Synthesis and Reactivity of Cp*Ru^{II} η^6-π-Adducts of Functionalized Arenes with Useful Side Chains: X-ray Molecular Structure of [Cp*Ru(η^6-*N*-succinimidyl 3-(4-methoxyphenyl)propionate)][CF_3SO_3]

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Several novel organoruthenium complexes [Cp*Ru(η^6-arene)][CF_3SO_3] (**3**, **4**, **6**) were prepared in which the arene unit possesses an alkyl chain terminated with carboxylic acid, ester, and activated ester functions. These compounds were fully characterized by spectroscopic methods, and in particular, the activated ester complex [Cp*Ru(η^6-$MeOC_6H_4(CH_2)_2$-COONS)][CF_3SO_3] (**6**) (NS = *N*-succinimidyl) was identified by X-ray analysis. The reactivity of **6** with respect to benzylamine and β-alanine ethyl ester was examined and afforded quantitatively the stable conjugates [Cp*Ru(η^6-$MeOC_6H_4CH_2CH_2CONHCH_2Ph$][$CF_3SO_3$] (**7**) and [Cp*Ru($\eta^6$-$MeOC_6H_4(CH_2)_2CONH(CH_2)_2COOEt$][$CF_3SO_3$] (**8**). Furthermore, the stability and reactivity of **6** relative to the analogous dicationic organoiridium complex [Cp*Ir(η^6-$MeOC_6H_4(CH_2)_2COONS$)][BF_4]$_2$ (**10**) and the neutral metallocarbonyl derivatives of the type [L_nMCpCOONS] (**12**−**14**) [L_nM = Fe(CO)$_2$Me, Mo(CO)$_3$Me, Co(CO)$_2$] are presented and discussed.

Introduction

The use of (pentamethylcyclopentadienyl)metal fragments to form stable complexes in coordination chemistry is a widely documented area.[1] Recently these species [Cp*M] (M = Rh, Ir, Ru) have been employed as organometallic synthons to bind amino acids[2] or amino acid derivatives,[2a] prompted by the roles of metals in biochemistry and amino acids in producing chiral catalysts.[3,4] Further it has been shown that organometallic complexes of the type [Cp*(Cl)Rh-{peptide−OR−H$^+$}] exhibit chiral centers both at the α-carbon in the ligand and at the metal and possess considerable potential for the enantioselective synthesis of peptides.[5] On the other hand, the presence of the organometallic moiety [Cp*M] helped to bring about the crystallization of the modified amino acid or amino acid derivatives; for instance, Grotjahn and co-workers have isolated and determined the X-ray molecular structures of the stable conjugates [Cp*Ir(*N*-tosylglycine)] and [Cp*Ir(*N*-tosylphenylglycine)].[2a,6]

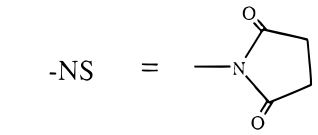
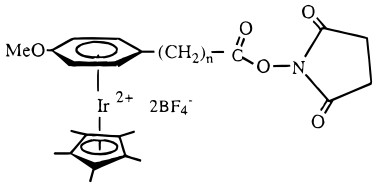


Figure 1.



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n = 1, 2, 3

Figure 2.

We reported previously the preparation of a series of organometallic succinimidyl esters (see Figure 2) in which a [Cp*Ir] unit is coordinated at the arene possessing an alkyl chain terminated by a succinimidyl ester moiety.[7] Such derivatives can be regarded as Bolton−Hunter reagents, in which the aryl ring bears a [Cp*Ir] moiety. The use of such derivatives for selective labeling of amino acids in peptides has proved to be a valuable method. Unfortunately these dicationic iridium derivatives showed signs of decomposition even in the solid state. Thus we focused our efforts to prepare the analogous monocationic complex but using the [Cp*Ru] unit.

In this paper we describe the high-yield synthesis of [Cp*Ru(η^6-$MeOC_6H_4(CH_2)_2COONS$)][CF_3SO_3] (**6**) as well as its X-ray molecular structure. Two general synthetic routes were followed to attain our objective: (a) preparation of the organometallic carboxylic acid [Cp*Ru(η^6-

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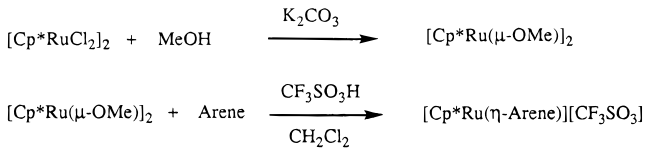
Scheme 1



$MeOC_6H_4(CH_2)_2COOH][CF_3SO_3]$ (**3**) followed by attempted esterification with *N*-hydroxysuccinimide in the presence of dicyclohexyldiimide (DCC); (b) direct complexation of of the succinimidyl ester $MeOC_6H_4(CH_2)_2$-COONS (**5**) by Cp*Ru. Method b turned out to be more convenient to attain our goal.

