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A Facile Route to 1-Trifluoromethyl-2,3,4,5-tetramethylcyclopentadienyl Ruthenium Half- and Mixed-Sandwich Compounds

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Summary: A series of half- and mixed-sandwich ($Cp^{\ddagger}$ = 1-trifluoromethyl-2,3,4,5-tetramethylcyclopentadienide) ruthenium compounds have been synthesized from a new $Cp^{\ddagger}Ru$ synthon, $[Cp^{\ddagger}Ru(NCCH_3)_3](PF_6)$. $[Cp^{\ddagger}Ru(NCCH_3)_3](PF_6)$ is efficiently generated by photolysis of $[Cp^{\ddagger}RuBz](PF_6)$ in acetonitrile with a quantum yield of approximately 0.34. The methods described here should be useful for the synthesis of other compounds that contain the $Cp^{\ddagger}Ru$ group.

Introduction

Ruthenium half-sandwich complexes with the auxiliary η^5-cyclopentadienide (Cp), η^5-pentamethylcyclopentadienide (Cp*), or other substituted η^5-cyclopentadienide ligands have been of interest because they give stable compounds with a wide range of ligands in the remaining three coordination sites.[1−14] Many of the CpRu and Cp*Ru compounds are catalytically active,[15] and they frequently have interesting electrochemical and spectroscopic properties.[4,6,7,10,16] It has also been observed that the differences in the Cp and Cp* ligands produce complexes with unique reactivity and properties through a combination of steric and electronic effects at the metal center.[17]

In 1992, Gassman, Mickelson, and Sowa introduced a new ligand, 1-trifluoromethyl-2,3,4,5-tetramethylcyclopentadienide ($Cp^{\ddagger}$), that is electronically similar to Cp,[18,19] but sterically similar to Cp*.[19] So far, only a few $Cp^{\ddagger}Ru$ compounds have been studied.[20−22] $Cp^{\ddagger}Ru(CO)_2I$ has allowed new $Cp^{\ddagger}Ru$ half-sandwich compounds to be prepared, but the possibilities are limited to complexes with at least one carbonyl ligand.[20] More recently, $[Cp^{\ddagger}RuCl_2]_2$, the $Cp^{\ddagger}$ analogue of $[Cp^{*}RuCl_2]_2$, was reported,[21] but its synthetic utility is somewhat limited[22] and the procedures involve multistep syntheses. The synthesis of more useful $Cp^{\ddagger}$ analogues of the Cp**Ru and CpRu synthons has been hampered by the instability of simple salts containing the $Cp^{\ddagger}$ anion.[19] It was clear that a new $Cp^{\ddagger}Ru$ synthon was required to produce a wider range of complexes for comparison with existing CpRu and Cp*Ru complexes. We chose as a target $[Cp^{\ddagger}Ru(NCCH_3)_3]^+$, an analogue of $[CpRu(NCCH_3)_3]^+$ [23−25] with high versatility for preparing sandwich and half-sandwich compounds under very mild reaction conditions. Other analogues of this reactant ($[Cp^{*}Ru(NCCH_3)_3]^+$ [25−28] and $[CpOs(NCCH_3)_3]^+$ [29,30]) have previously been developed. The synthesis of $[Cp^{\ddagger}Ru(NCCH_3)_3]^+$ and its initial development as a synthon for half-sandwich $Cp^{\ddagger}Ru$ complexes is reported herein.

Experimental Section

General Considerations. All reactions were carried out using standard Schlenk line techniques under a nitrogen or argon atmosphere. Solvents were supplied by Fisher Scientific

