)tetracarbonyliron (80.4 mg, 0.35 mmol) and 2 (50.0 mg, 0.118 mmol) were weighed into a Schlenk tube equipped with a magnetic stir bar and purged with nitrogen. A 5-mL volume of dry hexane was added, and the contents were stirred overnight at room temperature. An orange solid gradually precipitated from solution (see below). The red hexane solution was filtered under nitrogen, rinsing the red-brown insoluble residue with an additional portion of hexane. The clear red filtrate was evaporated under vacuum, and the resulting solid residue was warmed under vacuum to remove residual $Fe(CO)_4(NMe_3)$, leaving 6.4 mg (9.5%) of crude red tricarbonyliron complex 12. This product was recrystallized twice from cold hexane to give the pure complex as deep red prisms. Proton NMR (C_6D_6): δ 1.92 (s, 6 H), 1.85 (d, J = 3 Hz, 2 H), 1.62 (s, 18 H), 1.08 (s, 6 H), 0.05 (d, J = 3 Hz, 2 H). MS: *m/e* 564 (M^+). IR (hexane): 2022 (vs), 1959 (vs), 1945 cm^{-1} (vs). Anal. Calcd for $C_{27}H_{34}FeO_3Ru$: C, 57.55; H, 6.08. Found: C, 57.59; H, 6.18.

$\{\mu_2\text{-}[\eta^2,\eta^5\text{-}C_6Me_5(CH_2)]\}\{\mu_2\text{-}[\eta^1,\eta^6\text{-}C_6Me_5CH_2CO]\}Fe(CO)_3Ru$ (13). The orange solid collected above in the preparation of the tricarbonyliron complex was rinsed with hexane and then dissolved in warm toluene and precipitated by addition of hexane to give 26.0 mg (37%) of analytically pure plates after filtration in air and rinsing with hexane. Proton NMR (C_6D_6): δ 3.33 (s, 2 H), 1.74 (s, 6 H), 1.73 (s, 2 H), 1.23 (s, 6 H), 1.19 (s, 3 H), 1.14 (s, 3 H), 0.97 (s, 6 H), 0.87 (s, 6 H). MS: *m/e* 480 ($M^+ - 4CO$, parent ion not observed). IR (THF): 2005 (s), 1915 (s), 1890 (vs), 1635 cm^{-1} (w). Anal. Calcd for $C_{28}H_{34}FeO_4Ru$: C, 56.86; H, 5.79. Found: C, 56.64; H, 6.05.

$[Ru(C_6H_6)(1,2\text{-}C_6H_4Me_2)](PF_6)_2$ (7). $[RuCl_2(C_6H_6)]_2$ (0.50 g, 1.01 mmol) and anhydrous sublimed aluminum trichloride (0.60 g, 4.53 mmol) were weighed into a reaction vessel under nitrogen. A 20-mL volume of 1,2-dichloroethane, freshly distilled from CaH_2,

Scheme I



3: X=R=Me
4: X=H, R=Me

2: X=R=Me
5: X=H, R=Me

was injected into the reaction vessel and brought to reflux temperature with magnetic stirring. After about 20 min the aluminum trichloride had completely dissolved, and *o*-xylene, freshly distilled from CaH_2, was injected into the hot solution. A precipitate formed immediately in the dark solution, which was refluxed under nitrogen for 7 h and then cooled to room temperature and evaporated under vacuum to a light colored solid residue. Hexane (20 mL) and water (40 mL) were added, and the two phases were stirred vigorously to dissolve all soluble material. The phases were separated, and the aqueous layer was filtered through diatomaceous earth on a glass frit. Addition of NH_4PF_6 to the light green aqueous filtrate gave a white precipitate which was collected on a frit, rinsed with water and then diethyl ether, and dried in air to give 0.69 g (60%) of the crude white 7. The product was recrystallized by addition of ethanol to a concentrated acetonitrile solution to give microcrystalline product. Proton NMR (CD_3CN): δ 6.75 (s, 10 H), 2.45 (s, 6 H).