Finally the reactivity of $[Cp^*Ru(\eta^6\text{-}MeOC_6H_4(CH_2)_2$-$COONS)][CF_3SO_3]$ (**6**) with benzylamine and β-alanine ethyl ester was investigated and afforded the corresponding stable adducts $[Cp^*Ru(\eta^6\text{-}MeOC_6H_4CH_2CH_2$-$CONHCH_2Ph][CF_3SO_3]$ (**7**) and $[Cp^*Ru(\eta^6\text{-}MeOC_6H_4$-$(CH_2)_2CONH(CH_2)_2COOEt][CF_3SO_3]$ (**8**). The stability and reactivity of **6** was compared to those of the analogous dicationic iridium derivative $[Cp^*Ir(\eta^6\text{-}MeOC_6H_4$-$(CH_2)_2COONS)][BF_4]_2$ (**10**) and the neutral metallocarbonyl succinimidyl derivatives $[L_nMCpCOONS]$ (**12**−**14**) [L_nM = $Fe(CO)_2Me$, $Mo(CO)_3Me$, $Co(CO)_2$].

Results and Discussion

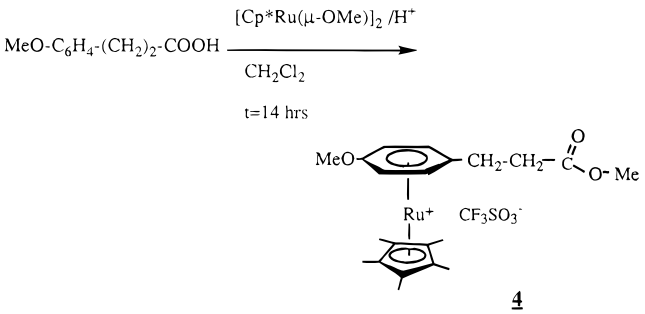
The organometallic fragment "Cp*Ru" is a very strong areneophile and often forms compounds which are stable in the solid state. There are several methods to introduce a Cp*Ru unit to an arene: (i) Reflux of isolobal $[Cp^*Ru(CH_3CN)_3][CF_3SO_3]$ with an arene affords the desired $[Cp^*Ru\text{-}\pi\text{-arene}][CF_3SO_3]$.[8] (ii) Reduction of $[Cp^*RuCl_2]_2$ with zinc powder followed by addition of the arene in the presence of KPF_6 also gives the corresponding π-arene complexes of ruthenium(II).[9] (iii) Preparation of $[Cp^*Ru(\mu\text{-OMe})]_2$ followed by addition of CF_3SO_3H in CH_2Cl_2 in the presence of the arene affords the Cp*Ru-complexed arenes as shown in (Scheme 1).[10]

We have found that method iii was the most convenient to prepare our compounds, since this type of arene possesses functional groups such as an ester, an activated ester, and carboxylic chains which hydrolyze easily.

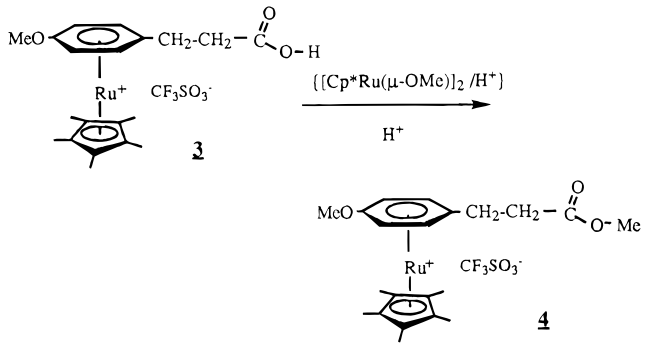
(a) Reaction of $[Cp^*Ru(\mu\text{-OMe})]_2$ (1) with MeO-$C_6H_4(CH_2)_2COOH$ (2). Treatment of $[Cp^*Ru(\mu\text{-OMe})]_2$ (**1**) with 3-(4-methoxyphenyl)propanoic acid (**2**) in CH_2Cl_2 and in the presence of CF_3SO_3H for 14 h afforded unexpectedly the methyl ester adduct $[Cp^*Ru(\eta^6\text{-}MeOC_6H_4(CH_2)_2COOMe][CF_3SO_3]$ (**4**) see Scheme 2.

