ELSEVIER

Journal of Organometallic Chemistry 533 (1997) 25–30

Journal of Organometallic Chemistry

Regioselective synthesis of η^3-(*N*-methoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-dienyl)-η^5-(C_5Me_5)RuCl complexes

Zhengming Chen [a], Lubin Luo [a], Steven P. Nolan [a], Jeffrey L. Petersen [b], Mark L. Trudell [a,*]

[a] *Department of Chemistry, University of New Orleans, New Orleans, LA 70148, USA*
[b] *Department of Chemistry, West Virginia University, Morgantown, WV 26506-6045, USA*

Received 25 June 1996; revised 23 September 1996

Abstract

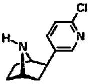
The reactions of Cp*Ru(COD)Cl and CpRu(COD)Cl with *N*-methoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-diene derivatives were found to give η^3-[$N(CO_2Me)C_6H_3(2\text{-}p\text{-}MeC_6H_4SO_2)(6\text{-}CO_2Me)(5\text{-}Me)$]CpRuCl and η^3-[$N(CO_2Me)$-7-azabicyclo[2.2.1]heptadienyl]Cp*RuCl complexes in good yields (54–78%). The coordination reaction was found to take place regioselectively at the least substituted π-bond of the *N*-methoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-diene derivatives. The structures of the complexes were determined by ^1H and ^{13}C NMR and the structure of η^3-[$N(CO_2Me)C_6H_3(2\text{-}p\text{-}MeC_6H_4SO_2)(6\text{-}CO_2Me)(5\text{-}Me)$]Cp*RuCl was unequivocally established by X-ray crystallography.

Keywords: 7-Azabicyclo[2.2.1]heptadienes; Regioselective; Ruthenium; Olefin complexes

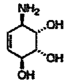
---

1. Introduction

The [4 + 2] cycloaddition reaction of *N*-acylpyrrole substrates with electron deficient acetylene equivalents has proven to be a useful method for the one-step construction of highly functionalized 7-azabicyclo[2.2.1]heptadiene derivatives [1]. These compounds have proven to be useful for the synthesis of the potent analgesic non-opioid alkaloid (−)-epibatidine **1** and the glycosidase inhibitory conduramine alkaloids **2** [2] (review of recent syntheses of epibatidine), [3]. As part of an ongoing program aimed at the synthesis of epibatidine-related analogs, it became necessary to develop a method for the chemical differentiation between the two π-bonds of various substituted 7-azabicyclo[2.2.1]heptadienes. To achieve this goal an organometallic approach was envisaged.



1



2

There are numerous examples in the literature where transition metals have been employed to chemically differentiate between two olefinic sites in a molecule [4]. The coordination of transition metals (Fe, Mo) with 7-azabicyclo[2.2.1]heptadiene derivatives has been reported to result in the formation of stable organometallic complexes which upon thermolysis give deaminated aromatic derivatives [5–9]. It has been shown that the transition metal coordinates stereoselectively to the *exo*-side of the 7-azabicyclo[2.2.1]heptadiene with both the lone pair of the nitrogen atom and a π-bond. In simple 7-aza-bicyclo[2.2.1]heptadiene systems, transition metal complexes have been obtained in moderate yields but poor regioselectivity between the two π-bonds of the bicyclic diene was observed. Typically, a mixture of both *exo*-isomers and in some cases mixtures of dimers have been obtained [9]. Although these mixtures

---

[*] Corresponding author. Tel.: +(504) 286-7337; Fax: +(504) 286-6860; E-mail: MLTCM@UNO.EDU.

0022-328X/97/$17.00 Copyright © 1997 Elsevier Science S.A. All rights reserved.
PII S0022-328X(96)06827-1

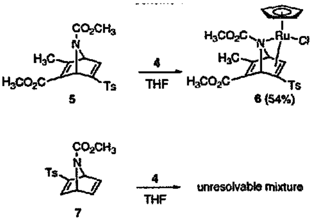
of *exo*-coordinated organometallic species do not generally inhibit the nitrene-extrusion reaction to give aromatic compounds, they are unsuitable for further regioselective chemical modification of the bicyclic ligand [5,9]. Herein, we wish to report the regioselective syntheses of η^3-(*N*-methoxycarbonyl-7-azabicyclo[2.2.1]heptadienyl)Cp*RuCl complexes.

