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Ru(II)-Catalyzed rearrangement of 2-aryl-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidates

Lingling Peng, Xiu Zhang, Jie Ma, Jianbo Wang*

Beijing National Laboratory of Molecular Sciences (BNLMS) and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

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ABSTRACT

$[RuCl_2(p\text{-cymene})]_2$ efficiently catalyzes the rearrangement of 2-aryl-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate to afford (*Z*)-2,2,2-trichloro-*N*-(4-aryl-1-(phenylthio)penta-2,4-dien-2-yl) acetamide. Ru carbene is assumed as the reactive intermediate in this rearrangement.

1. Introduction

Allene chemistry is a hot research topic in synthetic organic chemistry in recent years. In particular, the transition-metal-catalyzed reaction of allene derivatives has led to many synthetically useful transformations [1–26]. However, there are rare reported examples in which metal carbene is supposed as intermediates in transition-metal-catalyzed reactions of allenes [27–36].

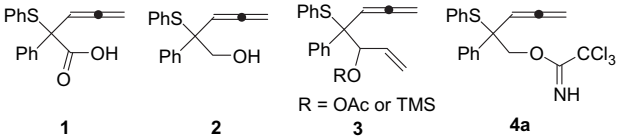
We have recently reported the reaction of $[RuCl_2(p\text{-cymene})]_2$- or $PtCl_2$-catalyzed rearrangement of β-carbonyl allenic sulfides which afford furan products in high yields [31]. The reaction proceeds through 1,4-migration of the sulfanyl group and presumably involves a metal carbene intermediate which is trapped intramolecularly by a carbonyl group (Scheme 1).

Since the carbonyl group of β-carbonyl allenic sulfides can be easily transferred into other functional group, we proceed to extend this investigation by exploring transition-metal-catalyzed reactions of various allenic sulfide derivatives. In this paper we report $[RuCl_2(p\text{-cymene})]_2$-catalyzed rearrangement of allenic sulfides bearing a β-trichloroethanimidyl group. The reaction gives 1, 3-butadiene derivatives in high yields.

2. Results and discussion

The reaction shown in Scheme 1 demonstrates that Ru(II) carbene is generated efficiently from β-carbonyl allenic sulfides. The electron-deficient Ru(II) carbene is then trapped by carbonyl oxygen to afford furan derivative as final product. To further extend this chemistry, we conceived that novel transformations should be possible by converting the carbonyl group into various nucleophilic functional groups.

A series of β-allenic sulfide esters or ketones were prepared from Cu(I)- or Rh(II)- catalyzed reaction of α-diazo carbonyl compounds and propargyl sulfide [37,38]. The ester or ketone group was subsequently converted into various functional groups. Allenic sulfide derivatives **1**, **2**, **3**, and **4a** are prepared and their reactions with transition metals were investigated. Preliminary study shows that no reaction occurs for allenic sulfide derivatives **1**, **2** and **3** under the catalysis with $[RuCl_2(p\text{-cymene})]_2$ or $PtCl_2$. To our delight, we found that $[RuCl_2(p\text{-cymene})]_2$-catalyzed reaction of substrate **4a** leads to clean rearrangement. We then proceeded to study this rearrangement in details.



1 **2** **3** **4a**

* Corresponding author. Tel.: +8610 6275 7248; fax: +8610 6275 1708.
E-mail address: wangjb@pku.edu.cn (J. Wang).

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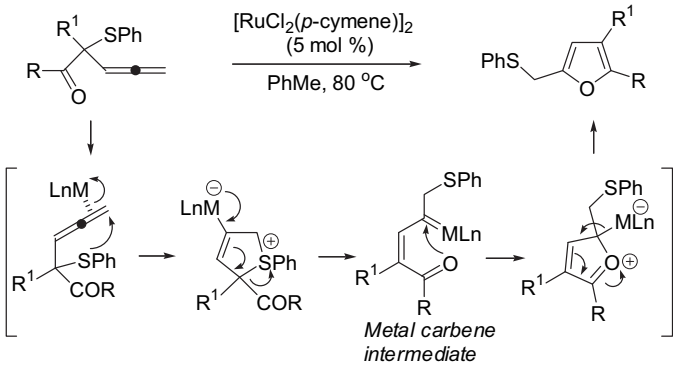
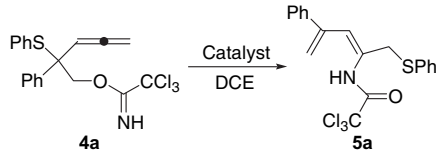


Scheme 1. Ru(II)-Catalyzed reaction of β-carbonyl allenic sulfides.