Deprotonation of $[Ru(C_6H_6)(1,2\text{-}C_6H_4Me_2)](PF_6)_2$. A THF solution (5 mL) of potassium *tert*-butoxide (0.16 g, 1.42 mmol) was added dropwise to a 5-mL THF slurry of 7 (0.20 g, 0.36 mmol) at minus 78 °C under nitrogen with magnetic stirring. The THF solution became yellow, and most of the insoluble cation appeared to be consumed. After 30 min the cold bath was removed and the solvent was removed under vacuum, leaving a bright yellow solid residue. This solid was extracted with dry hexane and collected on a frit under nitrogen. It was investigated for its solubility in a number of dry solvents and found to be insoluble in benzene, methylene chloride, acetonitrile, and DMSO. The solid appeared to be air sensitive.

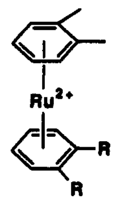
Deprotonation of $[Ru(1,2\text{-}C_6H_4Me_2)_2](PF_6)_2$.[11] Potassium *tert*-butoxide (0.20 g, 1.75 mmol) was weighed into a Schlenk tube and dissolved in 5 mL of dry THF under nitrogen; the solution was then cooled to −78 °C. A cooled THF slurry of $[Ru(1,2\text{-}C_6H_4Me_2)_2](PF_6)_2$[11] (0.26 g, 0.44 mmol) was cannulated in small portions into the cold butoxide solution, while stirring magnetically. The THF solution became bright yellow as the insoluble ruthenium dication was consumed. After 40 min at −78 °C, the solution was warmed to 0 °C and the solvent removed under vacuum to give a yellow residue. This residue was extracted into toluene and filtered through a Schlenk frit, and the bright yellow filtrate was evaporated under vacuum to give a light yellow powder. No additional purification was attempted. Proton NMR (C_6D_6): δ 4.86–4.62 (14 H, complex pattern), 3.53 (q AA′BB′, 2 H), 1.76 (s, 6 H). MS: *m/e* 312 (M^+), also ions observed at *m/e* 340, 355 and a large cluster around *m/e* 413, 467, and 511. An *m/2e* peak was not observed.

Results and Discussion

Synthesis of *o*-Xylylene Complexes. Treatment of a THF slurry of dication 3 with excess potassium *tert*-butoxide at −78 °C (Scheme I) gave bright yellow crystals of the neutral *o*-xylylene complex 2 after recrystallization from hexane. The crystals were moderately air stable and could be collected on a frit in air, dried, and stored under an atmosphere of dry nitrogen. The X-ray crystal structure of 2 has been reported elsewhere.[6]

Deprotonation of the mixed-sandwich complex 4 gave only the product 5 arising from double deprotonation of the hexamethylbenzene ligand (Scheme I), as indicated by the number of methyl group resonances in the proton NMR. The deprotonation of 4 to give preferentially the permethylated *o*-xylylene complex 5 rather than the product from deprotonation of coordinated *o*-xylene is not surprising in light of previous work with $[FeCp(arene)]^+$ systems in which deprotonated complexes were not stable when the arene ligand bears less than six methyls.[12] Complex 5 gave a ^1H NMR spectrum typical of a coordinated *o*-xylylene ligand but failed to give a satisfactory elemental analysis; 5 precipitated as a powder, and attempts to recrystallize a high-purity sample were unsuccessful.

Attempts to prepare a complex of the parent ligand 1 by deprotonation of $[Ru(o\text{-xylene})_2]^{2+}$ (6)[11] resulted in a complex mixture of products by proton NMR and mass spectral analysis, including a doubly deprotonated species which appeared to arise from one deprotonation of each *o*-xylene ligand. The mass spectrum also indicated higher molecular weight fragments, possibly arising from ligand coupling. The mixed-ligand complex $[Ru(benzene)(o\text{-xylene})]^{2+}$ (7) was prepared from $[RuCl_2(C_6H_6)]_2$, $AlCl_3$, and *o*-xylene in refluxing 1,2-dichloroethane according to a procedure previously reported[13] and gave a ^1H NMR spectrum characteristic of a bis(arene) dicationic complex.[9] Treatment of 7 with potassium *tert*-butoxide at −78 °C gave a yellow solution indicative of the neutral deprotonated products, but warming and attempted isolation gave only an insoluble yellow oxygen-sensitive powder. The attempted deprotonation of either 6 or 7, where no permethylated ring was available, demonstrates the instability of non-methylated bis(arene)ruthenium(0) systems. While the deprotonation of 7 may give a stable *o*-xylylene complex at low temperatures, additional experiments with this complex were not attempted.