2. Results and discussion

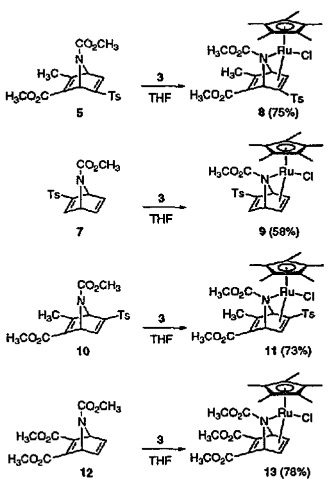
The transition metal complex Cp*Ru(η^4-COD)Cl (3) [10] has been shown to readily substitute the 1,5-cyclooctadiene (COD) ligand for norbornadiene (NBD) to furnish the stable complex Cp*Ru(η^4-NBD)Cl [11]. Based on these results it was believed that the readily available ruthenium complexes Cp*Ru(η^4-COD)Cl (3) and CpRu(η^4-COD)Cl (4) [12] would be excellent candidates for the synthesis of stable complexes of 7-azabicyclo[2.2.1]hepta-2,5-diene derivatives.

The reaction of 7-azabicyclo[2.2.1]heptadiene derivative 5 [1] with 4 in tetrahydrofuran (THF) at room temperature under an inert atmosphere of nitrogen gave the η^3-complex 6 as a pink solid in 54% yield as the sole product (Scheme 1). The structure of 6 was easily determined by ^{1}H NMR [7,8]. η^3-Coordination of the CpRu(II)Cl moiety to the monosubstituted π-bond resulted in an upfield shift of the NMR signal of H(3) of 6 (δ 5.74 ppm) relative to the free ligand 5 (δ 7.70 ppm). In addition, the broad singlet corresponding to the *N*-methoxycarbonyl group of 5 was considerably sharper in 6 since the interconversion of rotamers was no longer possible. The η^3-complex 6 was found to be surprisingly stable for a ruthenium(II) complex; exposure to air over several months resulted in no decomposition and the compound could be readily purified by silica gel column chromatography.

The regioselectivity observed for the η^3-coordination of the CpRu(II)Cl moiety was believed to result from the steric differential between the two π-bonds of 5. Coordination at the least hindered monosubstituted π-bond was found to take place exclusively over coordination at the less accessible disubstituted π-bond of 5. However, this regioselectivity was not observed with 2-*p*-toluenesulfonyl-7-azabicyclo[2.2.1]hepta-2,5-diene (7) [1]. When 7 was allowed to react with 4 under similar reaction conditions a complex mixture of isomers was obtained (Scheme 1). The lack of regioselectivity observed in this reaction was presumed to be due to an insufficient steric differential between the π-bonds of 7 and the CpRu(II)Cl moiety.



Scheme 1.



Scheme 2.

To address the problem of low regioselectivity observed for the simple 7-azabicyclo[2.2.1]heptadiene derivative 7, coordination of the bulkier Cp*Ru(II)Cl moiety with 7-azabicyclo[2.2.1]heptadiene derivatives was investigated. The bulkier Cp*Ru(II)Cl moiety was expected to be more sensitive to steric constraints about the π-bonds and thus exhibit enhanced regioselectivity. Similar to the CpRu(II)Cl system, the reaction of Cp*Ru(COD)Cl (3) with 5 afforded the η^3-complex 8 in 75% yield as the sole product (Scheme 2). In addition, the reaction of 7 with 3 afforded the η^3-complex 9 regioselectively. The complex 9 was isolated as the sole product after chromatography in 58% yield. This result confirmed that the regioselectivity observed for these coordination reactions was governed by steric interactions between the 7-azabicyclo[2.2.1]heptadiene ligand and the organoruthenium species. Moreover, the Cp*Ru(II)Cl moiety exhibited a much greater sensitivity to the steric environment of the π-bonds of the ligand than did the CpRu(II)Cl moiety. The reactions of

3 with 7-azabicyclo[2.2.1]heptadiene derivatives **10** [1] and **12** [1] also regioselectively afforded the η^3-complexes **11** and **13** respectively in high yield. In all cases, the coordination of the Cp* Ru(II)Cl species was established by NMR based on the shielding effect experienced by the vinyl protons of the π-bond coordinated to the ruthenium moiety.