According to the previous reaction condition for furan formation, allenic sulfide **4a** was firstly treated with 5 mol% [$RuCl_2$(*p*-cymene)]$_2$. It afforded a diene product **5a** in 88% yield in DCE at 60 °C (Table 1, entry 1). The reaction took only 30 min to complete at 60 °C, while the reaction needed 4 h when carried out at room temperature (entry 2). We also examined the reactions of **4a** with other transition metal catalysts in DCE at 60 °C. $PtCl_2$ was also an effective catalyst and afforded **5a** in 50% yield (entry 3). $Rh_2(O_2CCF_3)_4$ only gave **5a** in 8% yield (entry 4). Au catalysts were found not effective for this rearrangement (entries 5–9). AgOTf and Pd(II) catalysts were also not effective (entries 10–12).

Table 1
Reaction of **4a** with various transition-metal complexes.

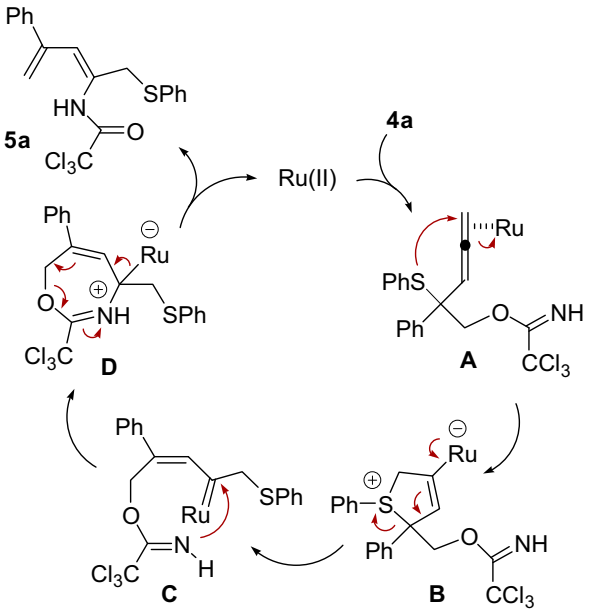


Entry	Catalyst[a]	*T*(°C)	*t*(h)	yield(%)[b]
1	[$RuCl_2$(*p*-cymene)]$_2$	60	0.5	88
2	[$RuCl_2$(*p*-cymene)]$_2$	25	4	90
3	$PtCl_2$	60	4	50
4	$Rh_2(CO_2CF_3)_4$	60	4	8
5	AuCl	60	5	–[c]
6	$AuPPh_3Cl$	60	19	–
7	AuCl + AgOTf	60	22	trace[d]
8	AuCl + $AgBF_4$	60	22	trace
9	AuCl + $AgSbF_6$	60	22	trace
10	AgOTf	60	24	trace
11	$Pd(OAc)_2$	60	19	trace
12	$Pd_2(dba)_3$	60	22	trace

[a] Reactions were carried out with 5 mol % catalyst except for Rh(II) catalyst, in which case 1 mol % catalyst was used.
[b] Isolated yields after column chromatography.
[c] No product **5a** can be identified by TLC.
[d] Small amount of product **5a** can be identified from TLC, most starting material remained or decomposed.

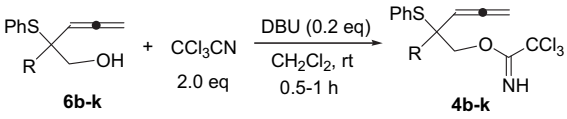
The structure of **5a** was unambiguously confirmed by X-ray analysis of single crystal (Fig. 1) [Appendix A].

Based on our previous study [31], a mechanism for the formation of diene product is proposed as shown in Scheme 2. The metal carbene intermediate **C** is first formed through a similar process as described in Scheme 1. From **C**, the nitrogen atom of the trichloroethanimidyl group interacts with the electron-deficient carbene carbon atom to give **D**, subsequent rearrangement leads to the formation of **5a**, with release of the metal catalyst. As comparison, it is noted that the [33] rearrangement of allyl or propargyl trichloroethanimidate under heating condition (Overman rearrangement) is a general process [39].



Scheme 2. Mechanistic hypothesis for the formation of diene product.

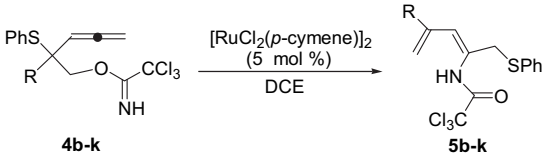
To examine the scope of this novel rearrangement, we then prepared a series of β-trichloroethanimidyl allenic sulfides **4b-k** by DBU-catalyzed reaction of β-allenic sulfide alcohols **6b-k** with trichloroacetonitrile (eq. (1)) [40].