Complex **4** was identified by spectroscopic methods: The ^{1}H-NMR spectrum recorded in CD_3CN showed the presence of a pair of doublets for the π-complexed arene in the range of 5.5−6.0 ppm and a multiplet attributed to the ethylene chain ($-CH_2CH_2-$) at 2.58 ppm. Further we note the presence of two singlets at 3.72 and 3.60 ppm attributed to the MeO− groups of the phenyl and that of the ester function. The ^{13}C-NMR also confirms the formation of **4** (see Experimental Section),

Scheme 2



Scheme 3



and in particular the presence of a singlet at 52.35 ppm is attributed to the methyl group of the ester function.

Esterification of carboxylic acids by MeOH in the presence of acidic medium (H^+) as catalyst is a well-known process.[11] We feel that the formation of **4** results from the esterification of the organometallic carboxylic acid intermediate $[Cp^*Ru(\eta^6\text{-}MeOC_6H_4(CH_2)_2COOH]$-$[CF_3SO_3]$ (**3**) mediated by the couple $[Cp^*Ru(\mu\text{-OMe})]_2$/$H^+$ as a source of MeOH unit and catalyzed by the acidic medium (CF_3SO_3H) (see Scheme 3). Another explanation[13] could be that several equivalents of MeOH remained in the crude $[Cp^*Ru(\mu\text{-OMe})]_2$ (**1**) obtained after solvent removal, and this explains the successful esterification of the carboxylic acid intermediate $[Cp^*Ru$-$(\eta^6\text{-}MeOC_6H_4(CH_2)_2COOH][CF_3SO_3]$ (**3**).

In order to isolate the organometallic carboxylic acid intermediate **3**, we repeated the previous experiment, but the reaction mixture was stirred for only 30 min. Reaction workup afforded a dark brown precipitate identified as $[Cp^*Ru(\eta^6\text{-}MeOC_6H_4(CH_2)_2COOH][CF_3$-$SO_3]$ (**3**), while the supernatant phase gave a mixture of the carboxylic acid adduct **3** and the corresponding methyl ester derivative $[Cp^*Ru(\eta^6\text{-}MeOC_6H_4(CH_2)_2$-$COOMe][CF_3SO_3]$ (**4**). The ^{1}H-NMR spectrum of **3** recorded in $(CD_3)_2CO$ exhibits the usual pair of doublets for the arene in the area 5.4−6.1 ppm downfield relative to the free ligand and we also note the presence of a broad peak at 5.5 ppm attributed to the hydroxyl unit of the carboxylic function.

It has been reported previously that treatment of $[Cp^*Ru(\mu\text{-OMe})]_2$ (**1**) with benzoic acid gave the benzoate zwitterion species [Cp*Ru(PhCOO)]. When the previous reaction was repeated in the presence of CF_3SO_3H, the corresponding organometallic benzoic acid was obtained

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(13) We appreciate the insight of a reviewer who pointed this out.

[Cp*Ru(PhCOOH)][CF_3SO_3]. These compounds were identified by spectroscopic methods, and the X-ray molecular structure of [Cp*Ru(PhCOO)] was reported and found to be disordered. The disorder in the structure of the latter was attributed to the presence of the corresponding methyl ester derivative [Cp*Ru(PhCOOMe)][CF_3SO_3] with an occupancy factor of 30%. The authors suggested the esterification of the benzoato-adduct [Cp*Ru(PhCOO)] during the reaction course.[12]

In order to attain our target compound [Cp*Ru(η^6-$MeOC_6H_4(CH_2)_2COONS$)][CF_3SO_3] (**6**) we attempted to treat the crude mixture of [Cp*Ru(η^6-$MeOC_6H_4(CH_2)_2$-$COOH$][CF_3SO_3] (**3**)/[Cp*Ru(η^6-$MeOC_6H_4(CH_2)_2COOMe$] (**4**) by *N*-hydroxysuccinimide (NHS) in the presence of dicyclohexyldiimide (DCC) in THF for 12 h. Analysis of the reaction mixture by ^{1}H-NMR suggested the formation of our desired product but in low yield (10% by integration) while the major compounds were the starting materials. Further, we found that separation of these cationic species is a difficult task and time consuming, so we decided to attain our target complex by first preparing the organic *N*-hydroxysuccinimide ester species $MeOC_6H_4(CH_2)_2COONS$ (**5**) and then in a second step to treat it with [Cp*Ru(μ-OMe)]$_2$ (**1**) in the presence of CF_3SO_3H.