Further structural characterization of **8** was achieved by X-ray crystallography (Fig. 1). Selected interatomic distances and angles are given in Table 1. From the X-ray structure of **8**, coordination of the Cp* Ru(II)Cl species clearly takes place at the nitrogen atom and at the least substituted π-bond to give a classical three-legged piano stool complex. The orientation of the ligands about the ruthenium(II) metal is such that the steric interactions between the substituents on the rigid 7-azabicyclo[2.2.1]heptadiene ligand **5** and the Cp* ligand are minimized. As a result, the distance between the ruthenium atom and the centroid of the Cp* ligand [Ru–Cp*(c)] was found to be 1.842 Å. This distance is similar to that observed in the less sterically constrained Cp* Ru(COD)Cl (**3**) complex [Ru–Cp*(c), 1.885(2) Å] [13]. It is also interesting to note the slight asymmetry of the ruthenium coordination to the π-bond. The Ru–C(11) bond distance (2.101 Å) is slightly shorter than the Ru–C(12) (2.141(2) Å) bond distance. This slight distortion may result from the electron-withdrawing effect of the *p*-toluenesulfonyl substituent on C(12) or assist in relieving the steric interactions between the Cp* ligand and the *p*-toluenesulfonyl substituent. In addition, the elongation of the C(11)–C(12) bond [1.431(4) Å] relative to the uncoordinated C(14)–C(15) bond [1.333(4) Å] was also consistent with bonding trends observed in other η^3-(7-azabicyclo[2.2.1]heptadienyl) transition metal complexes [7].

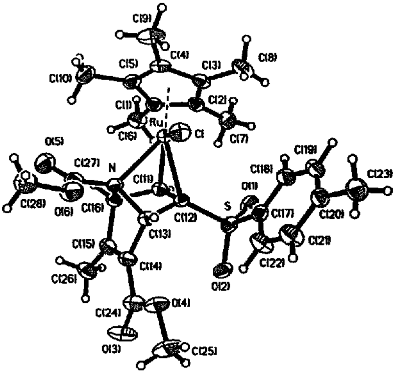


Fig. 1. ORTEP diagram of η^3-[N(CO$_2$Me)-C$_6$H$_3$(SO$_2$C$_6$H$_4$Me)(CO$_2$Me)Me]-η^5-(C$_5$Me$_5$)RuCl (**8**).

Table 1

Selected bond distances (Å) and bond angles (deg) for η^3-[N(CO$_2$Me)C$_6$H$_3$(SO$_2$C$_6$H$_4$Me)(CO$_2$Me)Me]-η^5-(C$_5$Me$_5$)RuCl (**8**)

Bond distances [a,b]			
Ru–C(11)	2.101(3)	S–O(1)	1.438(2)
Ru–C(12)	2.141(2)	S–O(2)	1.446(2)
Ru–N	2.269(2)	S–C(12)	1.735(3)
Ru–Cp*(c)	1.842	S–C(17)	1.759(3)
Ru–C(1)	2.207(3)	N–C(13)	1.512(3)
Ru–C(2)	2.168(3)	N–C(16)	1.504(4)
Ru–C(3)	2.158(3)	N–C(27)	1.409(7)
Ru–C(4)	2.235(3)	C(11)–C(12)	1.431(4)
Ru–C(5)	2.259(3)	C(14)–C(15)	1.333(4)
Bond angles [a,b]			
C(11)–Ru–C(12)	39.43(10)	N–Ru–Cp*(c)	139.8
C(11)–Ru–Cl	125.53(7)	N–Ru–Cl	85.15(7)
C(11)–Ru–N	60.47(9)	O(1)–S–O(2)	117.78(13)
C(11)–Ru–Cp*(c)	116.1	O(1)–S–C(12)	108.11(13)
C(12)–Ru–Cl	87.77(8)	O(1)–S–C(17)	108.18(13)
C(12)–Ru–N	60.09(9)	O(2)–S–C(12)	108.11(12)
C(12)–Ru–Cp*(c)	145.4	O(2)–S–C(17)	107.28(13)
Cl–Ru–Cp*(c)	117.2	C(12)–S–C(17)	106.90(13)

[a] Atom labels correspond to those shown in Fig. 1.