(1)

The [$RuCl_2$(*p*-cymene)$_2$]-catalyzed reaction of **4b-k** was then investigated under the optimized reaction conditions and the results are collected in Table 2. When R is an aryl group, the

Table 2
[$RuCl_2$(*p*-cymene)]$_2$-catalyzed reaction of **4b-k**.



Entry	**4b-k**, R	*T*(°C)	*t*(h)	yield (%)[a]
1	**4b**, *p*-BrC_6H_4	25	4	93
2	**4c**, *p*-$MeOC_6H_4$	25	4	94
3	**4d**, 3,4-$Cl_2C_6H_3$	25	5	86
4	**4d**, 3,4-$Cl_2C_6H_3$	60	0.5	84
5	**4e**, *p*-ClC_6H_4	25	4	89
6	**4f**, *p*-$O_2NC_6H_4$	60	3	70
7	**4g**, *m*-MeC_6H_4	25	5	86
8	**4h**, *m*-$MeOC_6H_4$	25	5	88
9	**4i**, *m*-ClC_6H_4	25	5	81
10	**4i**, *m*-ClC_6H_4	60	0.5	80
11	**4j**, 1-naphthyl	25	23	–[b]
12	**4k**, H	60	72	–

[a] Isolated yields after column chromatography.
[b] The starting material decomposed, but no diene product **5j** or **5k** was identified.

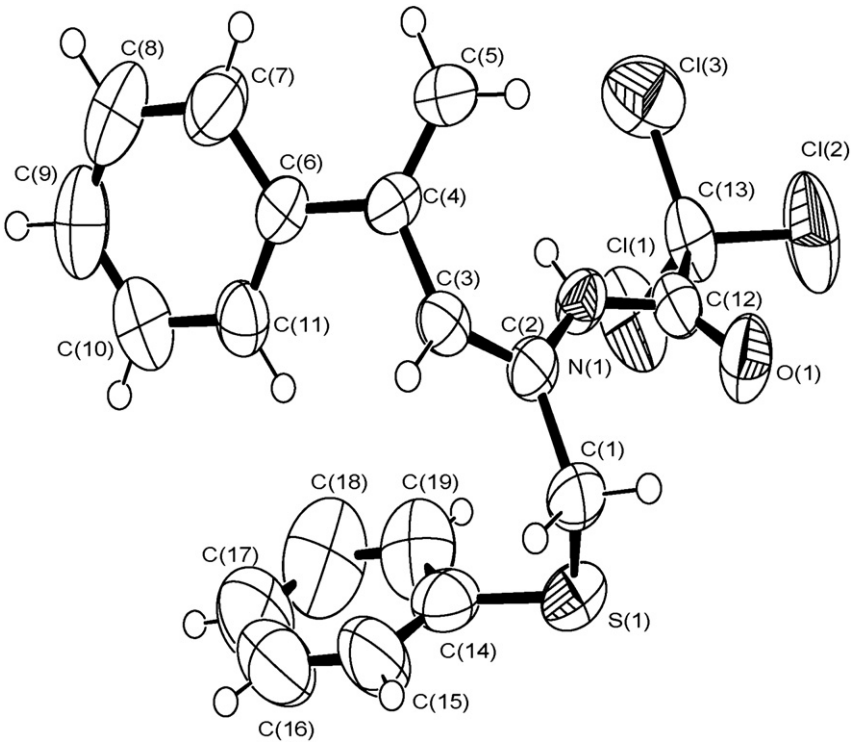


Fig. 1. The X-ray structure of 5a.

reaction proceeds smoothly and affords the corresponding diene products in excellent yields (entries 1–8), except in the case when R is 1-naphthyl group (entry 9). It is noted that when there is electron-deficient substitute on the R group, the reaction is too sluggish at room temperature and the reaction temperature needs to be increased to 60 °C (entries 3, 5). When the R is H, the reaction gave complex mixture after a long reaction time (entry 10). We have also attempted to extend the reaction substrates to these derived from secondary β-allenic sulfide alcohols. However, we failed to synthesize these substrates by the reaction of secondary β-allenic sulfide alcohols with trichloroacetonitrile, presumably due to the steric hindrance of the secondary alcohols.

