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11. Compound **3**, a mixture of two diastereomers: TLC(SiO₂, 9:1 ethyl acetate/methanol) *R_f*=0.57; IR 1208 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 3.38 (d), 4.48 (dd), 4.9 (dd), 5.58 (s), 5.69 (dd), 5.92 (dd), 6.12 (d), 6.28 (d), 6.13 (d), 6.44 (d), 7.21-7.41 (m), 7.88 (s), 7.98 (s), 8.10 (s), 8.16 (s).
12. Compound **4**: TLC(SiO₂, 9:1 ethyl acetate/methanol) *R_f*=0.64; IR 1212, 1400 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 3.38 (d, 2H), 4.65 (dd, 1H), 5.61 (brs, 2H), 5.81 (dd, 1H), 6.23 (d, 1H), 6.37 (dd, 1H), 7.22-7.38 (m, 15H), 7.86 (s, 1H), 8.11 (s, 1H).
13. Compound **5**, a mixture of two diastereomers: TLC(SiO₂, 9:1 ethyl acetate/methanol) *R_f*=0.80; IR 1210 cm⁻¹; ¹H-NMR (CDCl₃, 80 MHz) δ 3.40-3.52 (m), 3.97-4.25 (m), 5.42-5.64 (m), 5.81-6.00 (m), 7.10-7.35 (m), 7.70-7.88 (m), 9.73 (brs).
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15. Compound **6**: TLC(SiO₂, 9:1 ethyl acetate/methanol) *R_f*=0.60; mp. 216-218°C (Ref.³, mp. 217-219°C); ¹H-NMR (CDCl₃, 80 MHz) δ 3.15 (d, 1H), 3.52 (d, 2H), 4.08-4.39 (m, 3H), 5.37 (d, 1H), 5.86 (d, 1H), 7.22-7.46 (m, 15H), 7.94 (d, 1H).
16. Compound **7**: mp. 209-211°C (Ref.², mp. 208.5-215°C); [α]_D²⁵ +126.5 (c 0.5, H₂O) (Ref.², +126); ¹H-NMR (CDCl₃, 200 MHz) δ 3.90-4.04 (m, 2H), 4.05-4.15 (m, 1H), 4.23 (dd, 1H), 4.52 (dd, 1H), 5.97 (d, 1H), 6.29 (d, 1H), 7.96 (d, 1H).

Synthesis of 4-Carboxy-5-aryl-5,6-dihydro-2H-1,2,6-thiadiazine 1,1-Dioxides

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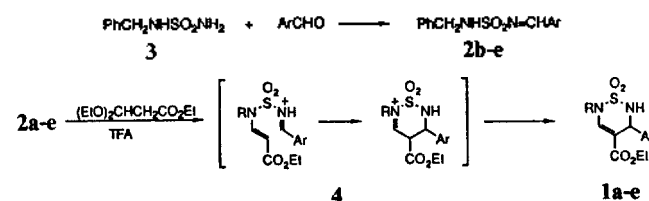
In recent years an increasing number of articles describing the synthesis, properties and biological activities of various heterocycles containing sulfamide unit have appeared,¹ and we have demonstrated that the intramolecular α-sulfamidoalkylation transformations of N-alkylsulfamides could provide those kinds of heterocycles, such as 5,6-dihydro-2H-1,2,6-thiadiazine 1,1-dioxide derivatives.² Two general, acid-mediated procedures have been reported for the preparation of such 1,2,6-thiadiazine 1,1-dioxides.³ The first entails the reac-

Table 1. Synthesis of N-Arylidenesulfamides **2** and 1,2,6-Thiadiazine 1,1-Dioxides **1**

Compound	mp. (°C)	yield (%)	Compound	mp (°C)	yield (%)
2a^b	105-106	65	1a	oil	42
2b	106-108	75	1b	122-124	50
2c	81-83	68	1c	oil	43
2d	118-120	81	1d	116-118	53
2e	130-133	73	1e	oil	40

tion of sulfamides with an equimolar amounts of 1,3-difunctionalized compounds and the second process entails the treatment of sulfamides with two equivalents of a carbonyl compound containing an acidic alpha hydrogen.

