

## Synthesis and Reactivities of (Arylsulfonyl)amido Complexes of Ruthenium(II)

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### Introduction

Although early transition metal amide complexes are well documented, mononuclear amido complexes of later transition metals are rather uncommon.<sup>1</sup> Low-valent late transition metals have a strong tendency to form dimeric and oligomeric amide complexes in order to avoid the unfavorable  $p\pi(N)-d\pi(M)$  antibonding interaction. Our interest in (arylsulfonyl)amido complexes ( $M-NHSO_2Ar$ ) comes from the belief that the electron-withdrawing sulfonyl group may relieve the  $p\pi(N)-d\pi(M)$  antibonding interaction by formation of an  $N=S$  double bond. Additionally, tosylamido complexes ( $M-NHTs$ ,  $Ts = tosyl$ ) are potential precursors to tosylimido species ( $M=NTs$ ) that are believed to be the active intermediates in metal-catalyzed olefin aziridination reactions.<sup>2</sup> Recently, Templeton and Brookhart and their co-workers reported that  $W-H$  undergoes insertion reaction with tosyl azide to give  $W-NHTs$ , which can be further oxidized to give  $W=NTs$  species.<sup>3</sup> This finding prompts us to study the analogous reaction with Ru(II) hydrides. We here report the synthesis and molecular structure of tosylamido complexes of Ru(II).

### Experimental Section

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried, distilled, and degassed prior to use. NMR spectra were recorded on a JEOL EX 400 spectrometer. Chemical shifts (in ppm) were reported referenced to  $Si(CH_3)_4$  ( $^1H$ ) and  $H_3PO_4(aq)$  ( $^{31}P$ ). Infrared spectra were obtained on a Perkin-Elmer 16PC FT-IR spectrophotometer. Mass spectra were recorded on a Finnigan MAT-95 mass spectrometer. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

$p-t-BuC_6H_4SO_2Cl$  and  $2,4,6-i-Pr_3C_6H_2SO_2Cl$  were obtained from Aldrich and used as received.  $Ru(Et_2dtc)(PPh_3)_2(CO)H$  ( $Et_2dtc = N,N'$ -diethyldithiocarbamate) was synthesized according to the literature method.<sup>4</sup>  $ArSO_2N_3$  ( $Ar = p-CH_3C_6H_4$ ,  $p-t-BuC_6H_4$ ,  $2,4,6-i-Pr_3C_6H_2$ ) were prepared from  $ArSO_2Cl$  and  $NaN_3$  as described elsewhere.<sup>5</sup>

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**Preparation.  $Ru(Et_2dtc)(PPh_3)_2(CO)(NHSO_2C_6H_4CH_3-p)$  (1).** To a solution of  $Ru(Et_2dtc)(PPh_3)_2(CO)H$  (0.92 g, 1.17 mmol) in toluene (20 mL) was added 1 equiv of  $p-CH_3C_6H_4SO_2N_3$  (0.23 g, 1.17 mmol), and the mixture was stirred at room temperature overnight. The solvent was pumped off, and the residue was recrystallized from  $CH_2Cl_2$ /hexane to give bright yellow crystals (yield 0.89 g, 81%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.44 (t, 3H,  $CH_2CH_3$ ), 0.68 (t, 3H,  $CH_2CH_3$ ), 2.31 (s, 3H,  $p-CH_3$ ), 2.63 (q, 2H,  $CH_2CH_3$ ), 2.90 (q, 2H,  $CH_2CH_3$ ), 6.05 (d, 2H, Ph *m*), 6.85 (d, 2H, Ph *o*), 7.26–7.58 (m, 30H, PPh<sub>3</sub>).  $^{31}P$  NMR ( $CDCl_3$ ):  $\delta$  37.7 (s). MS(FAB):  $m/z$  973 ( $M + 1$ )<sup>+</sup>. IR ( $cm^{-1}$ ): 3369  $\nu(N-H)$ , 1934  $\nu(C=O)$ . Anal. Calcd for  $C_{49}H_{48}N_2O_3P_2S_3Ru$ : C, 60.6; H, 4.9; N, 2.9. Found: C, 60.3; H, 4.8; N, 2.9.