6: R=Me
7: R=H

Protonation of 2. The chemical reactivity of 2 centers mainly on the exomethylene carbon atoms.[6] Scheme II shows the observed reactivity of the permethylated *o*-xylylene complex 2. The acid/base chemistry of the $[Ru(C_6Me_6)_2]^{2+}/[Ru(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_6Me_5CH_2)]^+$ system has been previously reported.[6] Complex 2 is unstable in protic solvents in which it is converted to $[Ru(C_6Me_6)_2]^{2+}$. Careful protonation of 2 with 1 equiv of CF_3SO_3H gave the cyclohexadienyl complex 8 very cleanly by proton NMR. Larger quantities of 8 were prepared by mono deprotonation of 3 with 1 equiv of potassium *tert*-butoxide. Interestingly, 2 behaves as a base and will abstract a proton from its dicationic precursor, $[Ru(C_6Me_6)_2]^{2+}$. Thus, when equimolar quantities of 2 and $[Ru(C_6Me_6)_2]^{2+}$ were placed together in acetonitrile-d_3, complete equilibration to the cyclohexadienyl complex 8 occurred within a few minutes. The failure of 8 to give a satisfactory elemental analysis as the BPh_4^- salt was attributed to some contamination from the triflate salt as a result of metathesis.[6] The ^1H

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[11] Prepared from $[RuCl_2(o\text{-xylene})]_2$ and $AgBF_4$ in the presence of excess *o*-xylene according to ref 9.

[12] Astruc, D.; Roman, E. E.; Hamon, J. R.; Batail, P. *J. Am. Chem. Soc.* **1979**, *101*, 2240.

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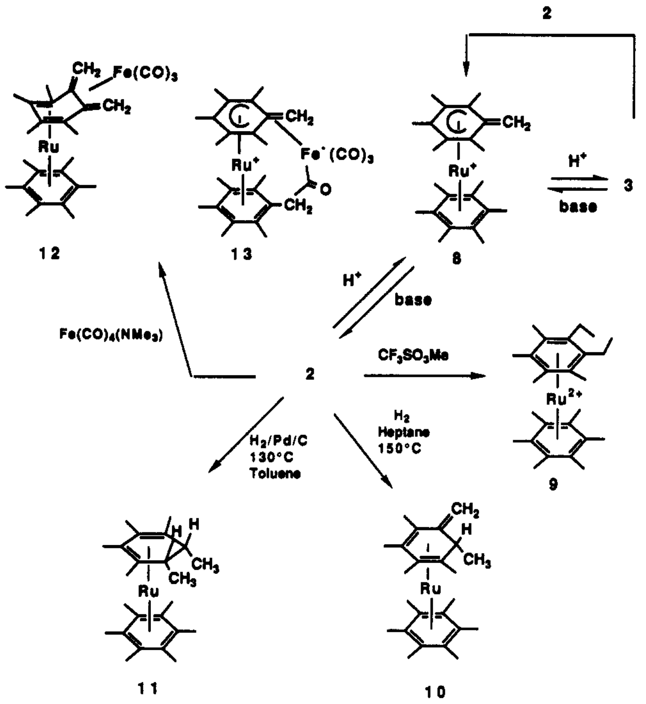
Scheme II

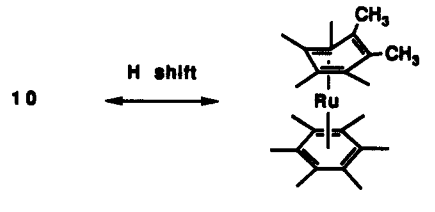


and ^{13}C NMR spectra of the cyclohexadienyl ligand of 8 were similar to those previously reported for the isoelectronic complexes $FeCp(\eta^5\text{-}C_6Me_5CH_2)$[14] and $Mn(\eta^5\text{-}C_6Me_5CH_2)(CO)_3$.[15] In all three of these complexes the characteristic unbound quaternary ring carbon of the cyclohexadienyl ligand gave a ^{13}C NMR signal around 145 ppm, and the exomethylene carbon gave a triplet in the undecoupled spectra around 85 ppm. The hydrogens bound to the exomethylene carbon atom gave a singlet in the ^1H NMR around 3.7 ppm in all three complexes.[6,14,15]