3. Conclusion

In summary, we have reported the $[RuCl_2(p\text{-cymene})]_2$-catalyzed reaction of 2-aryl-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate, which affords 1,3-diene derivatives in excellent yields [41–45]. The reaction proceeds through 1,4-migration of the sulfanyl group and presumably involves a Ru carbene intermediate which interacts with tethered trichloroethanimidyl group to complete the transformation. This result further demonstrates the diverse reactivity of metal carbene generated from allenic sulfide precursors.

4. Experimental section

4.1. General

All reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask. All solvents were distilled prior to use. Toluene and THF was distilled over sodium, DCE was distilled over NaH. For chromatography, 200–300 mesh silica gel (Yantai, China). ^1H and ^{13}C NMR spectra were recorded at 300 MHz (or 200 MHz) and 75 MHz (or 50 MHz) with Varian Mercury 300 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. Mass spectra were obtained on a VG ZAB-HS mass spectrometer.

4.2. Preparation of 2-aryl-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate 4a-i

Under a nitrogen atmosphere, 2-phenylthio-3,4-pentadienyl alcohol **6a-i** (2.0 mmol) and trichloroacetonitrile (4.0 mmol) were mixed in anhydrous CH_2Cl_2 (20 mL) in a 50 mL round-bottomed flask. To the solution was then added DBU (0.4 mmol) at 0 °C (ice-bath). The reaction was continued at room temperature until completed as judged by TLC. Removal of the solvent in *vacuo* gave a crude residue, which was purified by silica gel column. Elution with petroleum ether/ethyl acetate (200:1) afforded pure product of **4a-i**.

2-Phenyl-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate (**4a**). yield 90%; IR (film) 3338, 3058, 1953, 1663, 1303, 1086, 796, 749, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ = 4.43 (d, J = 11.1 Hz, 1H), 4.51 (dd, J = 11.1, 6.6 Hz, 1H), 4.62 (d, J = 11.1 Hz, 1H), 4.81 (dd, J = 11.1, 6.6 Hz, 1H), 5.67 (t, J = 6.6 Hz, 1H), 7.24–7.45 (m, 8H), 7.60–7.63 (m, 2H), 8.19 (s, 1H); ^{13}C NMR ($CDCl_3$,75 MHz) δ = 56.85, 72.04, 78.80, 91.15, 93.56, 127.61,127.96, 128.03, 128.44, 129.33, 130.83, 137.98, 140.02, 162.30, 207.68. EI-MS (m/z, relative intensity): 411 (M^+, 0.6), 302 (35), 250 (27), 141 (100), 115 (77), 109 (32), 91 (24), 77 (27), 44 (63). HRMS calcd for $C_{19}H_{16}O^{35}Cl_3SN$ [M^+] 411.0018; Found: 411.0000.

2-(4-Bromophenyl)-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate (**4b**). yield 74%; IR (film) 3337, 1953, 1663, 1488, 1302, 1079, 1009, 825, 796, 750, 734, 693 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ = 4.42 (d, J = 11.1 Hz, 1H), 4.51–4.59 (m, 2H), 4.81 (dd, J = 11.1,

6.6 Hz, 1H), 5.60 (t, J = 6.6 Hz, 1H), 7.26–7.50 (m, 9H), 8.22 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 56.40, 71.78, 79.06, 91.00, 93.22, 121.67, 128.51, 129.46, 129.78, 130.34, 131.02, 137.87, 139.18, 162.07, 207.61. EI-MS (m/z, relative intensity): 491 (M^+, 1), 414 (3), 382 (44), 330 (30), 318 (18), 249 (29), 219 (95), 140 (100), 109 (85), 44 (61). HRMS calcd for $C_{19}H_{15}ONS^{35}Cl_3^{79}Br$ [M^+] 488.9123; Found: 488.9119.

2-(4-Methoxyphenyl)-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate (**4c**). yield 85%; IR (film) 3341, 2955, 2835, 1953, 1663, 1510, 1300, 1252, 1182, 1086, 1031, 828, 795, 750, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.79 (s, 3H), 4.40 (d, J = 11.1 Hz, 1H), 4.50 (dd, J = 10.8, 6.6 Hz, 1H), 4.58 (d, J = 11.1 Hz, 1H), 4.79 (dd, J = 10.8, 6.6 Hz, 1H), 5.65 (t, J = 6.6 Hz, 1H), 6.83–6.88 (m, 2H), 7.25–7.56 (m, 7H), 8.19 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 55.21, 56.47, 72.10, 78.73, 91.18, 93.75, 113.31, 128.42, 129.15, 129.26, 131.01, 132.02, 137.92, 158.89, 162.31, 207.60. EI-MS (m/z, relative intensity): 441 (M^+, 8), 332 (15), 318 (14), 280 (66), 171 (50), 133 (100), 77 (22), 44 (92). HRMS calcd for $C_{20}H_{18}O_2^{35}Cl_3SN$ [M^+] 441.0124; Found: 441.0114.