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or Mallinckrodt. Acetonitrile and dichloromethane were dried over P_2O_5 and distilled under nitrogen, hexanes and heptane were dried over 4 Å molecular sieves, and anhydrous diethyl ether and methanol were used as received. Ruthenium trichloride hydrate was supplied by Johnson Matthey, anhydrous ammonium hexafluorophosphate was supplied by Aldrich and was used as received, and 1-trifluoromethyl-2,3,4,5-tetramethylcyclopentadiene (HCp‡) was prepared by the literature method.[31] Triphenylphosphine was supplied by Aldrich and sublimed before use. Elemental analyses were carried out by MHW Laboratories, Phoenix, AZ. NMR spectra were obtained with Varian VI 300, VXR 300 (^{19}F and ^{31}P), or VI 500 spectrometers. ^{1}H spectra are referenced to the residual protons of the solvent which are referenced to TMS, ^{19}F spectra are referenced to $CFCl_3$ internal standard, and ^{31}P spectra are referenced to 80% phosphoric acid external standard. UV−vis absorption spectra were recorded with a Cary 17 or Tracor Northern 6500 system as noted. FT-IR spectra were obtained on a Nicolet Magna 550 with an attenuated total reflectance (ATR) cell; samples were deposited on the ATR ZnSe crystal from dichloromethane solution.

Materials. [Cp‡RuBz]Cl·1.25 H$_2$O. η^5-1-Trifluoromethyl-2,3,4,5-tetramethylcyclopentadienyl-η^6-benzene ruthenium chloride was synthesized through a multiple-step reaction, similar to Chaudret's method used for the analogous [Cp*Ru(arene)]$^+$ complexes.[32] A flask was charged with $RuCl_3 \cdot xH_2O$ (2.62 g, 10.0 mmol) and 200 mL of nitrogen-saturated methanol and was brought to reflux under a nitrogen atmosphere. A neat aliquot of HCp‡ (2.3 mL, 13 mmol) was added to the reddish orange mixture, which became more brown in color. This mixture was refluxed for 48 h and cooled, and granulated zinc metal (297 mg, 4.54 mmol) was added. Heating was reinitiated, and the reaction mixture turned purple. After 2 h, 50 mL of benzene was added and the mixture was allowed to reflux for an additional 36 h. The dark reddish brown reaction mixture was cooled, 50 mL of charcoal was added with stirring (15 min), and the mixture was filtered through Celite, to give a clear reddish orange filtrate. The filtrate was rotoevaporated to dryness, and the residue was triturated (3 × 100 mL of H$_2$O) and rotoevaporated to dryness again. The resulting residue was redissolved in 12 mL of acetonitrile and placed on a 2 × 20 cm column of neutral alumina. A green band moved with the solvent front and was discarded. Subsequently, a very pale yellow clear solution containing the product was eluted. A total of 5 L of acetonitrile was used to elute the product. The clear acetonitrile solution was rotoevaporated in an aluminum foil-covered flask to give 1.45 g (3.45 mmol) of pale yellow crude product (35% yield based on ruthenium). The crude product was recrystallized from wet acetonitrile and ether to give 1.42 g (99% recovery) of a hygroscopic white precipitate. A water peak observed in the ^{1}H NMR is consistent with the hygroscopic behavior observed in the combustion analysis. ^{1}H NMR (CDCl$_3$) (shift (ppm), multiplicity, J_{HH}, J_{HF}, integration): 6.29, s, 6H; 2.21, s, 6H; 2.18, q, $J_{HF} = 0.9$ Hz, 6H. ^{19}F NMR (CDCl$_3$): −55.79, s. Anal. Calcd for [Cp‡RuBz]Cl·1.25 H$_2$O: C, 45.07; H, 4.85; F, 13.39. Found: C, 45.09; H, 4.72; F, 13.40.

[Cp‡RuBz](PF$_6$).[21a] A solution of NH$_4$(PF$_6$) (1.50 g, 9.20 mmol) in 2 mL of H$_2$O was added to a solution of [Cp‡RuBz]Cl (1.19 g, 2.95 mmol) in a minimal amount (<5 mL) of H$_2$O filtered through Celite. The resulting white precipitate of [Cp‡RuBz](PF$_6$) (1.45 g, 2.82 mmol) was collected (96% yield). ^{1}H NMR (CD$_2$Cl$_2$) (shift (ppm), multiplicity, J_{HH}, J_{HF}, integration): 6.02, s, 6H; 2.15, q, $J_{HF} = 1.2$ Hz, 6H; 2.09, s, 6H. Anal. Calcd for [Cp‡RuBz](PF$_6$): C, 37.44; H, 3.53; F, 33.31. Found: C, 37.31; H, 3.63; F, 33.18.