(b) Reaction of [Cp*Ru(OMe)]$_2$ (1) with $MeOC_6H_4(CH_2)_2COONS$ (5). As described previously, $MeOC_6H_4(CH_2)_2COONS$ (**5**) was added to a brown solution of [Cp*Ru(μ-OMe)]$_2$/H^+ and the reaction mixture was stirred for 1 h affording the desired compound [Cp*Ru(η^6-$MeOC_6H_4(CH_2)_2COONS$)][CF_3SO_3] (**6**) in 70% yield. The ^{1}H-NMR spectrum of **6** showed the expected pair of doublets for the π-complexed arene in the range 6−6.2 ppm; we also note the presence of the $-CH_2CH_2-$ chain of complex **6** appearing as pair of triplets at 3.10 and 2.80 ppm and two signals at 3.90 and 2.90 ppm attributed to the methoxy group and to the methylene groups of the *N*-hydroxysuccinimidyl unit. The ^{13}C-NMR data also confirmed the formation of the target compound (see Experimental Section). The infrared showed three carbonyl absorptions at 1815, 1784, and 1739 cm^{-1}. In order to confirm the structure of the activated ester complex [Cp*Ru(η^6-$MeOC_6H_4CH_2CH_2$-$COONS$][CF_3SO_3] (**6**) without ambiguity, we carried out an X-ray structural determination of **6** (see below).

(c) X-ray Molecular Structure of [Cp*Ru(η^6-$MeOC_6H_4CH_2CH_2COONS$][CF_3SO_3] (6). Crystals of **6** suitable for an X-ray analysis were grown from a CH_2Cl_2/hexane solution. The compound crystallizes in the monoclinic unit cell $P2_1/c$. Figure 3 shows the ORTEP view of [Cp*Ru(η^6-$MeOC_6H_4CH_2CH_2COONS$]$^+$, and crystal data are shown in Table 1. The structure shows that the organometallic fragment Cp*Ru is coordinated symmetrically to the arene unit with a d(Ru---C_{1-6}) average of 2.21 Å. The C9--O10 bond distance is 1.188 Å and is typical of a double bond.[14a,15]

This bond distance is similar to those carbonyls of the succinimidyl unit;[13a] we also note that the C9−O11 bond distance is 1.367 Å. Furthermore, the angle between the plane of the succinimidyl unit C13−N12−C16 and that of the ester defined by O11−C9−O10−C8 is θ = 93°, while that between the arene C1−6 and the succinimidyl unit is θ = 20°. The structure also shows that the *N*-succinimidyl unit (−NS) is situated away from the organometallic fragment; this implies that there is no steric influence created by the organometallic entity; hence, we would expect to observe a high reactivity of complex **6** with respect to amines and amino esters in view of formation of stable conjugates with peptide linkage. Finally we are not aware of any other X-ray structure reported for cationic species belonging to such a family of organometallic activated-ester complexes.

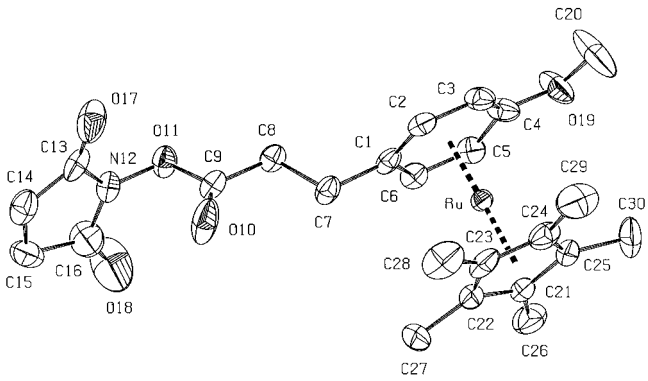

Figure 3. Molecular structure and atom labeling for [Cp*Ru(η^6-$MeOC_6H_4(CH_2)_2COONS$)][CF_3SO_3] (**6**). Selected bond distances (Å) and angles (deg): Ru−C1 = 2.215(3), Ru−C(2) = 2.191(3), Ru−C3 = 2.28(3), Ru−C4 = 2.272(3), Ru−C5 = 2.204(3), Ru−C6 = 2.192(3), Ru−C21 = 2.190-(3), Ru−C22 = 2.179(3), Ru−C22 = 2.179(3), Ru−C23 = 2.157(3), Ru−C24 = 2.181(3), Ru−C25 = 2.201(3), C4−O19 = 1.346(4), O19−C20 = 1.438(5), C1−C7 = 1.519(4), C9−O10 = 1.188(4); C8−C9−O10 = 127.6(3), C8−C9−O11 = 111.1(2), O10−C9−O11 = 121.3(3), C4−O19−C20 = 116.4-(3).