[b] Numbers in parentheses are the estimated standard deviations.

In summary, the reactions of **3** and **4** with 7-azabicyclo[2.2.1]heptadiene derivatives were found to proceed regioselectively to furnish air-stable η^3-*exo*-coordinated complexes. The ability of the Cp* Ru(II)Cl moiety to chemically differentiate between disubstituted, monosubstituted and unsubstituted π-bonds of 7-azabicyclo[2.2.1]heptadienes will prove to be useful for the characterization and synthesis of complex 7-azabicyclo[2.2.1]heptadiene derivatives. Moreover, the availability of air-stable η^3-*exo*-coordinated 7-aza-bicyclo[2.2.1]heptadiene complexes may prove useful for the synthesis of 7-azabicyclo[2.2.1]heptane-related alkaloids.

3. Experimental section

All chemicals were purchased from Aldrich Chemical Co., Milwaukee, WI, unless otherwise noted. Tetrahydrofuran (E.M. Science) was dried by distillation from Na/benzophenone. Chromatography refers to flash chromatography on silica gel (Silica Gel 60, 230–400 mesh, E.M. Science). Melting points were recorded on a Mel-Temp apparatus and are uncorrected. NMR spectra were recorded on a Varian Multiprobe 300 MHz spectrometer. Mass spectral data were obtained on Finnigan TSQ 700 (EI) and KRATOS MS50 (HRMS) spectrometers at Iowa State University, Ames, IA. Elemental analyses were obtained from Atlantic Microlabs, Inc., Norcross, GA.

3.1. Crystallographic studies of η^3-[$N(CO_2Me)C_6H_3(2\text{-}p\text{-}MeC_6H_4SO_2)(6\text{-}CO_2Me)(5\text{-}Me)$]-$Cp^*RuCl$ (8)

A reddish orange crystal of **8**, grown by evaporation of a saturated CH_2Cl_2/benzene solution, having approximate dimensions $0.12 \times 0.30 \times 0.40\,mm^3$ was selected and sealed under nitrogen in a capillary tube and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The reflections that were used for the determination of the dimensions of the triclinic unit cell were located and indexed by the automatic peak search routine XSCANS [14]. The corresponding lattice parameters and orientation matrix were provided from a non-linear least-squares fit of the orientation angles of 40 reflections ($10° < 2\theta < 25°$) at 22 °C. The refined lattice parameters and other pertinent crystallographic information are summarized in Table 2.

Intensity data were measured with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and variable ω-scans (2.5–$10.0°\,min^{-1}$). Background counts were measured at the beginning and end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured periodically during data collection and gave no indication of crystal decay or sample movement. The data were corrected for Lorentz–polarization and the symmetry-equivalent reflections were averaged. An empirical absorption correction (range of transmission coefficients 0.683–0.797) based upon the ψ-scans measured for eight reflections ($\chi = -90°$, $2\theta = 17$–$41°$) was applied.

Table 2
Crystal data and refinement for η^3-[$N(CO_2Me)C_6H_3(SO_2C_6H_4Me)(CO_2Me)Me$]-$\eta^5$-($C_5Me_5$)RuCl (8)·1/2$C_6H_6$