**$Ru(Et_2dtc)(PPh_3)_2(CO)(NHSO_2C_6H_4-t-Bu-p)$  (2).** This was prepared as for **1** from  $Ru(Et_2dtc)(PPh_3)_2(CO)H$  (0.75 mg, 0.95 mmol) and  $p-t-BuC_6H_4SO_2N_3$  (0.233 mg, 0.94 mmol). The product was recrystallized from THF as bright yellow crystals (yield 0.66 g, 69%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.46 (t, 3H,  $CH_2CH_3$ ), 0.68 (t, 3H,  $CH_2CH_3$ ), 1.3 (s, 9H, *t*-Bu), 2.63 (q, 2H,  $CH_2CH_3$ ), 2.89 (q, 2H,  $CH_2CH_3$ ), 6.74 (d, 2H, Ph *m*), 7.04 (d, 2H, Ph *o*), 2.26–7.54 (m, 30H, PPh<sub>3</sub>).  $^{31}P$  NMR ( $CDCl_3$ ):  $\delta$  37.5 (s). MS(FAB):  $m/z$  1016 ( $M + 1$ )<sup>+</sup>. IR ( $cm^{-1}$ ), 3306  $\nu(N-H)$ , 1932  $\nu(C=O)$ . Anal. Calcd for  $C_{52}H_{54}N_2O_3P_2S_3Ru$ : C, 61.6; H, 5.3; N, 2.7. Found: C, 61.5; H, 5.3; N, 2.7.

**$Ru(Et_2dtc)(PPh_3)_2(CO)(NHSO_2C_6H_2-2,4,6-i-Pr_3)$  (3).** This was prepared as for **1** from  $Ru(Et_2dtc)(PPh_3)_2(CO)H$  (0.75 g, 0.95 mmol) and  $2,4,6-i-Pr_3C_6H_2SO_2N_3$  (0.29 g, 0.95 mmol). The product was recrystallized from  $Et_2O$  at 0 °C as yellow blocks, which were suitable for a diffraction study (yield 0.51 g, 50%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.45 (t, 3H,  $CH_2CH_3$ ), 0.71 (t, 3H,  $CH_2CH_3$ ), 0.87 (d, 6H,  $CH(CH_3)_2$ ), 0.92 (d, 6H,  $CH(CH_3)_2$ ), 1.20 (d, 6H,  $CH(CH_3)_2$ ), 2.71 (q, 2H,  $CH_2CH_3$ ), 2.81 (sept, 1H,  $CH(CH_3)_2$ ), 2.93 (q, 2H,  $CH_2CH_3$ ), 3.58 (sept, 1H,  $CH(CH_3)_2$ ), 3.74 (sept, 1H,  $CH(CH_3)_2$ ), 6.73 (s, 1H, Ph *m*), 6.95 (s, 1H, Ph *m*), 7.09–7.64 (m, 30H, PPh<sub>3</sub>).  $^{31}P$  NMR ( $CDCl_3$ ):  $\delta$  38.0 (s). MS(FAB):  $m/z$  1084 ( $M + 1$ )<sup>+</sup>. IR ( $cm^{-1}$ ), 3330  $\nu(N-H)$ , 1938  $\nu(C=O)$ . Anal. Calcd for  $C_{57}H_{54}N_2O_3P_2S_3Ru$ : C, 58.0; H, 5.4; N, 2.4. Found: C, 57.0; H, 5.5; N, 2.4.