Table 1. Experimental Details for 6[a]

cryst description	brownish yellow cube; 0.30 × 0.30 × 0.30
instrument	Enraf-Nonius CAD4 diffractometer
corrs	Lorentz polarization
max 2θ	54.0
hkl ranges	h = −12 to 12 k = 0 to 23 l = −19 to 0
no. of refls measd	6439 tot., 6017 unique
no. of unobsd	0
refls included	4656 with $F_o^2 > 3.0\sigma(F_o^2)$
solution	direct methods
least-squares details	
H atoms	included as fixed contributions to the structure factors
params refined	352
unweighted agreement factor	0.059
weighted agreement factor	0.095
GOF	1.96
convergence, largest shift/error	0.01
minimization function	$w(\|F_o\| - \|F_c\|)^2$, where $w = 4F^2/\sigma^2(F^2)$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$, with $\sigma^2(F^2) = \sigma^2(I) + (pF^2)^2$
instrument instability factor, p	0.08
high peak in final diff map	0.31(8) e/Å^3
low peak in final diff map	0.00(8) e/Å^3

[a] X-ray data abstract: $C_{26}H_{30}F_3NO_7RuS$, fw = 658.66; space group $P2_1/c$ (No. 14); a = 9.949(1), b = 18.442(2), c = 15.657(2) Å; β = 106.19(1)°; V = 2758.76(92) Å^3; Z = 4; D_{calc} = 1.586 g/cm^3; radiation = Mo Kα (λ = 0.710 73 Å); μ = 6.9 cm^{-1}; $F(000)$ = 1344; temperature = −150 ± 0.5 °C; final R = 0.059; number of observed reflections = 4656.

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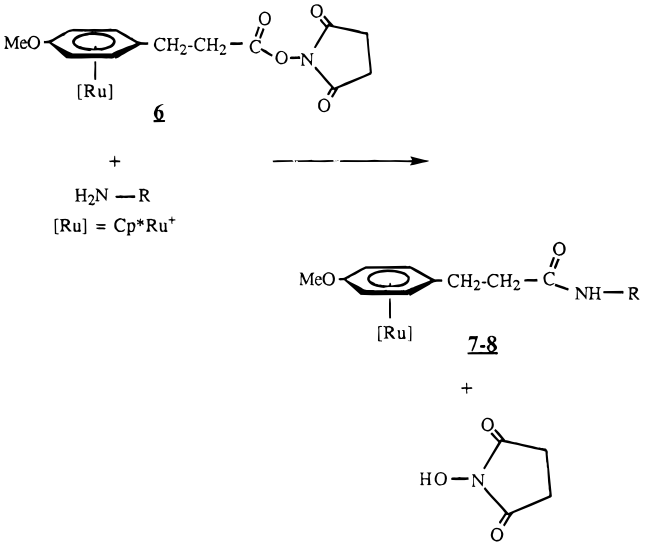
Scheme 4

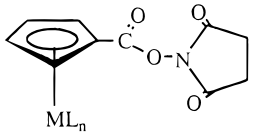


(d) Reactivity of 6 with Benzylamine and β-Alanine Ethyl Ester. Scheme 4 describes the reaction of **6** with amines and amino esters.

Treatment of **6** with benzylamine for 1 h gave the stable conjugate adduct [Cp*Ru(η^6-MeOC$_6$H$_4$CH$_2$CH$_2$-CONHCH$_2$Ph][CF$_3$SO$_3$] (**7**) in quantitative yield. The ^{1}H-NMR spectrum of **7** recorded in CD_2Cl_2 showed the expected pair of doublets in the range of 5.5−5.8 ppm; we also note the presence of a broad peak at 7.32 ppm attributed to the −NH unit, while the phenyl protons appear as a multiplet at 7.24 ppm. It is worth mentioning that separation of the cationic conjugate adduct **7** from the starting material could be achieved by simple addition of ether to the reaction mixture, thus affording **7** as a precipitate while the organic reagents remain soluble in the supernatant phase.