[Cp‡Ru(NCCH$_3$)$_3$](PF$_6$). A solution of [Cp‡Ru(Bz)](PF$_6$) (1.35 g, 2.63 mmol) in 350 mL of freshly distilled acetonitrile was placed in a quartz photochemical reaction well. The clear solution was purged with nitrogen for 20 min prior to and during the photolysis. Light for the photolysis was provided by a 400 W medium-pressure mercury lamp (converted Sylvania type H33 street lamp). After 2 h of photolysis at 10 ± 5 °C, the reaction was determined to be complete by ^{1}H NMR. The solvent was removed from the amber solution in vacuo to give 1.25 g (2.23 mmol, 85% yield) of the bright orange "tris" complex. ^{1}H NMR (CD$_2$Cl$_2$) (shift (ppm), multiplicity, J_{HH}, J_{HF}, integration): 2.40, s, 9H; 1.72, q, J_{HF} 0.9 Hz, 6H; 1.68, s, 6H. ^{19}F NMR (CD$_2$Cl$_2$) (shift (ppm), multiplicity, J_{HF}, integration): −52.92, q, CF$_3$, J_{HF} 0.8 Hz; −73.13, PF$_6$, d, J_{PF} 710 Hz. Anal. Calcd for [Cp‡Ru(NCCH$_3$)$_3$](PF$_6$): C, 34.42; H, 3.79; N, 7.53; F, 30.62. Found: C, 34.14; H, 3.94; N, 7.40; F, 30.48.

[Cp‡Ru(C$_{10}$H$_8$)](PF$_6$). Solid [Cp‡Ru(NCCH$_3$)$_3$](PF$_6$) (78 mg, 0.14 mmol) and naphthalene (29.7 mg, 0.23 mmol) were placed in a 50 mL round-bottom flask. The flask was evacuated and backfilled with Ar three times. The flask was protected from light with aluminum foil, and 7 mL of freshly distilled dichloromethane was added under positive pressure of argon. The resulting solution was allowed to stir for 36 h, at which time it was determined to be complete by ^{1}H NMR. To precipitate the product, 40 mL (dried over sieves) of degassed hexanes was added to the reaction mixture. The product was filtered and washed with a 12 mL of a 5:1 mixture of hexanes and dichloromethane. The microcrystalline cream-colored product was dried in vacuo to give 59 mg (0.10 mmol, 69% yield). ^{1}H NMR (CD$_2$Cl$_2$) (shift (ppm), multiplicity, J_{HH}, integration): 7.81 (dd, 2.0 H), J_{HH} 6.9 Hz, J_{HH} 3.3 Hz; 7.59 (dd, 2.0H) J_{HH} 6.9 Hz, J_{HH} 3.3 Hz; 7.59 (dd, 2.0H) J_{HH} 6.9 Hz, J_{HH} 3.3 Hz; 6.69 (dd, 2.0H) J_{HH} 4.5 Hz, J_{HH} 2.4 Hz; 6.18 (dd, 2.0H) J_{HH} 4.5 Hz, J_{HH} 2.4 Hz; 1.75 (q, 6.0H) J_{HF} 1.2 Hz; 1.72 (s, 6.0H) J_{HF} 1.2 Hz. ^{19}F NMR (CD$_2$Cl$_2$): −54.79 (unresolved m), CF$_3$; −72.68, PF$_6$, (d), J_{PF} 711 Hz. Anal. Calcd for [Cp‡Ru(C$_{10}$H$_8$)](PF$_6$): C, 42.64; H, 3.58.; F, 30.35. Found: C, 42.47; H, 3.79; F, 30.13.