**$(CO)(Et_2dtc)(PPh_3)Ru(\mu-Et_2dtc)(\mu-I)Ru(CO)I(PPh_3)$  (4).** To a solution of **2** (0.3 g, 0.3 mmol) in  $CH_2Cl_2$  at 0 °C was added a solution of  $I_2$  in  $CH_2Cl_2$  (0.075 g in 15 mL) dropwise. The resulting red solution was stirred at room temperature overnight. The solvent was pumped off in vacuo, and the residue was recrystallized from  $CH_2Cl_2/Et_2O$  to give red plates (yield 0.13 g, 50%). X-ray-quality crystals were obtained by recrystallization from a saturated  $CH_2Cl_2$ /hexane solution.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.86 (t, 3H,  $CH_3CH_2$ ), 0.98 (t, 3H,  $CH_3CH_2$ ), 1.09 (t, 3H,  $CH_3CH_2$ ), 1.23 (t, 3H,  $CH_3CH_2$ ), 3.32 (q, 2H,  $CH_3CH_2$ ), 3.47 (q, 2H,  $CH_3CH_2$ ), 3.74 (q, 2H,  $CH_3CH_2$ ), 3.91 (q, 2H,  $CH_3CH_2$ ), 7.20–7.64 (m, 30H, PPh<sub>3</sub>). IR ( $cm^{-1}$ ): 1940  $\nu(C=O)$ . Anal. Calcd for  $C_{48}H_{50}N_2I_2O_2P_2S_4Ru_2$ : C, 36.0; H, 3.8; N, 2.1. Found: C, 37.1; H, 3.8; N, 2.3.

**Reaction of **2** with HCl.** To a solution of **2** (0.1 g, 0.1 mmol) in  $CH_2Cl_2$  (15 mL) was added 1 equiv of HCl (ca. 0.1 mL of a 1 M solution in ether) at room temperature, and the mixture was stirred for 2 h. The solvent was evaporated to dryness, and the residue was washed with  $Et_2O$ . The yellow solid obtained was characterized as  $Ru(Et_2dtc)(PPh_3)_2(CO)Cl$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.56 (t, 3H,  $CH_2CH_3$ ), 0.75 (t, 3H,  $CH_2CH_3$ ), 2.69 (q, 2H,  $CH_2CH_3$ ), 3.01 (q, 2H,  $CH_2CH_3$ ), 7.16–7.79 (m, 30H, PPh<sub>3</sub>). IR ( $cm^{-1}$ ): 1940  $\nu(C=O)$ . Evaporation of the  $Et_2O$  washings afforded a white solid, which was identified as  $p-t-BuC_6H_4SO_2NH_2$  by NMR and IR spectroscopy.

**X-ray Analysis.** All X-ray data were collected on a Rigaku AFC7R diffractometer at 295 K using graphite-monochromated Mo  $K\alpha$  radiation. Pertinent crystallographic parameters and refinement data are listed in Table 1. Intensities of three standard reflections were monitored showing neither significant decay of crystals nor instrument instability. Empirical absorption corrections based on  $\psi$  scans of several strong reflection with  $\chi$  close to 90° were applied for both structures. All calculations were performed on a Silicon Graphic workstation with teXsan<sup>6</sup> software package. Both structures were solved by direct methods (SIR88).<sup>7</sup> Full-matrix least-squares refinements with aniso-

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**Table 1.** Crystallographic Data for **3** and **4**·0.5CH<sub>2</sub>Cl<sub>2</sub>