In a similar manner when **6** was treated with β-alanine ethyl ester in CH_2Cl_2 for 1 h the amide counterpart [Cp*Ru(η^6-MeOC$_6$H$_4$(CH$_2$)$_2$CONH(CH$_2$)$_2$COOEt][CF$_3$-SO$_3$] (**8**) was obtained quantitatively. The ^{1}H-NMR spectrum of **8** recorded in CD_2Cl_2 shows the expected pair of doublets for the coordinated arene in the range of 5.5−6.0 ppm and a broad triplet attributed to the −NH unit of the peptide linkage at 7.0 ppm; all other signals were assigned without ambiguity (see Experimental Section). At this stage it is worth comparing the reactivity of the monocationic organoruthenium complex **6** with that of the analogous bicationic iridium complex [Cp*Ir(η^6-MeOC$_6$H$_4$CH$_2$CH$_2$COONS]$^{2+}$ (**10**).

Previously we reported the synthesis of a series of dicationic iridium complexes of the type [Cp*Ir(η^6-MeOC$_6$H$_4$(CH$_2$)$_n$COONS]$^{2+}$ (n = 1, 2, 3) (**9**−**11**) and found that these complexes decompose during the reaction course with primary amines and amino esters.[7] The instability of these species was attributed to the presence of the dicationic fragment [Cp*Ir]$^{2+}$ on the aromatic ring of the succinimidyl esters **9**−**11**, which weakens the "CH$_2$−COO" bond of the ester unit and facilitates its cleavage, affording several side products in their reactions with amino substrates. On the other hand, we have found that the neutral succinimidyl derivatives of the type [L$_n$MCpCOONS] (**12**−**14**) [L$_n$M = Fe(CO)$_2$Me, Mo(CO)$_3$Me, Co(CO)$_2$] (Figure 4) react with amino substrates to give the conjugate products which possess the primary amide linkage.[14] It is worth mentioning that the reaction proceeds slowly and an average of 12 h was required to attain the conjugate species, and this should be compared to that of **6** which needs only 1 h to give the corresponding amide counterpart.



ML$_n$ =Fe(CO)$_2$Me (**12**); Mo(CO)$_3$Me (**13**), Co(CO)$_2$; (**14**)

Figure 4.

In conclusion we feel that the monocationic ruthenium derivative exhibits a higher stability relative to the analogous iridium species, yet this compound is more reactive than the neutral metallocarbonyl succinimidyl derivatives of the type [L$_n$MCpCOONS] (**12**−**14**) [L$_n$M = Fe(CO)$_2$Me, Mo(CO)$_3$Me, Co(CO)$_2$]. Efforts are currently directed toward the study of the reactivity and selectivity of **6** with peptides possessing several reactive sites. These investigations will be the subject of future reports.

Experimental Section

General Procedures. All manipulations were carried out under argon atmosphere using Schlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques. All reagents obtained from commercial sources were used without further purification. ^{1}H and ^{13}C NMR were recorded on Bruker AM 250MHz instrument. ^{1}H-NMR chemical shifts are reported in parts per million referenced to residual solvent proton resonance. Infrared spectra were obtained on a FT Bruker IR45 spectrometer from samples prepared either on KBr disks or in CH_2Cl_2 solutions. All absorptions are expressed in wavenumbers (cm^{-1}). Elemental analyses were performed by the Microanalytical Laboratory of the CNRS of the University of Paris VI.

Synthesis of [Cp*Ru(η^6-MeOC$_6$H$_4$CH$_2$CH$_2$COOH]-[CF$_3$SO$_3$] (3). This compound was prepared in a similar way to that of **4** (see below), but the reaction mixture was stirred for only 30 min and using the following reagents and quantities: [Cp*RuCl$_2$]$_2$ (0.2 g, 0.32 mmol), K_2CO_3 (0.6 g, 4.28 mmol), triflouromethanesulfonic acid (80 μL, 0.70 mmol), and MeOC$_6$H$_4$-CH$_2$CH$_2$COOH (**2**) (180 mg, 1.0 mmol). Compound **3** was obtained as a dark brown precipitate by addition of Et$_2$O (30 mL) to the solution mixture, while the supernatant phase gave a mixture of **3** and **4** in a ratio of 1/1 (54 mg).

Total yield for **3**: 134 mg, 50%. IR (ν/cm^{-1}) (KBr): −OH, 3458, C═O, 1733. ^{1}H NMR (CD_3CN): δ 5.95 (d, 2H, aromatic), 5.85 (d, 2H, aromatic), 5.45 (b, 1H, −COOH), 3.75 (s, 3H, −MeO), 2.55 (m, 4H, −CH$_2$CH$_2$−), 1.90 (s, 15H, −Cp*). ^{13}C NMR (CD_3)$_2$CO): δ, 173.13 (COO), 133.16 (C$_{ipso}$), 122.10 (CF$_3$, q, $^1J_{CF}$ = 320.6 Hz), 101.19 (C$_{ipso}$), 96.30 (−Cp*, −C═C−), 87.73, 76.63 (aromatics, −C═C−), 57.33 (MeO−), 35.39 (−CH$_2$−), 28.03 (−CH$_2$−), 10.39 (Cp*, Me−). An analysis could not be obtained for this compound, since it hydrolyzes rapidly when exposed to air and becomes gummy.