We now wish to report on the use of the above α-sulfamidoalkylation process for the preparation of 4-carboxy-5-aryl-5,6-dihydro-2H-1,2,6-thiadiazine 1,1-dioxides **1** from N-arylidenesulfamides **2** and ethyl 3,3-diethoxypropionate in trifluoroacetic acid.



a R=H, Ar=phenyl. **b** R=benzyl, Ar=phenyl. **c** R=benzyl, Ar=1-naphthyl. **d** R=benzyl, Ar=4-methoxyphenyl. **e** R=benzyl, Ar=4-bromophenyl

N-Benzylidenesulfamide (**2a**) and N-benzylsulfamide (**3**) were prepared following the known procedures^{2b,4,5} and the N-arylidene-N'-benzylsulfamides **2b-e** were prepared by condensing aromatic aldehydes with N-benzylsulfamide (**3**) in the presence of *p*-toluenesulfonic acid (see Table 1). Reaction of these N-arylidenesulfamides **2** with ethyl 3,3-diethoxypropionate in trifluoroacetic acid then afforded the 4-carboxy-5-aryl-5,6-dihydro-2H-1,2,6-thiadiazine 1,1-dioxides **1** (see Table 1) by undergoing intramolecular α-sulfamidoalkylation process through iminium ion **4**.

The typical procedure for the synthesis of **1** is as follows: A solution of **2d** (305 mg, 1 mmol) and ethyl 3,3-diethoxypropionate (190 mg, 1 mmol) in trifluoroacetic acid (10 ml) was stirred at rt for 48 hr and then concentrated in vacuo. Column chromatography (chloroform) of the residue afforded 220 mg (53% yield) of **1d**: IR (KBr) 3350, 1705, 1355, 1125 cm⁻¹; ¹H-NMR (CDCl₃) δ 0.97 (t, 3H, *J*=7.0, -CH₃), 3.77 (s, 3H, -OCH₃), 3.92-3.97 (m, 2H, -OCH₂-), 4.63 (d, 1H, *J*=15.2 Hz, CH₂Ph), 4.68 (d, 1H, *J*=8.2 Hz, CHAr), 4.75 (d, 1H, *J*=15.2 Hz, CH₂Ph), 5.50 (d, 1H, *J*=8.2 Hz, NH), 6.83 (d, 2H, *J*=11.6 Hz), 7.20 (d, 2H, *J*=11.6 Hz), 7.35-7.45 (m, 5H), 7.38 (s, 1H, =CH-) ppm; ¹³C-NMR (CDCl₃) δ 13.88, 52.37, 55.21, 59.14, 60.33, 108.00, 114.02, 128.34, 128.49, 128.92, 129.00, 129.48, 130.16, 134.85, 140.77, 159.58 ppm.

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Heteroleptic Crown Thioether Chemistry. Synthesis and Characterization of the Group 9 Metal Complexes of 1,4,7-Trithiacyclononane

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Owing to the unique electronic and structural properties, 1,4,7-trithiacyclononane(9S3), a nine-membered crown thioether, has been successfully employed in the development of crown thioether chemistry.¹⁻³ Particularly, 9S3 derives its strong chelating ability from the retention of endodentate conformation on binding to a trigonal face of a metal, leading to an observation of large set of homoleptic complexes of lower oxidation state transition metal ions³ as well as *p*-block metal ion.⁴ On the other hand, heteroleptic 9S3 complexes, which appear in the form of metal carbonyls,⁵ metal halides,⁶ metal hydride,⁷ metal oxides⁸ or organometallic compounds,⁹ constitute a newly emerging class. Described herein are brief accounts of synthesis and structural characterization of the type [L_nM(9S3)]^{z+}, a set of novel heteroleptic crown thioether complexes with varying L, c and the Group 9 metal M.