Alkylations. Both of the methylene groups in 2 were alkylated by the use of a strong alkylating agent such as $CF_3SO_3CH_3$. The dimethylated product 9 gave a proton NMR spectrum which confirmed that the two ethyl groups were adjacent to each other. This was not necessarily required, as the intermediate, analogous to 8, could undergo nondegenerate proton shifts on the same ring, or between the two rings, which would result in isomeric alkylated products. That the cyclohexadienyl analogue was formed was indicated by an intermediate color change from yellow to red during treatment of 2 in benzene with excess methyl triflate, with subsequent precipitation of white dicationic complex 9. The second alkylation occurred at a sufficient rate to give the 1,2-diethyl complex as a single product. The ditriflate salt of 9 failed to give a satisfactory elemental analysis[6] probably due to solvent contamination. Treatment of 2 with methyl iodide did not result in clean alkylation, giving instead products of uncertain composition. The triflate esters were found to be superior due to their strong alkylating capability, their nonoxidizing nature,[16] and the stable and nonnucleophilic trifluoromethanesulfonate counterion produced in the reaction.

Hydrogenations. Either one or both of the methylene double bonds of 2 were hydrogenated with hydrogen gas at higher temperatures in the presence of a catalyst. Treatment of 2 in heptane with 26 psig of hydrogen gas at 150 °C gave the monohydrogenated complex 10 in 65% yield. At this temperature, a small amount of thermal decomposition occurred which gave a black precipitate of ruthenium metal; this presumably served as the hydrogenation catalyst. When no black solid precipitated, no hydrogenation occurred. Treatment of 2 in toluene with 50 psig of hydrogen gas at 130 °C in the presence of a small amount of palladium on carbon gave the doubly hydrogenated complex 11 in 54% yield. The need for a catalyst in the hydrogenation reactions rules out intramolecular ruthenium-assisted hydrogen addition and lends support to the assigned stereochemistry of 10 and 11 involving addition of hydrogen from the distal side of the *o*-xylylene ligand. The 300-MHz proton NMR spectrum of the dihydrogenated complex 11 indicated that the two saturated methyl groups (formerly the methylene carbons of 2) are cis to one another, giving rise to a symmetrical double of doublets at 0.87 ppm, due to coupling from the *magnetically* nonequivalent methyls and methine protons. A decoupling experiment indicated the position of the methine protons as a multiplet at 1.69 ppm. Irradiation of this position caused the methyl doublet of doublet to collapse to a singlet. Though the NMR data indicate relative cis stereochemistry, they do not unequivocally prove the stereochemistry of the cyclohexadiene ligand. It would seem likely, however, that addition of hydrogen will occur readily from the unhindered distal side of the ligand, rather than from the coordinated, or proximal, side. This has been observed with the zinc–HCl hydrogenation of $[Rh(C_6Me_6)_2]^{2+}$, which gave the rhodium analogue of 11.[17]

Interestingly, the monohydrogenated complex 10 can be viewed as a tautomer of Fisher's η^4-bonded complex $Ru(C_6Me_6)_2$ (14).[18] The difference in stability of the two complexes is striking; 10 can be readily handled in air with no decomposition, while 14 is oxidized immediately in air. The unstable nature of 14 relative to its oxidized form is due to the bend aromatic ligand, confirmed by X-ray structure,[19] which can assume a normal planar η^6 structure upon two-electron oxidation. No such driving force exists for 10, which would require a 1,3-proton shift to revert to an aromatic system upon oxidation of the ruthenium center.