Synthesis of [Cp*Ru(η^6-MeOC$_6$H$_4$CH$_2$CH$_2$COOMe]-[CF$_3$SO$_3$] (4). The general procedure for the preparation of these Cp*Ru π-adducts is as follows: K_2CO_3 (0.6 g, 4.28 mmol) was added to a solution of [Cp*RuCl$_2$]$_2$ (0.5 g, 0.817 mmol) in MeOH (20 mL), and the mixture was refluxed for 1 h under argon. The suspension becomes deep red, and then the solvent was removed under vacuum, 30 mL of CH_2Cl_2 was added, and the mixture was filtered with care. A total of 300 μL (3.4 mmol) of triflouromethanesulfonic acid was added to the deep red sensitive solution of [Cp*Ru(μ-OMe)]$_2$ (**1**), which changes rapidly to brown yellow. The mixture was stirred for 15 min,

and then a CH_2Cl_2 solution of 3-(4-methoxyphenyl)propionic acid (400 mg, 2.22 mmol) was added and the reaction mixture stirred for 14 h. The solution was concentrated under vacuum, and 30 mL of Et_2O was added affording a brown precipitate. The supernatant phase was removed, and the precipitate was washed with Et_2O several times, recrystallized from CH_2Cl_2/Et_2O, and dried under vacuum. Yield: 350 mg, 70%.

IR (ν/cm^{-1}) (KBr): C═O, 1740; CF_3SO_3, 1025, 640. ^{1}H NMR (CD_3CN): δ 5.73 (d, 2H, aromatic), 5.66 (d, 2H, aromatic), 3.72 (s, 3H, −MeO), 3.60 (s, 3H, COOMe), 2.58 (m, 4H, $-CH_2CH_2-$), 1.89 (s, 15H, Me−Cp). ^{13}C NMR (CD_3CN): δ 173.24 (C═O), 133.11 (C_{ipso}), 100.89 (C_{ipso}), 96.59 (Cp*, −C═C−), 87.52 (aromatics, C═C), 76.53 (aromatics, C═C), 57.63 (MeO−), 52.34 (COOMe), 35.64 ($-CH_2-$), 28.11 (−CH2−), 10.60 (Cp*, Me−). An analysis could not be obtained for this compound, since it hydrolyzes rapidly when exposed to air and becomes gummy.

Synthesis of [Cp*Ru(η^6-MeOC$_6$H$_4$CH$_2$CH$_2$COONS][CF$_3$SO$_3$] (6). This compound was prepared in a similar way to that of **4** but using the following reagents and quantities: 0.1 g, 0.16 mmol, of $[Cp^*RuCl_2]_2$, 0.3 g, 0.490 mmol, of K_2CO_3, 40 mL, 0.35 mmol, of triflouromethanesulfonic acid, and 100 mg, 0.35 mmol, of $MeOC_6H_4CH_2CH_2COONS$ (**5**). Yield: 150 mg, 70%. IR (ν/cm^{-1}) (KBr): −OH, 3509; C═O, 1815, 1784, 1739; CF_3SO_3, 1031, 638. ^{1}H NMR ($(CD_3)_2CO$): δ 6.10 (d, 2H, aromatic), 6.05 (d, 2H, aromatic), 3.90(s, 3H, −MeO), 3.05 (t, 2H, $-CH_2-$), 2.90 (s, 4H, $-CH_2-$, −NS), $-CH_2$ signal obscured by residual H_2O in $(CD_3)_2CO$, 2.01 (s, 15H, −Cp*) ^{13}C NMR (CD_2Cl_2): δ 168.72 (CON), 167.09 (COO), 131.99 (Cipso), 97.75 (Cipso), 95.59 (−Cp*, −C═C−), 86.33 (aromatics, −C═C−), 56.57 (MeO−), 32.17 ($-CH_2-$), 27.17 ($-CH_2-$), 25.25 (−NS), 9.91 (Cp*, Me−). Anal. Calcd for $C_{25}H_{30}O_8NF_3SRu\cdot CH_2Cl_2$: C, 41.76; H, 4.28; N, 1.87. Found: C, 38.81; H, 4.20; N, 1.76.