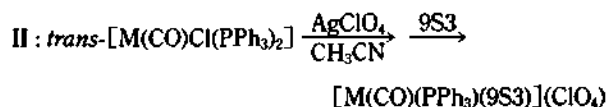
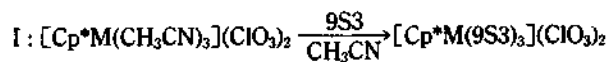
Dicationic [Cp^{*}M(9S3)]²⁺ (1: M=Co; 2: M=Rh; 3: M=Ir) and monocationic [M(CO)(PPh₃)(9S3)]⁺ (4: M=Rh; 5: M=Ir) were prepared as perchlorate salts according to the reaction Scheme I and II, respectively.¹⁰ In the Scheme I acetonitrile solutions of [Cp^{*}M(CH₃CN)₃](ClO₄)₂ (M=Co, deep purple;

Table 1. Spectroscopic Data for 9S3 Complexes of Group 9 Metals.

[Cp [*] M(9S3)](ClO ₄) ₂ (CH ₃ CN)			
M	NMR	Cp [*]	9S3
Co	¹ H (CD ₃ CN) ^a	1.70 (s, 15H)	2.91-3.16 (m, 12H)
	¹³ C (CD ₃ CN) ^a	10.2 (C ₅ Me ₅)	38.9
		104 (C ₅ Me ₅)	
Rh	¹ H (d ₆ -DMSO)	1.94 (s, 15H)	3.18-3.27 (m, 12H)
	¹³ C (d ₆ -DMSO)	9.04 (C ₅ Me ₅)	36.7
		106 (C ₅ Me ₅ , ¹ J _{Rh-C} =6.3 Hz)	
Ir	¹ H (CD ₃ CN)	2.04 (s, 15H)	2.84-2.96 (m, 12H)
	¹³ C (CD ₃ CN)	9.27 (C ₅ Me ₅)	38.5
		102 (C ₅ Me ₅)	
[M(CO)(PPh ₃)(9S3)](ClO ₄)			
M	ν_{CO} ^b , cm ⁻¹	¹ H-NMR (d ₆ -DMSO)	³¹ P{ ¹ H}-NMR ^c (d ₆ -DMSO)
Rh	1950	2.41-2.73 (m, 12H, 9S3)	42.4 (d, J _{Rh-P} =128 Hz)
		7.53-7.72 (m, 15H, PPh ₃)	
Ir	1932	2.33-2.73 (m, 12H, 9S3)	12.4
		7.50-7.69 (m, 15H, PPh ₃)	

^a Referenced to TMS. ^b KBr. ^c Referenced to 85% aq H₃PO₄.

Rh, yellow; Ir, orange) were generated *in situ* by stirring the slurry of Cp^{*}Co(CO)I₂¹¹ or [Cp^{*}MCl₂]₂ (M=Rh, Ir) with stoichiometric amount of AgClO₄ in acetonitrile for 1.5-2 h followed by filtration. Addition of 9S3 to the filtrate, stirring the resulting solutions for a period of 12-18 h at r.t., and filtration resulted in orange-red, pale green and pale yellow solution for M=Co, Rh, and Ir, respectively. Recrystallization (CH₃CN/Et₂O) of the solids obtained by treating the foregoing solutions with large amount of Et₂O afforded analytically pure crystalline (ClO₄)₂ · 1 · (CH₃CN) (orange-red; 35%; Anal. Found (Calc.) C, 35.2 (35.2); H, 4.85 (4.92); N, 2.05 (2.28)), (ClO₄)₂ · 2 · (CH₃CN) (green; 80%; Anal. Found (Calc.): C, 32.3 (32.8); H, 4.59 (4.59); N, 1.85 (2.12)) and (ClO₄)₂ · 3 · (CH₃CN) (pale-yellow; 70%; Anal. Found (Calc.): C, 29.2 (28.9); H, 3.98 (4.04); N, 1.69 (1.87)). In the Scheme II, analogous work-up yielded spectroscopically pure



crystalline orange-red 4 · (ClO₄) and yellow 5 · (ClO₄).

Solid infrared spectra of [Cp^{*}M(9S3)](ClO₄)₂(CH₃CN) are all similar and contain the features of Cp^{*}, 9S3, ClO₄ and CH₃CN, which and other spectroscopic data listed in Table 1 indicate that the three complexes have the same structural core whose nature for M=Rh was determined by single crystal X-ray analysis.¹² The structure of cationic species 2, displayed in Figure 1, reveals endo-tridentate ligating nature