Empirical formula	$C_{31}H_{37}ClNO_6RuS$
Formula weight	688.20
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 10.736(2)$ Å, $\alpha = 68.80(1)°$ $b = 11.732(3)$ Å, $\beta = 83.82(1)°$ $c = 13.398(2)$ Å, $\gamma = 81.31(1)°$
Volume	1552.7(6) $Å^3$
Z	2
Density (calc.)	1.472 $g\,cm^{-3}$
Absorption coefficient	7.01 cm^{-1}
$F(000)$	710
Crystal size	$0.12 \times 0.30 \times 0.40\,mm^3$
θ range for data collection	1.92 to 25.00°
Index ranges	$0 \leq h \leq 12$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$
Reflections collected	5594
Independent reflections	5290 ($R_{int} = 0.0211$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5020/20/410
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0385$, $wR_2 = 0.0881$
R indices (all data)	$R_1 = 0.0544$, $wR_2 = 0.0962$
Largest diff. peak and hole	0.544 and -0.441 e $Å^{-3}$

The initial coordinates of the Ru atom were determined by Patterson methods and the coordinates for the remaining non-hydrogen atoms were obtained from subsequent Fourier summations calculated with the algorithms provided by SHELXTL-93 operating on a Silicon Graphics IRIS Indigo workstation [15]. As the refinement proceeded it became apparent that the methoxycarbonyl substituent on the nitrogen atom suffered from a two-site (50:50) disorder and that a solvent molecule of benzene resided on a center of inversion. The methoxycarbonyl disorder was refined by restraining the C(27)–O(5) double bond and C(27)–O(6) single bond of the two equally-weighted sites to 1.20 ± 0.02 and 1.32 ± 0.02 Å respectively. The three unique carbon atoms of the benzene molecule, C(29)–C(31), were refined by restraining the adjacent C–C bonds and the shortest non-bonding C–C separations within the ring to 1.39 ± 0.02 and 2.41 ± 0.02 Å respectively. The large refined thermal parameters for the benzene carbon atoms indicate that its position is poorly-defined in the crystal lattice. Idealized positions for all of the hydrogen atoms were included as fixed contributions using a riding model with isotropic temperature factors set at 1.2 times that of the adjacent carbon. The positions of the methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. A full-matrix least-squares refinement, based upon the minimization of $\Sigma w_i|F_o^2 - F_c^2|^2$, with $w_i^{-1} = [\sigma^2(F_o^2) + (0.0494P)^2 + 0.608P]$ where $P = (\max(F_o^2, 0) + 2F_c^2)/3$, was performed with SHELXL-93 operating on a Silicon Graphics IRIS Indigo workstation [15]. After convergence, the final discrepancy indices were $R_1 = 0.0385$, $wR_2 = 0.0881$ for 4344 reflections with $I > 2\sigma(I)$ and the overall GOF value was 1.046. The discrepancy indices were calculated from the expressions $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma(w_i(F_o^2 - F_c^2)^2)/\Sigma(w_i(F_o^2)^2)]^{1/2}$ and the standard deviation of an observation of unit weight (GOF) is equal to $[\Sigma(w_i(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters varied during the last refinement cycle. The atomic coordinates and equivalent isotropic displacement parameters are provided in Table 3.

3.2. η^5-(C_5H_5)-η^3-(N-methoxycarbonyl-6-methoxycarbonyl-5-methyl-2-p-toluenesulfonyl-7-azabicyclo[2.2.1]hepta-2,5-dienyl)RuCl (6)

Under an argon atmosphere, a 100 ml flask was charged with CpRu(COD)Cl (**4**) [13] (500 mg, 1.6 mmol) in dried THF (40 ml). A solution of **5** [1] (900 mg, 2.4 mmol) in THF (10 ml) was then added in one por-

Table 3
Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for η^3-[N(CO$_2$Me)C$_6$H$_3$-(SO$_2$C$_6$H$_4$Me)(CO$_2$Me)Me]-η^5-(C$_5$Me$_5$)RuCl (8)·1/2C$_6$H$_6$ [a]