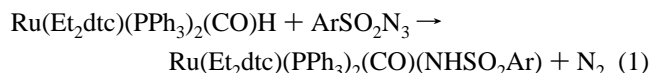
	<b>3</b>	<b>4</b> ·0.5CH <sub>2</sub> Cl <sub>2</sub>
empirical formula	C <sub>57</sub> H <sub>64</sub> N <sub>2</sub> O <sub>3</sub> P <sub>2</sub> S <sub>3</sub> Ru	C <sub>48.5</sub> H <sub>51</sub> N <sub>2</sub> Cl <sub>1.2</sub> O <sub>2</sub> P <sub>2</sub> S <sub>4</sub> Ru <sub>2</sub>
<i>a</i> , Å	13.597(5)	10.960(1)
<i>b</i> , Å	24.348(8)	26.355(3)
<i>c</i> , Å	20.665(5)	19.862(2)
β, deg	108.31(3)	103.92(2)
<i>V</i> , cm <sup>3</sup>	6306(3)	5568.4(9)
<i>Z</i>	4	4
fw	1084.34	1375.54
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)
λ, Å	0.710 73	0.710 73
<i>T</i> , °C	22	22
ρ, g cm <sup>-3</sup>	1.142	1.641
μ, cm <sup>-1</sup>	4.37	19.44
<i>R</i> <sup>a</sup>	0.075	0.049
<i>R</i> <sub>w</sub> <sup>b</sup>	0.113	0.064
GOF	1.77	3.10

<sup>a</sup>  $R = \sum |F_o| - |F_c| / |F_o|$ . <sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|]^2$ . <sup>c</sup> GOF =  $[\sum w(|F_c| - |F_o|)^2 / (N_{obs} - N_{param})]^{1/2}$ .

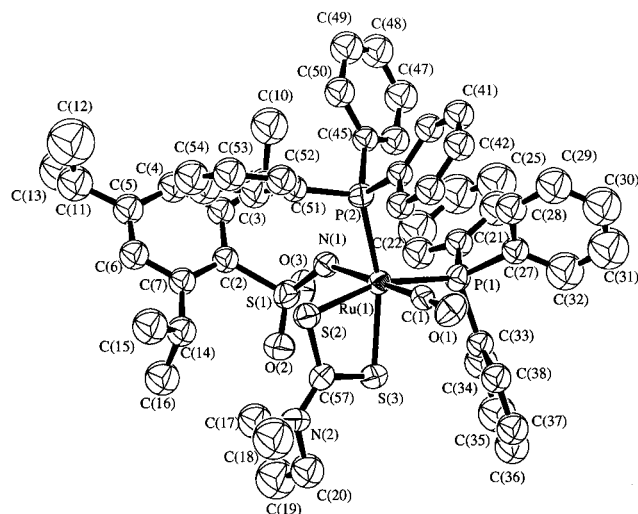
tropic thermal displacement parameters for Ru, S, P, O, N and two carbon atoms in **3** and Ru, I, S, P, O, N and carbon atoms of Et<sub>2</sub>dtc ligands in **4**·0.5CH<sub>2</sub>Cl<sub>2</sub> were carried out. For crystal **3**, the refinement converged to *R* = 7.5% and *R*<sub>w</sub> = 11.3%. For crystal **4**·0.5CH<sub>2</sub>Cl<sub>2</sub>, a 2-fold positional disorder of one phenyl [C(26)–C(27)–C(28)–C(29)–C(30), C(50)–C(51)–C(52)–C(53)–C(54)] ring on the triphenylphosphine was encountered. Subsequently, the atoms belonging to this ring were refined with occupancies 0.5. There is a partially disordered dichloromethane solvent molecule in the crystal lattice. The chlorine atoms of the solvent molecules were refined with an occupancy factor 0.5, while the carbon was not refined. With this model, the refinement converged to *R* = 4.9% and *R*<sub>w</sub> = 6.4%. Final difference Fourier maps revealed no significant features for either structure.

## Results and Discussion

Reactions of low-valent Ru carbonyls with organic azides, depending on the experimental conditions, are known to give the urylene and isocyanate complexes.<sup>8</sup> In this work, we found that the Ru carbonyl hydride Ru(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>(CO)H undergoes insertion with ArSO<sub>2</sub>N<sub>3</sub> (Ar = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, *p*-*t*-BuC<sub>6</sub>H<sub>4</sub>, 2,4,6-*i*-PrC<sub>6</sub>H<sub>2</sub>) to give the corresponding (arylsulfonyl)amido complexes Ru(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>(CO)(NHSO<sub>2</sub>Ar) in good yields (eq 1). No isocyanate or urylene complexes were detected.