2-(3,4-Dichlorophenyl)-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate (**4d**). Yield 87%; IR (film) 3340, 1953, 1664, 1469, 1380, 1302, 1086, 1029, 855, 824, 795, 751, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 4.40 (d, J = 11.1 Hz, 1H), 4.52 (d, J = 11.1 Hz, 1H), 4.58 (dd, J = 11.1, 6.6 Hz, 1H), 4.85 (dd, J = 11.1, 6.6 Hz, 1H), 5.57 (t, J = 6.6 Hz, 1H), 7.26–7.48 (m, 7H), 7.72 (d, J = 2.1 Hz, 1H), 8.25 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 56.08, 71.68, 79.35, 90.98, 93.04, 127.47, 128.67, 129.72, 129.83, 130.04, 130.48, 131.71, 132.10, 137.93, 140.49, 162.09, 207.69. EI-MS (m/z, relative intensity): 479 (M^+, 0.4), 370 (13), 318 (8), 209 (100), 175 (21), 139 (36), 109 (52). HRMS calcd for $C_{19}H_{14}ONS^{35}Cl_5$ [M^+] 478.9239; Found: 478.9255.

2-(4-Chloroheny)-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate (**4e**). Yield 82%; IR (film) 3341, 1953, 1663, 1491, 1303, 1093, 1013, 827, 795, 750, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 4.42 (d, J = 11.1 Hz, 1H), 4.52–4.59 (m, 2H), 4.82 (dd, J = 11.1, 6.6 Hz, 1H), 5.61 (t, J = 6.6 Hz, 1H), 7.26–7.44 (m, 7H), 7.52–7.57 (m, 2H), 8.22 (s, 1H); ^{13}C NMR($CDCl_3$, 75 MHz) δ = 56.39, 71.91, 79.08, 91.05, 93.33, 128.11, 128.56, 129.49, 130.44, 133.48, 137.92, 138.68, 162.19, 207.68. EI-MS (m/z, relative intensity): 445 (M^+, 0.6), 336 (43), 272 (18), 193 (27), 175 (100), 139 (68), 109 (93). HRMS calcd for $C_{19}H_{15}ONS^{35}Cl_4$ [M^+] 444.9629; Found: 444.9632.

2-(4-Nitrophenyl)-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate (**4f**). Yield 89%; IR (film) 3338, 1953, 1665, 1520, 1348, 1302, 1085, 855, 833, 795, 750, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 4.51 (d, J = 11.1 Hz, 1H), 4.62–4.68 (m, 2H), 4.89 (dd, J = 11.1, 6.6 Hz, 1H), 5.63 (t, J = 6.6 Hz, 1H), 7.27–7.43 (m, 5H), 7.76 (dd, J = 6.9, 2.1 Hz, 2H), 8.18 (dd, J = 6.9, 2.1 Hz, 2H), 8.28 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 56.48, 71.69,79.54, 90.89, 92.89, 123.06, 128.75, 129.20, 129.72, 129.85, 137.86, 147.09, 147.61, 162.01, 207.79. EI-MS (m/z, relative intensity): 456 (M^+, 2), 379 (6), 347 (32), 295 (34), 218 (27), 186 (100), 139 (61), 109 (76), 44 (77). HRMS calcd for $C_{19}H_{15}O_3N_2S^{35}Cl_3$ [M^+] 455.9869; Found: 455.9859.

2-(3-Methylphenyl)-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate (**4g**). Yield 97%; IR (film) 3340, 1953, 1663, 1303, 1087, 998, 852, 831, 796, 752, 702, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.34 (s, 3H), 4.40 (d, J = 11.1 Hz, 1H), 4.48 (dd, J = 11.1, 6.6 Hz, 1H), 4.57 (d, J = 11.1 Hz, 1H), 4.79 (dd, J = 11.1, 6.6 Hz, 1H), 5.66 (t, J = 6.6 Hz, 1H), 7.07–7.09 (m, 1H), 7.19–7.47 (m, 8H), 8.18 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 21.52, 56.78, 71.96, 78.72, 91.17, 93.62, 124.90, 127.90, 128.35, 128.39, 128.69, 129.29, 130.90, 137.52, 138.04, 139.86, 162.27, 207.57. EI-MS (m/z, relative intensity): 425 (M^+, 0.6), 316 (14), 264 (8), 155 (100), 128 (10), 77 (6). HRMS calcd for $C_{20}H_{18}ONS^{35}Cl_3$ [M^+] 425.0175; Found: 425.0161.