Atom	x	y	z	U_{eq} [b]
Ru	2050(1)	1722(1)	1456(1)	35(1)
S	5315(1)	690(1)	1460(1)	44(1)
Cl	2353(1)	2100(1)	3058(1)	54(1)
O(1)	5454(2)	1444(2)	346(2)	61(1)
O(2)	6075(2)	−496(2)	1819(2)	57(1)
O(3)	5096(3)	−3660(2)	3444(2)	90(1)
O(4)	5168(2)	−2184(2)	4120(2)	69(1)
N	1962(2)	−258(2)	2561(2)	41(1)
C(1)	1101(3)	2266(2)	−58(2)	43(1)
C(2)	2085(3)	3025(2)	−176(2)	43(1)
C(3)	1750(3)	3670(2)	547(2)	50(1)
C(4)	544(3)	3331(3)	1088(2)	53(1)
C(5)	168(3)	2470(3)	714(2)	49(1)
C(6)	982(3)	1554(3)	−762(2)	59(1)
C(7)	3153(3)	3192(3)	−1000(2)	60(1)
C(8)	2434(4)	4649(3)	648(3)	75(1)
C(9)	−182(4)	3861(3)	1871(3)	81(1)
C(10)	−1016(3)	1849(3)	1079(3)	71(1)
C(11)	3026(2)	284(2)	993(2)	37(1)
C(12)	3741(2)	453(2)	1761(2)	37(1)
C(13)	3325(2)	−490(2)	2846(2)	41(1)
C(14)	3700(3)	−1796(2)	2856(2)	47(1)
C(15)	3035(3)	−1959(2)	2144(2)	48(1)
C(16)	2220(3)	−737(2)	1649(2)	43(1)
C(17)	5664(2)	1524(2)	2232(2)	43(1)
C(18)	5501(3)	2791(3)	1828(3)	58(1)
C(19)	5872(3)	3441(3)	2396(3)	60(1)
C(20)	6434(3)	2851(3)	3357(2)	51(1)
C(21)	6551(4)	1592(3)	3758(3)	69(1)
C(22)	6176(3)	922(3)	3206(2)	64(1)
C(23)	6905(3)	3576(3)	3934(3)	68(1)
C(24)	4716(3)	−2664(3)	3489(2)	60(1)
C(25)	6203(4)	−2927(4)	4756(3)	103(2)
C(26)	3050(3)	−3028(2)	1790(3)	61(1)
C(27)	1018(3)	−749(3)	3352(3)	64(1)
O(5)	12(5)	−871(5)	3054(5)	83(2)
O(6)	1239(5)	−932(5)	4357(4)	72(2)
C(28)	163(3)	−1383(4)	5035(3)	78(2)
O(5′)	1200(3)	−944(4)	4248(3)	59(2)
O(6′)	36(3)	−896(4)	2985(3)	77(2)
C(28′)	−1007(3)	−1179(4)	3879(3)	102(3)
C(29)	8760(6)	−5171(11)	5560(6)	338(9)
C(30)	9129(6)	−4735(10)	4538(8)	307(7)
C(31)	10145(8)	−4467(11)	3947(7)	306(6)

[a] Numbers in parentheses are the estimated standard deviations.

[b] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

tion. After stirring for 10 h, the solution color changed from yellow–brown to red and a pink precipitate formed. The solid was collected by filtration. The pink solid was then washed with THF/hexane (2:1, 3 × 2 ml) and dried under vacuum to give **6** (510 mg, 54% yield). M.p. 101–105 °C (dec.). ^{1}H NMR (CDCl$_3$): δ 7.73 (d, $J = 7.4$ Hz, 2H), 7.34 (d, $J = 7.9$ Hz, 2H), 5.74 (s, 1H), 5.59 (s, 1H), 5.26 (s, 1H), 4.95 (s, 5H), 3.79 (s, 3H), 3.58 (s, 3H), 2.44 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (CDCl$_3$): δ 162.3, 159.7, 144.0, 142.3, 136.7, 129.5, 129.4, 129.3, 129.1, 83.3, 81.9, 78.0, 55.2, 53.0, 51.6, 21.8, 14.0. Anal. Found: C, 43.70; H, 4.02; N, 2.21. C$_{23}$H$_{24}$ClNO$_6$SRu · CH$_2$Cl$_2$ Calc.: C, 43.42; H, 3.95; N, 2.11%.