Synthesis of [Cp*Ru(η^6-MeOC$_6$H$_4$CH$_2$CH$_2$CONHCH$_2$Ph][CF$_3$SO$_3$] (7). A 40 μL (0.192 mmol) amount of benzylamine was added to a CH_2Cl_2 solution (20 mL) of **6**, and the reaction mixture turned rapidly to deep orange. The mixture was stirred for 1 h and 45 min, and then the solution was concentrated under vacuum to 1 mL. Addition of Et_2O (30 mL) afforded a brown precipitate, which was filtered off and washed several times with ether and then dried under vacuum. Yield: 45 mg, 90%. IR (ν/cm^{-1}) (KBr): −OH, 3432; C═O, 1680; CF_3SO_3, 1030, 638. ^{1}H NMR (CD_2Cl_2): δ 7.32 (b, 1H, −NH), 7.23 (m, 5H, aromatics), 5.68 (d, 2H, aromatics), 5.54 (d, 2H, aromatics), 4.30 (d, 2H, $-CH_2-$), 3.73 (s, 3H, −MeO), 2.57 (s, 4H, $-CH_2CH_2-$). Anal. Calcd for $C_{28}H_{34}O_5NF_3SRu\cdot 3H_2O$: C, 47.45; H, 5.65. Found: C, 47.34; H, 5.34.

Synthesis of [Cp*Ru(η^6-MeOC$_6$H$_4$(CH$_2$)$_2$CONH(CH$_2$)$_2$-COOEt][CF$_3$SO$_3$] (8). A 50 μL (0.45 mmol) amount of NEt_3 was added to a warm THF solution (20 mL) of β-alanine ethyl ester·HCl (85 mg, 0.45 mmol) to give a white precipitate ($NEt_3\cdot$HCl). The mother liquor was filtered and then added dropwise to a CH_2Cl_2 solution (20 mL) of **6** (70 mg, 0.1 mmol). The reaction mixture was stirred for 1 h. The solvent was reduced under vacuum, and then Et_2O (30 mL) was added to give an oil-like precipitate. This compound was washed several times with Et_2O and then dried under vacuum. Yield: 65 mg, 93%. IR (ν/cm^{-1}) (KBr): −OH, 3500; −C═O ester, 1733; −C═O amide, 1680; CF_3SO_3, 1030, 638. ^{1}H NMR (CD_2Cl_2): δ 7.00 (t, 1H, −NH), 5.73 (d, 2H, arene), 5.64 (d, 2H, arene), 4.09 (m, 2H, $-COOCH_2-$), 3.40 (m, 2H, $-CONCH_2-$), 2.48 (t, 2H, $-CONCCH_2-$), 1.91 (s, 15H, −Cp*), 1.24 (t, 3H, $-COOCCH_3$). ^{13}C NMR (CD_2Cl_2): δ 171.55 (CON), 170.65 (COO), 131.51 (C_{ipso}), 120.34 (CF_3, q, $^1J_{CF}$ = 320.2 Hz), 99.97 (C_{ipso}), 95.17 (−Cp*, −C═C−), 86.337 (aromatics, −C═C−), 75.26 (aromatics, −C═C−), 60.15 ($COOCH_2-$), 56.31 (MeO−), 36.69 ($-CH_2CONH$), 34.78 ($-CH_2COO$), 31.20 ($-CH_2$), 27.87 ($-CH_2$), 13.57 (CH_3-), 9.91 (Cp*, Me−).

Structural Determination of [Cp*Ru(η^6-MeOC$_6$H$_4$CH$_2$-CH$_2$COONS][CF$_3$SO$_3$] (6). Single crystals were grown from a CH_2Cl_2/hexane solution using the slow diffusion method. Data were collected at −150 ± 0.5 °C on an Enraf Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator . The crystal structure was solved and refined using the Enraf Nonius MOLEN package. The compound crystallizes in space group $P2_1/c$ (No. 14), with a = 9.949(1) Å, b = 18.442(2) Å, c = 15.657(2) Å, β = 106.19-(1)°, V = 2758.76(92) Å^3, Z = 4, d_{calc} = 1.586 g/cm^3, μ = 6.9 cm^{-1}, and F(000) = 1344. A total of 6439 unique reflections were recorded in the range $2° \le 2\theta \le 54.0°$ of which 1783 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 4656 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were R = 0.059, R_w = 0.095, and GOF = 1.96.

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Supporting Information Available: Tables S1−S4, listing bond lengths and angles, atomic coordinates and B values, and anisotropic displacement coefficients (4 pages). Ordering information is given on any current masthead page.

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