These complexes are air-stable in the solid state and moderately air-stable in solution. The structure of the ((2,4,6-triisopropylphenylsulfonyl)amido) derivative **3** has been established by X-ray crystallography. Figure 1 shows a perspective view of the molecule; selected bond distances and angles are given in Table 2. The geometry around Ru is octahedral with the CO and amido group trans to each other. The trans disposition of the carbonyl and amide ligands are in agreement with the bonding picture for Ru(H)(X)[P(*t*-Bu)<sub>2</sub>Me]<sub>2</sub> (X = OR, NHR) suggested by Caulton and co-workers.<sup>9</sup> Remarkably, the Ru–N distance of 2.21(1) Å is significantly longer than that expected for Ru(II)–N(sp<sup>2</sup>). In fact it is not only longer than

**Figure 1.** Perspective view of **3**.**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **3**

Ru(1)–S(2)	2.427(4)	Ru(1)–S(3)	2.417(4)
Ru(1)–P(1)	2.401(4)	Ru(1)–P(2)	2.392(4)
Ru(1)–N(1)	2.21(1)	Ru(1)–C(1)	1.82(1)
S(1)–N(1)	1.57(1)	O(1)–C(1)	1.15(1)
S(1)–Ru(1)–S(2)	72.0(1)	S(2)–Ru(1)–P(1)	162.4(1)
S(2)–Ru(1)–P(2)	89.8(1)	S(2)–Ru(1)–N(1)	90.3(3)
S(2)–Ru(1)–C(1)	89.1(4)	S(3)–Ru(1)–P(1)	90.9(1)
S(3)–Ru(1)–P(2)	161.8(1)	S(3)–Ru(1)–N(1)	92.9(3)
S(3)–Ru(1)–C(1)	86.8(4)	P(1)–Ru(1)–P(2)	107.2(1)
P(1)–Ru(1)–N(1)	94.8(3)	P(1)–Ru(1)–C(1)	85.7(4)
P(2)–Ru(1)–N(1)	86.5(3)	P(2)–Ru(1)–C(1)	93.6(4)
N(1)–Ru(1)–C(1)	179.4(5)	Ru(1)–N(1)–S(1)	138.4(6)
Ru(1)–C(1)–O(1)	176(1)	N(1)–S(1)–C(2)	107.6(6)

a Ru–phenylamide bond (e.g. Ru–N distance in Ru(PMe<sub>3</sub>)<sub>4</sub>H–(NHPh) is 2.160(6) Å<sup>10</sup>) but also longer than a Ru(II)–amine bond (e.g. the Ru–N in [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(Cy<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PCy<sub>2</sub>)(C<sub>8</sub>H<sub>17</sub>NH<sub>2</sub>)<sup>+</sup> is 2.174(8) Å<sup>11</sup>). The long Ru–N bond in **3** may indicate that pπ(N)–dπ(Ru) interaction is not important. Accordingly, the ν(C≡O) for **1–3** (ca. 1932 cm<sup>-1</sup>) are higher than those for the amido–carbonyl complex RuH(NHPh)(CO)[P(*t*-Bu)<sub>2</sub>Me]<sub>2</sub> (1898 cm<sup>-1</sup>), in which the Ru–CO back-bonding is thought to be enhanced by π-donation from the amide.<sup>9</sup> It might also be noted that the N–S distance in **3** of 1.57(1) Å is slightly shorter than that in Tp<sup>+</sup>W(CO)<sub>2</sub>(NHTs)<sup>+</sup> (Tp<sup>+</sup> = hydrotris(3,5-dimethyl-1-pyrazolyl)borate, 1.641(5) Å)<sup>3</sup>, indicative of double-bond character of the S–N bond. Therefore the Ru(II) (arylsulfonyl)amide may be represented by the following resonance structures:



Treatment of **1–3** with HCl gave the chloro complex Ru–(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>(CO)Cl and (arylsulfonyl)amides ArSO<sub>2</sub>NH<sub>2</sub> in good yields. In contrast to the case of other metal amides, no insertion reactions with CO<sub>2</sub> were observed for these complexes. Reaction of **2** with CO led to the isolation of a yellow solid, which shows ν(N–H) at 3400 cm<sup>-1</sup> and two ν(C≡O) bands at

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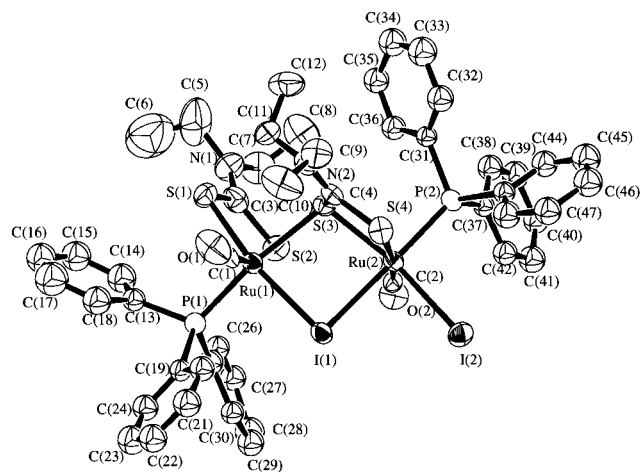


Figure 2. Perspective view of  $4 \cdot 0.5\text{CH}_2\text{Cl}_2$ .

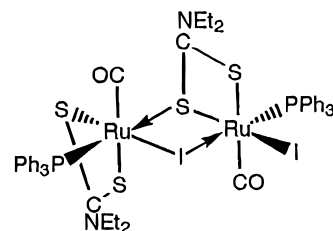
Table 3. Selected Bond Distances (Å) and Angles (deg) for  $4 \cdot 0.5\text{CH}_2\text{Cl}_2$

I(1)–Ru(1)	2.724(2)	I(1)–Ru(2)	2.773(1)
I(2)–Ru(2)	2.751(2)	Ru(1)–S(1)	2.367(4)
Ru(1)–S(2)	2.486(4)	Ru(1)–S(3)	2.448(4)
Ru(1)–P(1)	2.315(1)	Ru(1)–C(1)	1.87(2)
Ru(2)–S(3)	2.395(4)	Ru(2)–S(4)	2.482(4)
Ru(2)–P(2)	2.307(1)	Ru(2)–C(2)	1.85(2)
Ru(1)–I(1)–Ru(2)	88.39(4)	I(1)–Ru(1)–S(1)	168.6(1)
I(1)–Ru(1)–S(2)	98.8(1)	I(1)–Ru(1)–S(3)	82.41(9)
I(1)–Ru(1)–P(1)	91.58(4)	I(1)–Ru(1)–C(1)	96.0(5)
S(1)–Ru(1)–S(2)	71.9(1)	S(1)–Ru(1)–S(3)	89.2(1)
S(1)–Ru(1)–P(1)	95.5(1)	S(1)–Ru(1)–C(1)	92.6(5)
S(2)–Ru(1)–S(3)	78.7(1)	S(2)–Ru(1)–P(1)	94.0(1)
S(2)–Ru(1)–C(1)	163.6(5)	S(3)–Ru(1)–P(1)	169.7(1)
S(3)–Ru(1)–C(1)	96.2(4)	P(1)–Ru(1)–C(1)	92.8(4)
I(1)–Ru(2)–I(2)	86.40(4)	I(1)–Ru(2)–S(3)	83.08(9)
I(1)–Ru(2)–S(4)	91.3(1)	I(1)–Ru(2)–P(2)	176.05(5)
I(1)–Ru(2)–C(2)	83.9(4)	I(2)–Ru(2)–S(3)	164.9(1)
I(2)–Ru(2)–S(4)	97.7(1)	I(2)–Ru(2)–P(2)	95.46(4)
I(2)–Ru(2)–C(2)	89.5(4)	S(3)–Ru(2)–S(4)	71.8(1)
S(3)–Ru(2)–P(2)	95.73(9)	S(3)–Ru(2)–C(2)	100.1(4)
S(4)–Ru(2)–P(2)	91.9(1)	S(4)–Ru(2)–C(2)	171(4)
P(2)–Ru(2)–C(2)	92.6(4)		