3.3. η^3-(N-methoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-dienyl)-η^5-(C$_5$Me$_5$)RuCl (8)

Under an argon atmosphere a 100 ml flask was charged with Cp*Ru(COD)Cl (**3**) [11] (380 mg, 1 mmol) and dried THF (40 ml). A solution of the 7-azabicyclo[2.2.1]heptadiene **5** (565 mg, 1.5 mmol) [1] in THF (10 ml) was added in one portion. The reaction mixture was stirred for 10 h at room temperature. The solvent was then removed under reduced pressure and the residue chromatographed (SiO$_2$, 50% EtOAc/petroleum ether). This afforded the η^3-complex **8** in pure form (486 mg, 75%). M.p. 100–105 °C (dec.). ^{1}H NMR (CDCl$_3$): δ 7.71 (d, $J = 7.13$ Hz, 2H), 7.29 (d, $J = 7.13$ Hz, 2H), 5.56 (s, 1H), 4.97 (s, 1H), 4.89 (s, 1H), 3.79 (s, 3H), 3.53 (s, 3H), 2.43 (s, 3H), 2.21 (s, 3H), 1.61 (s, 15H). ^{13}C NMR (CDCl$_3$): δ 163.2, 158.7, 154.6, 143.3, 142.2, 137.3, 130.0, 129.0, 128.8, 128.4, 92.4, 82.1, 80.5, 56.8, 54.5, 51.4, 21.8, 13.8, 9.8. Anal. Found: C, 51.72; H, 5.36; N, 1.96. C$_{28}$H$_{34}$ClNO$_6$RuS Calc.: C, 51.81; H, 5.28; N, 2.16%.

3.4. η^3-(N-methoxycarbonyl-2-p-toluenesulfonyl-7-azabicyclo[2.2.1]hepta-2,5-dienyl)-η^5-(C$_5$Me$_5$)RuCl (9)

Compound **9** was prepared as described for **8** starting from **7** (458 mg, 1.5 mmol) [1]. This afforded **9** as a colorless oil (502 mg, 58%). ^{1}H NMR (CDCl$_3$): δ 7.71 (d, $J = 7.04$ Hz, 2H), 7.29 (d, $J = 7.04$ Hz, 2H), 6.81 (d, $J = 5.13$ Hz, 1H), 6.27 (d, $J = 5.13$ Hz, 1H), 5.36 (s, 1H), 5.13 (s, 1H), 4.81 (s, 1H), 3.54 (s, 3H), 2.43 (s, 3H), 1.62 (s, 15H). ^{13}C NMR (CDCl$_3$): δ 154.8, 146.3, 143.3, 137.8, 136.5, 129.1, 128.5, 92.2, 80.2, 59.8, 54.3, 29.7, 21.7, 9.8. MS (EI, 70 eV) m/z (%): 577.0 (10) [M$^+$], 232.2 (100). HRMS Found: 577.06333. C$_{25}$H$_{30}$NO$_4$RuClS Calc.: 577.06276.

3.5. η^3-(N-Methoxycarbonyl-5-methoxycarbonyl-6-methyl-2-p-toluenesulfonyl-7-azabicyclo[2.2.1]hepta-2,5-dienyl)-η^5-(C$_5$Me$_5$)RuCl (11)

Compound **11** was prepared as described for **8** starting from **10** (565 mg, 1.5 mmol) [1]. This afforded **11** as a colorless oil (710 mg, 73%). ^{1}H NMR (CDCl$_3$): δ 7.67 (d, $J = 7.13$ Hz, 2H), 7.28 (d, $J = 7.04$ Hz, 2H), 5.33 (s, 1H), 5.18 (s, 1H), 5.10 (s, 1H), 3.77 (s, 3H), 3.53 (s, 3H), 2.42 (s, 3H), 2.29 (s, 3H), 1.58 (s, 15H). ^{13}C NMR (CDCl$_3$): δ 169.5, 163.6, 154.4, 143.5, 137.6, 134.3, 129.1, 128.6, 128.4, 92.1, 81.9, 79.4, 77.9, 59.9, 54.5, 51.7, 21.8, 15.8, 9.7. MS (EI, 70 eV) *m/e* (%): 649.1 (20) [M^+], 272.1 (100). HRMS Found: 649.08391. $C_{28}H_{34}ClNO_6RuS$ Calc.: 649.08389.