2-(3-Methoxyphenyl)-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate (**4h**). Yield 92%; IR (film) 3337, 1953, 1663, 1291, 1260, 1086, 1039, 998, 853, 831, 796, 753, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.80 (s, 3H), 4.41 (d, J = 11.1 Hz, 1H), 4.50 (dd, J = 11.1, 6.6 Hz, 1H), 4.59 (d, J = 11.1 Hz, 1H), 4.80 (dd, J = 11.1, 6.6 Hz, 1H), 5.66 (t, J = 6.6 Hz, 1H), 6.80–6.84 (m, 1H), 7.20–7.47 (m, 8H), 8.19 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 55.23, 56.85, 72.03, 78.80, 91.13, 93.50, 113.18, 113.89, 120.25, 128.42, 128.95, 129.33, 130.79, 137.97, 141.60, 159.22, 162.25, 207.60. EI-MS (m/z, relative intensity): 441 (M^+, 0.4), 332 (16), 280 (17), 171 (100), 141 (25), 44 (20). HRMS calcd for $C_{20}H_{18}O_2NS^{35}Cl_3$ [M^+] 441.0124; Found: 441.0126.

2-(3-Chlorophenyl)-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate (**4i**). Yield 92%; IR (film) 3339, 1952, 1664, 1302, 1086, 999, 854, 829, 795, 750, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 4.40 (d, J = 11.1 Hz, 1H), 4.52–4.58 (m, 2H), 4.84 (dd, J = 11.1, 6.9 Hz, 1H), 5.61 (t, J = 6.9 Hz, 1H), 7.25–7.52 (m, 8H), 7.63 (s, 1H), 8.22 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 56.44, 71.78, 79.14, 91.01, 93.17, 126.13, 127.79, 128.56, 129.22, 129.56, 130.26, 133.92, 137.99, 142.15, 162.14, 207.64. EI-MS (m/z, relative intensity): 445 (M^+, 5), 368 (15), 336 (12), 284 (11), 175 (100), 139 (22), 109 (28). HRMS calcd for $C_{19}H_{15}ONS^{35}Cl_4$ [M^+] 444.9629; Found: 444.9636.

4.3. General procedure for [$RuCl_2$(p-cymene)]$_2$-catalyzed reaction of 2-aryl-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate **4a-i**

Under a nitrogen atmosphere, [$RuCl_2$(p-cymene)]$_2$ (0.025 mmol) and 2-aryl-2-(phenylthio)penta-3,4-dienyl 2,2,2-trichloroacetimidate **4a-i** were mixed in anhydrous DCE (5 mL) in a 25 mL round-bottomed flask. The reaction was continued at room temperature [for some examples the reaction temperature was 60 °C (oil-bath)] until completed as judged by TLC. Removal of the solvent in *vacuo* gave a crude residue, which was purified by silica gel column. Elution with petroleum ether/ethyl acetate (200:1) afforded pure product of **5a i**.

(*Z*)-2,2,2-Trichloro-*N*-(4-phenyl-1-(phenylthio)penta-2,4-dien-2-yl)acetamide (**5a**). IR (film) 3357, 3058, 1724, 1644, 1494, 902, 811, 766, 744, 706, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 4.18 (s, 2H), 5.21 (s, 1H), 5.52 (s, 1H), 5.64 (s, 1H), 6.96–6.99 (m, 2H), 7.21–7.50 (m, 8H), 7.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 38.53, 92.46, 117.84, 120.21, 126.58, 127.49, 128.38, 128.76, 129.03, 132.40, 132.63, 134.01, 138.68, 142.23, 158.38. EI-MS (m/z, relative intensity): 411 (M^+, 22), 302 (79), 230 (26), 156 (44), 141 (100), 115 (56), 77 (44). HRMS calcd for $C_{19}H_{16}O^{35}Cl_3SN$ [M^+] 411.0018; Found: 411.0020.