[Cp‡Ru(NCCH$_3$)$_2$(PPh$_3$)](PF$_6$). Solid [Cp‡Ru(NCCH$_3$)$_3$](PF$_6$) (46 mg, 0.082 mmol) and triphenylphosphine (93 mg, 0.36 mmol) were placed in a 50 mL round-bottom flask. The flask was evacuated and backfilled with Ar three times. To dissolve the reactants, 7 mL of freshly distilled dichloromethane was added under positive pressure of argon. The resulting solution was allowed to stir for 12 h, after which it was determined to be complete by proton NMR. Addition of 20 mL of hexanes produced a yellow oil, which clung to the sides of the flask from which the solvent was decanted. Redissolving the yellow film in 2 mL of dichloromethane and adding 25 mL of hexanes precipitated the product as a pale yellow powder (58 mg). The product was recrystallized one additional time from dichloromethane and hexanes to give microcrystalline material, which was dried in vacuo to give 39.2 mg (0.050 mmol, 62% yield). ^{1}H NMR (CD$_2$Cl$_2$) (shift (ppm), multiplicity, J_{HH}, integration): 7.5 (m, 15.0 H)*; 2.35 (d, 6.0H) J_{HP} 1.5 Hz; 1.66 (dq, 6.0H) J_{HP} 1.2 Hz, J_{HF} 1.2 Hz;1.36 (d, 6.0H) J_{HP} 1.2 Hz. ^{19}F NMR (CD$_2$Cl$_2$): −51.6 (d of unresolved m)*, CF$_3$, J_{FP} 4.5 Hz; −71.5 (d), PF$_6$, J_{PF} 708 Hz. ^{31}P NMR (CD$_2$Cl$_2$): 47.17 (unresolved m), PF$_6$; −142.75 (septet), J_{PF} 708 Hz. Anal. Calcd for [Cp‡Ru(NCCH$_3$)$_2$(PPh$_3$)](PF$_6$): C, 49.30; H, 4.27; N, 3.59. Found: C, 49.40; H, 4.37; N, 3.42.

[Cp‡Ru(NCCH$_3$)$_2$(CO)](PF$_6$). Freshly distilled dichloromethane (7 mL) was added to a 50 mL round-bottom flask containing [Cp‡Ru(NCCH$_3$)$_3$](PF$_6$) (253 mg, 0.453 mmol) to produce an orange solution. This solution was purged with carbon monoxide for 50 min, resulting in a more yellow solution. Upon layering with hexanes, the product crystallized as yellow needles that were filtered and dried in vacuo to give 48 mg (0.088 mmol, 70% yield). Several preparations of this

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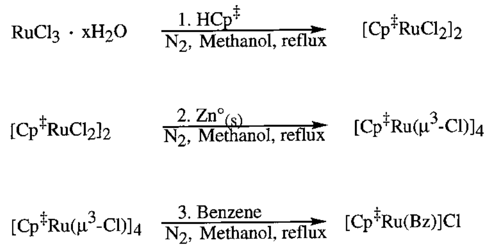
Scheme 1. Synthesis of [Cp‡Ru(Bz)]Cl



compound gave consistently low fluorine analyses. ^{1}H NMR (CD_2Cl_2) (shift (ppm), multiplicity, J_{HH}, integration): 2.48 (s, 6.0H); 1.96 (q, 6.0H) J_{HF} 1.2 Hz; 1.86 (s, 6.0 H). ^{19}F NMR (CD_2Cl_2): −54.2 (unresolved m); −73.1 (d), J_{PF} 711 Hz. IR: ν(CO), 2012 cm^{-1}. Anal. Calcd for [Cp‡Ru($NCCH_3$)$_2$(CO)](PF_6): C, 33.04; H, 3.33; F, 31.35. Found: C, 33.15; H, 3.19; F, 29.88.

CpCp‡Ru. Freshly distilled acetonitrile (5 mL) was added to a 50 mL round-bottom flask containing [Cp‡Ru($NCCH_3$)$_3$](PF_6) (253 mg, 0.453 mmol) to produce an orange solution. A solution of LiCp (110 mg, 1.53 mmol) in 20 mL of CH_3CN was added by cannula, and the orange solution became slightly lighter in color. After 4 h, the reaction was determined to be complete and the solvent was removed under vacuum. The residue was triturated with 3 × 25 mL of diethyl ether. The triturate was filtered through 1 cm activated alumina and rotoevaporated to dryness, yielding 141 mg (0.397 mmol, 88% yield) of the pale yellow microcrystalline mixed ruthenocene product. ^{1}H NMR (CD_2Cl_2) (shift (ppm), multiplicity, J_{HH}, integration): 4.18 (s, 5.0 H); 2.03 (q, 6.0H) J_{HF} 1.2 Hz; 1.98 (s, 6.0H). Anal. Calcd for CpCp‡Ru: C, 50.70; H, 4.82; F, 16.04. Found: C, 50.55; H, 5.01; F, 15.89.