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Reactions with $Fe(CO)_4(NMe_3)$. Treatment of 2 with $Fe(CO)_4(NMe_3)$ gave the tricarbonyliron complex 12 as a minor product in only a 10% yield. The formulation of 12 was based on mass spectral and elemental analytical data. The parent ion was observed at *m/e* 564 in the mass spectrum. The IR spectrum of the carbonyl region showed three strong stretches at 2022, 1959, and 1945 cm^{-1}, characteristic of tricarbonyliron diene complexes.[20] As

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expected, upon coordination of a metal to the exocyclic diene of 2, an upfield shift of the methylene doublets was observed, appearing at δ 1.85 and 0.05 ppm (J = 3 Hz) for 12.[20] This complex demonstrates that the exomethylenes of coordinated *o*-xylylene ligand in 2 can behave as a conjugated diene system, as was observed in the X-ray crystal structure,[6] capable of π-bonding to a transition metal.

The major product precipitated from hexane as a dark orange solid, was sparingly soluble in benzene or toluene, appeared to be somewhat thermally unstable above room temperature, and could be recrystallized from toluene/hexane. The formulation of the structure was based on the mass spectrum, elemental analysis, and ^{1}H NMR spectrum. The parent ion was not observed in the mass spectrum, indicating thermal instability relative to loss of coordinated CO. The highest mass peak is due to the ion resulting from the loss of four carbon monoxides (m/e 480). The postulated structure for this product is 13, which contains an iron acylate "strap" connecting the two hexamethylbenzene ligands. The 300-MHz proton NMR spectrum was consistent with the existence of two dissimilar rings, giving four singlets for four different pairs of methyls and two singlets half as intense for two different single methyl groups. The exomethylene coordinated to the $Fe(CO)_3$ moiety appears as a singlet at 1.73 ppm, consistent with a vertical mirror plane of symmetry which includes the ruthenium and iron atoms, and indicates that this methylene is probably π-bound to the iron atom. The upfield shift of this resonance relative to the uncomplexed exomethylene was also consistent with this assignment. The infrared spectrum of the carbonyl region revealed a relatively high energy CO stretch at 2005 cm^{-1}, with two lower-energy stretches at 1915 and 1890 cm^{-1}, with the latter being the strongest intensity. A weak stretch at 1635 cm^{-1} was observed which was assigned to the acyl moiety of the complex. To satisfy the 18-electron rule, 13 is formally a zwitterion, with a positive charge residing on the ruthenium atom and a negative charge on the iron atom. While the proposed structure of 13 is unusual, iron complexes with coordination about iron similar to that postulated for 13 have been reported.[21] Interestingly, benzylic functionalization of the hexamethylbenzene ligand of 2 has occurred, but structure 13 lends no information as to which ring originated as the coordinated *o*-xylylene ligand of 2.

Other Reactions. Attempts to carry out cycloaddition reactions with the coordinated *o*-xylylene ligand in 2 failed to give Diels–Alder type products. Complex 2 was not compatible with electron-deficient olefins such as maleic anhydride or acrylonitrile. An apparent competing reaction appeared to be initial electron transfer from the metal complex to the olefin, with subsequent rapid olefin polymerization. In these reactions the ruthenium-containing product could not be readily identified and may have become incorporated into the polymerized material. It is noteworthy that 2 formed a red complex with maleic anhydride, even in the solid state, presumably due to a charge-transfer complex. Not surprisingly, electron-rich 2 did not undergo electron-transfer reactions with more electron-rich olefins such as ethyl vinyl ether or 3,3-dimethyl-1-butene, nor did 2 undergo cycloaddition reactions with these olefins, even at higher temperatures (140 °C) in a sealed tube for up to 3 days. Under these conditions, unreacted 2 was recovered, and some thermal decomposition was noted. The electron-transfer reaction represents a major drawback to the use of a coordinated *o*-xylylene complex such as 2 in attempting cycloaddition reactions with electron-poor olefins.

Attempts to displace coordinated *o*-xylylene ligand from 2 using trimethyl phosphite in refluxing hexane, or by irradiation in benzene or hexane, resulted only in the recovery of unreacted 2. Clearly the *o*-xylylene ligand is firmly bound to the ruthenium center and would require more forcing conditions for displacement.

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