(*Z*)-2,2,2-Trichloro-*N*-(4-(4-bromophenyl)-1-(phenylthio) penta-2,4-dien-2-yl)acetamide (**5b**). IR (film) 3365, 3073, 1725, 1645, 1487, 1071, 1009, 902, 834, 817, 744, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 4.14 (s, 2H), 5.23 (s, 1H), 5.54 (s, 1H), 5.59 (s, 1H), 6.80 (d, J = 8.7 Hz, 2H), 7.33–7.49 (m, 7H), 7.93 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 38.62, 92.51, 117.88, 119.96, 122.44, 127.57, 128.18, 129.09, 131.71, 132.60, 132.75, 133.91, 137.62, 141.29, 158.38. EI-MS (m/z, relative intensity): 491 (M^+,32), 382 (100), 347 (11), 330 (13), 301 (14), 237 (31), 109 (46), 77 (26). HRMS calcd for $C_{19}H_{15}ONS^{35}Cl_3^{79}Br$ [M^+] 488.9123; Found: 488.9125.

(*Z*)-2,2,2-Trichloro-*N*-(4-(4-methoxyphenyl)-1-(phenylthio) penta-2,4-dien-2-yl)acetamide (**5c**). IR (film) 3356, 2958, 2836, 1723, 1644, 1606, 1509, 1250, 1178, 1031, 837, 814, 744, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.79 (s, 3H), 4.18 (s, 2H), 5.11 (s, 1H), 5.46 (s, 1H), 5.61 (s, 1H), 6.77 (dd, J = 6.9, 2.1 Hz, 1H), 6.91 (dd, J = 6.9, 2.1 Hz, 1H), 7.32–7.38 (m, 3H), 7.46–7.50 (m, 2H), 8.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 38.44, 55.32, 92.58, 114.10, 116.01, 120.29, 127.42, 127.84, 129.01, 131.08, 132.45, 132.57, 134.17, 141.61, 158.37, 159.88. EI-MS (m/z, relative intensity): 441 (M^+, 5), 332 (17), 296

(35), 187 (100), 159 (47), 115 (28), 44 (43). HRMS calcd for $C_{20}H_{18}O_2^{35}Cl_3SN$ [M^+] 441.0124; Found: 441.0127.

(*Z*)-2,2,2-Trichloro-*N*-(4-(3, 4-dichlorophenyl)-1-(phenylthio) penta-2,4-dien-2-yl)acetamide (**5d**). IR (film) 3367, 1726, 1645, 1496, 1136, 1029, 904, 817, 744, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) $\delta = 4.11$ (s, 2H), 5.27 (s, 1H), 5.55 (s, 1H), 5.60 (s, 1H), 6.74 (dd, $J = 8.4$, 2.1 Hz, 1H), 7.20–7.49 (m, 7H), 7.93 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 38.93, 92.48, 118.74, 119.76, 126.00, 127.80, 128.39, 129.20, 130.48, 132.40, 132.54, 132.82, 132.91, 133.74, 138.91, 140.49, 158.40. EI-MS (*m*/*z*, relative intensity): 479 (M^+, 35), 370 (49), 334 (25), 318 (43), 298 (20), 264 (18), 225 (87), 162 (30), 109 (100), 77 (40), 36 (64). HRMS calcd for $C_{19}H_{14}ONS^{35}Cl_5$ [M^+] 478.9239; Found: 478.9235.

(*Z*)-2,2,2-Trichloro-*N*-(4-(4-chlorophenyl)-1-(phenylthio) penta-2,4-dien-2-yl)acetamide (**5e**). IR (film) 3362, 3061, 1725, 1645, 1491, 1013, 902, 837, 814, 744, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) $\delta = 4.15$ (s, 2H), 5.23 (s, 1H), 5.54 (s, 1H), 5.60 (s, 1H), 6.87 (dd, $J = 6.6$, 1.8 Hz, 2H), 7.20 (dd, $J = 6.6$, 1.8 Hz, 2H), 7.34–7.40 (m, 3H), 7.46–7.49 (m, 2H), 7.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 38.63, 92.53, 117.81, 120.02, 127.57, 127.88, 128.76, 129.10, 132.63, 132.76, 133.95, 134.29, 137.17, 141.23, 158.40. EI-MS (*m*/*z*, relative intensity): 445 (M^+, 36), 336 (63), 300 (24), 284 (37), 191 (100), 128 (38), 109(45), 77 (31). HRMS calcd for $C_{19}H_{15}ONS^{35}Cl_4$ [M^+] 444.9629; Found: 444.9639.