3.6. η^3-(N-methoxycarbonyl-2,3-dimethoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-dienyl)-η^5-(C_5Me_5)RuCl (13)

Compound **13** was prepared as described for **8** starting from **12** (404 mg, 1.5 mmol) [1]. This afforded **13** as a colorless oil (630 mg, 78%). ^{1}H NMR ($CDCl_3$): δ 7.00 (d, $J = 5.13$ Hz, 1H), 6.45 (d, $J = 5.13$ Hz, 1H), 5.77 (s, 1H), 5.18 (s, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 3.55 (s, 3H), 1.54 (s, 15H). ^{13}C NMR ($CDCl_3$): δ 172.0, 170.8, 154.9, 146.3, 138.3, 92.8, 79.5, 78.2, 73.5, 65.8, 54.2, 51.7, 51.6, 29.7, 9.25. MS (EI, 70 eV) *m/z* (%): 539.1 (18) [M^+], 272.1 (100). HRMS Found: 539.065204. $C_{22}H_{28}NO_6RuCl$ Calc.: 539.06486.

4. Supplementary material available

Tables of atomic coordinates, selected distances and angles, anisotropic thermal parameters and hydrogen atom coordinates and isotropic displacement parameters for **8** are available from the corresponding author (MLT).

Acknowledgements

The National Institute on Drug Abuse (NIDA DA08055) is gratefully acknowledged by MLT for support of this research. The National Science Foundation (CHE-9305492) and the Louisiana Board of Regents are gratefully acknowledged by SPN for support of this research. The Chemical Instrumentation Program of the National Science Foundation (CHE-9120098) is gratefully acknowledged by JLP for the acquisition of the Siemens P4 X-ray diffractometer.

References

[1] Z. Chen and M.L. Trudell, *Chem. Rev.*, *96* (1996) 1179.
[2] C.A. Broka, *Med. Chem. Res.*, *4* (1994) 449.
[3] M. Balci, Y. Sutbeyaz and H. Secon, *Tetrahedron*, *46* (1990) 3715.
[4] S.G. Davies, *Organotransition Metal Chemistry: Applications to Organic Synthesis*, Pergamon Press, Oxford, 1982 and references cited therein.
[5] C.-H. Sun and T.J. Chow, *J. Chem. Soc., Chem. Commun.*, (1988) 535.
[6] C.-H. Sun and T.J. Chow, *Bull. Inst. Chem., Acad. Sin.*, *36* (1989) 23.
[7] C.-H. Sun, T.J. Chow and L.-K. Liu, *Organometallics*, *9* (1990) 560.
[8] T.J. Chow, J.J. Huang, C.-H. Sun and M.F. Ding, *Organometallics*, *12* (1993) 3762.
[9] C.-H. Sun and T.J. Chow, *Bull. Inst. Chem., Acad. Sin.*, *35* (1988) 9.
[10] P.J. Fagan, M.D. Ward, J.V. Caspar, J.C. Calabrese and P.J. Krusic, *J. Am. Chem. Soc.*, *110* (1988) 2981; P.J. Fagan, M.D. Ward, J.V. Caspar and J.C. Calabrese, *J. Am. Chem. Soc.*, *111* (1989) 1698; P.J. Fagan, W.S. Mahoney, J.C. Calabrese and J.D. Williams, *Organometallics*, *9* (1993) 1843.
[11] L. Luo and S.P. Nolan, *Organometallics*, *12* (1993) 4305.
[12] M.O. Albers, D.J. Robinson, A. Shaver and E. Singleton, *Organometallics*, *5* (1986) 2199.
[13] S.A. Serron, L. Luo, C. Li, M.E. Cucullu, E.D. Stevens and S.P. Nolan, *Organometallics*, *14* (1995) 5290.
[14] XSCANS (vers. 2.0), *Diffractometer Control System*, Siemens Analytical X-ray Instruments, Madison, WI.
[15] G.M. Sheldrick, SHELXL-93, *Single X-ray Structural Analysis Program*, University of Gottingen, Germany, 1993.