Thermal Ligand Exchange of [Cp‡RuBz]$^{+}$. No exchange of the coordinated benzene ring with acetonitrile was observed in the absence of light during the purification processes of [Cp‡RuBz]Cl and [Cp‡RuBz](PF_6) at temperatures that ranged between 25 and 50 °C. In separate experiments, specifically designed to investigate thermal arene replacement, a solution of [Cp‡RuBz](PF_6) in acetonitrile was stored at room temperature in the dark for 12 days. No decomposition of [Cp‡RuBz](PF_6) or formation of [Cp‡Ru($NCCH_3$)$_3$](PF_6) was observed. A room-temperature solution of [Cp‡RuBz](PF_6) and toluene in CD_2Cl_2 showed no arene exchange after 3 days.

Determination of Relative Quantum Yields. The relative quantum yield for the formation of [Cp‡Ru($NCCD_3$)$_3$](PF_6) from [Cp‡RuBz](PF_6) in acetonitrile-d_3 solution was estimated by comparing the percent conversion with time for this reaction and the analogous reactions with [CpRuBz](PF_6) and [Cp*RuBz](PF_6) by ^{1}H NMR. A solution of [Cp‡RuBz](PF_6) (0.0751 M, 13.5 mg, 0.0263 mmol, in 0.35 mL of CD_3CN), a solution of [CpRuBz](PF_6) (0.0747 M, 10.2 mg, 0.0262 mmol, in 0.35 mL of CD_3CN), and a solution of [Cp*RuBz](PF_6) (0.0759 M, 12.2 mg, 0.0266 mmol, in 0.35 mL of CD_3CN) were prepared and photolyzed in 4 mm quartz NMR tubes with the unfiltered output of a 100 W Hg lamp (USHIO 2D). The reactions were monitored by comparing the integration of the free benzene resonance (7.2 ppm) with the bound η^{6}-benzene peak at ~6 ppm. Between acquisitions of ^{1}H NMR spectra, the NMR tubes were protected from adventitious light.

Results and Discussion

When we started this work, no synthesis of [Cp‡RuBz]$^{+}$ was available, so we fashioned one (Scheme 1) after Chaudret's [Cp*Ru(arene)]$^{+}$ synthesis[32] that uses the [Cp*$RuCl_2$]$_2$ dimer. During the course of our work, a synthesis of the [Cp‡RuBz]$^{+}$ precursor from isolated [Cp‡$RuCl_2$]$_2$ was published.[21] In our hands, the isolation and purification of [Cp‡$RuCl_2$]$_2$ was problematic, so we generated and then reduced this compound in situ with zinc metal. We observe that the zinc reduction in Scheme 1 produces a blue air-sensitive intermediate, characteristic of mixed valence Ru(III)−Ru(II) compounds[18] and eventually the tetramer, [Cp‡RuCl]$_4$, the analogue of [Cp*RuCl]$_4$.[26] Addition of benzene to this mixture in step 3 leads to the formation of [Cp‡RuBz]Cl, which was readily isolated and separated from side products. Metathesis to the PF_6^- salt in water gives the mixed-sandwich complex as a water-insoluble white powder that may be recrystallized from dichloromethane/hexane.