2000 and  $1900\text{ cm}^{-1}$ , suggesting the formation of the dicarbonyl complex  $\text{Ru}(\text{PPh}_3)(\text{CO})_2(\text{Et}_2\text{dtc})(\text{NH}\text{SO}_2\text{C}_6\text{H}_4\text{-}i\text{-Bu-}p)$ .

In an attempt to synthesize the first Ru–(arylsulfonyl)imido complexes, the reactions between the (arylsulfonyl)amide complexes with bases and oxidants were studied. Addition of

$n\text{-BuLi}$  to **2** in  $\text{Et}_2\text{O}$  at  $-78\text{ }^\circ\text{C}$  resulted in the formation of an intractable red oil. Treatment of **2** with 1 equiv of  $\text{I}_2$  in  $\text{CH}_2\text{-Cl}_2$  at  $0\text{ }^\circ\text{C}$  afforded a red solution from which the crystalline Ru(II) dimer  $(\text{CO})(\text{Et}_2\text{dtc})(\text{PPh}_3)\text{Ru}(\mu\text{-Et}_2\text{dtc})(\mu\text{-I})\text{Ru}(\text{CO})\text{I}(\text{PPh}_3)$  (**4**) was isolated. Figure 2 shows a perspective view of **4**; selected bond distances and angles are given in Table 3. The structure of **4** consists of two  $[\text{Ru}(\text{Et}_2\text{dtc})(\text{PPh}_3)(\text{CO})\text{I}]$  units bridged by a dithiocarbamate sulfur and an iodine. The unsymmetrically bridging dithiocarbamate can be considered an  $\eta^2$  ligand of Ru(2) and coordinate to Ru(1) via one of the two sulfurs. The Ru(2)–S(3) and Ru(1)–S(3) distances are 2.395(4) and 2.448(4) Å, respectively. A similar bridging coordination mode for dithiocarbamate has been found for the previously reported cation  $[\text{Ru}_2(\text{Et}_2\text{dtc})_5]^+$ .<sup>12</sup> The Ru–Ru' separation is rather long (3.831 Å) indicative of the absence of direct Ru–Ru' bond. The Ru(1)–S(2) and Ru(2)–S(4) bonds, which are trans to CO, are longer than the other Ru–S bonds due to the trans influence of CO.



Complex **4** was possibly formed via the coupling of two coordinately unsaturated  $[\text{Ru}(\text{Et}_2\text{dtc})(\text{PPh}_3)(\text{CO})\text{I}]$  intermediates, the unisolated products of oxidation **2** by  $\text{I}_2$ .<sup>13</sup> The fate of the tosylamide ligand is not clear.

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**Supporting Information Available:** Listings of crystal data (Table S1 and S6), atomic coordinates and isotropic thermal parameters (Tables S2 and S7), anisotropic thermal parameters (Tables S3 and S8), and complete bond distances (Tables S4 and S9) and angles (Tables S5 and S10) (20 pages). Ordering information is given on any current masthead page.

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(13) The cyclic voltammogram of **2** in  $\text{CH}_2\text{Cl}_2$  at a glassy carbon electrode shows a reversible oxidation couple at ca. 0.21 V vs the ferrocenium–ferrocene couple.