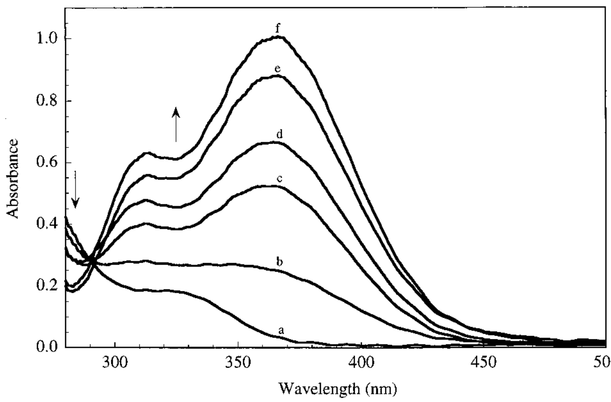
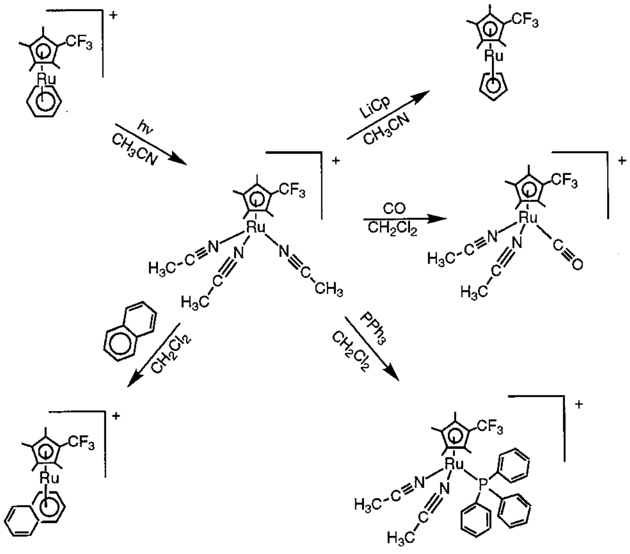


Figure 1. UV−vis absorbance changes during the photolysis of a 9.69 × 10^{-4} M solution of [Cp‡Ru(Bz)](PF_6) in acetonitrile with the unfiltered output of a 75 W xenon lamp (Osram XBO 75/2). The spectra were collected with a Tracor Northern 6500 diode array UV−vis spectrometer: (a), $t = 0$; (b) $t = 2.5$ min; (c) $t = 7.5$ min; (d) $t = 12.5$ min; (e) $t = 20$ min; (f) $t = 65$ min.

Scheme 2. Synthesis of [Cp‡Ru($NCCH_3$)$_3$]$^{+}$ and a Few Reactions Demonstrating Its Synthetic Utility



[Cp‡RuBz](PF_6) is inert to thermal arene bond cleavage as previously observed for [Cp*RuBz](PF_6) and [CpRuBz](PF_6). No arene exchange or replacement was observed in thermal control reactions; however, the photolysis of [Cp‡RuBz](PF_6) in acetonitrile to give the tris(acetonitrile) complex (step 1, Scheme 2) is facile and convenient. Figure 1 shows the progression of the photolysis monitored by UV−vis absorption spectroscopy. Clean conversion of the benzene complex to the tris(acetonitrile) complex, without the formation of an intermediate species, is indicated by the isosbestic

Table 1. Room-Temperature Electronic Spectra[a] of $[Cp^xRu(NCCH_3)_3](PF_6)$ and $[Cp^xRuBz](PF_6)$ Complexes in Acetonitrile

compound	λ(nm) ((ϵ(M^{-1} cm^{-1}))
$[CpRuBz](PF_6)$	320(136)
$[Cp^‡RuBz](PF_6)$	321(190)[b]
$[Cp^*RuBz](PF_6)$	321(221)[c]
$[CpRu(NCCH_3)_3](PF_6)$	309(860); 365(1071)
$[Cp^‡Ru(NCCH_3)_3](PF_6)$	310(784); 364(1074)[b]
$[Cp^*Ru(NCCH_3)_3](PF_6)$	317(870); 370(1287)[c]

[a] Recorded on a Cary 17 UV−vis spectrophotometer. [b] Reference 24. [c] Reference 27.

changes in the UV−vis absorption spectrum. The colorless solution gradually turns orange as $[Cp^‡Ru(NCCH_3)_3]^+$ is formed. The UV absorption peak (λ_{max} at 321 nm) decreases in intensity, while peaks at 364 and 310 nm increase as the orange product is formed. The conversion is quantitative in dry acetonitrile under a dry nitrogen atmosphere. Removal of the solvent in vacuo leaves essentially pure $[Cp^‡Ru(NCCH_3)_3](PF_6)$, which may be purified further by column chromatography. Scale-up of this general photolysis procedure to gram quantities results in excellent isolated yields.

UV−vis spectral data for $[Cp^‡RuBz](PF_6)$ and $[Cp^‡Ru(NCCH_3)_3](PF_6)$ are compared in Table 1 with data for the Cp and Cp* analogues. The close agreement of the values for the respective analogues is striking and is in agreement with the previously reported similarity in the electronic influence of Cp‡ and Cp in other ruthenium complexes.[18]

Another comparison that is of synthetic importance is the quantum yield for the production of $[Cp^‡Ru(NCCH_3)_3](PF_6)$ relative to the Cp and Cp* analogues. The photolyses of nearly equimolar solutions (vide supra) of $[CpRuBz](PF_6)$, $[Cp^‡RuBz](PF_6)$, and $[Cp^*RuBz](PF_6)$ were followed by ^1H NMR. The data collected gave percent conversion vs time plots shown in the Supporting Information. The relative percentage of conversion at a given time indicates that the quantum yield, Φ, is similar for the CpRu ($\Phi = 0.34$)[24,28] and Cp‡Ru analogues, which are larger than the Cp*Ru complex ($\Phi = 0.19$).[27] The curvature in the plots is due to the large inner-filter effect that has been noted previously.[24,29] Again the Cp‡ result is in close agreement with the Cp result, in line with the electronic, rather than steric control of the photochemical arene ring displacement.[24−28]

The synthetic utility of $[Cp^‡Ru(NCCH_3)_3]^+$ as a new Cp‡Ru synthon is demonstrated by the synthesis of a few new half- and mixed-sandwich compounds under very mild conditions (Scheme 2). The products were similar to those formed from the analogous $[CpRu(NCCH_3)_3]^+$,[22−25] $[Cp^*Ru(NCCH_3)_3]^+$,[25−28] and $[CpOs(NCCH_3)_3]^+$ [29,30] reactions under similar conditions, but generally the Cp‡Ru compounds have higher solubilities than the Cp or Cp* analogues. $[Cp^‡Ru(NCCH_3)_3]^+$ cleanly substitutes one acetonitrile ligand to form the bis(acetonitrile) monocarbonyl compound in dichloromethane solutions bubbled with carbon monoxide at atmospheric pressure and ambient temperature. Reaction with triphenyl phosphine in dichloromethane at room temperature yields the mono(triphenylphosphine) bis(acetonitrile) complex exclusively. Reaction of the tris(acetonitrile) compound with LiCp or with naphthalene in acetonitrile solution yields the neutral mixed ring ruthenocene and the η^6-naphthalene complex, respectively. All of the products reported here were characterized by ^1H and ^{19}F NMR, satisfactory elemental analyses, and, when appropriate, FT-IR spectroscopy and ^{31}P NMR spectrosopy. The salient feature of the ^1H NMR spectra of these compounds is the observation of two signals for the Cp‡ resonance, a singlet and a quartet; each peak integrated for six protons. The quartet is assigned to the methyl protons in the 2 position next to the CF_3 group with a J_{HF} coupling constant in the range 0.8−1.2 Hz for all the compounds investigated.

Conclusions

We have synthesized a new compound, $[Cp^‡Ru(NCCH_3)_3](PF_6)$, that functions as an effective synthon for the Cp‡Ru moiety. $[Cp^‡Ru(NCCH_3)_3](PF_6)$ is efficiently generated by photolysis of $[Cp^‡RuBz](PF_6)$ in acetonitrile with a quantum yield similar to one obtained previously for the Cp analogue. The utility of the new synthon is illustrated by the synthesis of several new open-face and mixed-sandwich ruthenium compounds under very mild conditions (room temperature/atmospheric pressure). The methods described here should be useful for the further development of synthetic chemistry designed to incorporate the Cp‡Ru group into other molecules of interest.

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Supporting Information Available: Plots of percent conversion vs time for the photolysis of $[CpRuBz](PF_6)$, $[Cp^‡RuBz](PF_6)$, and $[Cp^*RuBz](PF_6)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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