(*Z*)-2,2,2-Trichloro-*N*-(4-(4-nitrophenyl)-1-(phenylthio)penta-2,4-dien-2-yl)acetamide (**5f**). IR (film) 3309, 1703, 1649, 1594, 1517, 1492, 1343, 907, 856, 742, 734 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ = 4.12 (s, 2H), 5.42 (s, 1H), 5.66 (s, 1H), 5.71 (s, 1H), 7.07 (d, $J = 8.7$ Hz, 2H), 7.39–7.52 (m, 5H), 7.96 (s, 1H), 8.06 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 39.04, 92.40, 119.83, 120.24, 123.66, 127.37, 127.80, 129.24, 132.67, 132.97, 133.55, 140.75, 145.13, 147.41, 158.40. EI-MS (*m*/*z*, relative intensity): 456 (M^+, 30), 347 (98), 311 (37), 295 (31), 202 (100), 127 (38), 109 (47), 77 (26), 36 (73). HRMS calcd for $C_{19}H_{15}O_3N_2S^{35}Cl_3$ [M^+] 455.9869; Found: 455.9859.

(*Z*)-2,2,2-Trichloro-*N*-(4-(3-methylphenyl)-1-(phenylthio) penta-2,4-dien-2-yl)acetamide (**5g**). IR (film) 3346, 1723, 1642, 1493, 902, 816, 768, 744, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ = 2.29 (s, 3H), 4.17 (s, 2H), 5.19 (s, 1H), 5.46 (s, 1H), 5.66 (s, 1H), 6.76 (d, $J = 7.2$ Hz, 1H), 6.92 (s, 1H), 7.01–7.17 (m, 2H), 7.21–7.38 (m, 3H), 7.42–7.49 (m, 2H), 7.94 (s, 1H); ^{13}C NMR($CDCl_3$, 75 MHz) $\delta = 21.33$, 38.39, 92.42, 118.03, 120.29, 123.84, 127.16, 127.40, 128.78, 128.97, 129.17, 132.10, 132.36, 134.07, 138.53, 138.76, 142.43, 158.34. EI-MS (*m*/*z*, relative intensity): 425 (M^+, 34), 316 (100), 264 (48), 244 (43), 171 (77), 155 (78), 128 (52), 109 (44), 91 (38). HRMS calcd for $C_{20}H_{18}ONS^{35}Cl_3$ [M^+] 425.0175; Found: 425.0182.

(*Z*)-2,2,2-Trichloro-*N*-(4-(3-methoxyphenyl)-1-(phenylthio) penta-2,4-dien-2-yl)acetamide (**5h**). IR (film) 3345, 2937, 1722, 1643, 1576,1489, 1230, 1046, 905, 815, 769, 737, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ = 3.75 (s, 1H), 4.17 (s, 2H), 5.20 (s, 1H), 5.48 (s, 1H), 5.68 (s, 1H), 6.51–6.54 (m, 1H), 6.53 (d, $J = 7.8$ Hz, 1H), 6.72–6.74 (m, 1H), 6.81–6.84 (m, 1H), 7.17 (t, $J = 7.8$ Hz, 1H), 7.23–7.37 (m, 3H), 7.45–7.48 (m, 2H), 7.93 (s, 1H); ^{13}C NMR ($CDCl_3$,75 MHz) δ = 38.40, 55.19, 92.39, 112.20, 113.89, 118.41, 119.06, 120.28, 127.39, 128.98, 129.91, 132.17, 132.25, 134.09, 140.22, 142.25, 158.39, 159.96. EI-MS (*m*/*z*, relative intensity): 441 (M^+, 12), 332 (65), 280 (33), 260 (34), 187 (61), 171 (100), 128 (32), 109 (51), 77 (46). HRMS calcd for $C_{20}H_{18}O_2NS^{35}Cl_3$ [M^+] 441.0124; Found: 441.0139.

(*Z*)-2,2,2-Trichloro-*N*-(4-(3-chlorophenyl)-1-(phenylthio) penta-2,4-dien-2-yl)acetamide (**5i**). IR (film) 3365, 1725, 1644, 1495, 902, 813, 793, 769, 745, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) $\delta = 4.13$ (s, 2H), 5.25 (s, 1H), 5.53 (s, 1H), 5.61 (s, 1H), 6.80–6.83 (m, 1H), 7.09–7.49 (m, 8H), 7.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 38.76, 118.76, 119.76, 124.85, 126.56, 127.72, 128.35, 129.11, 129.91, 132.56, 132.60, 133.68, 134.63, 140.67, 141.18, 158.31. EI-MS (*m*/*z*, relative intensity): 445 (M^+, 20), 336 (100), 300 (20), 284 (19), 218 (19), 191 (41), 175 (78), 109 (70), 77 (39). HRMS calcd for $C_{19}H_{15}ONS^{35}Cl_4$ [M^+] 444.9629; Found: 444.9632.

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Appendix A. Supplementary material

CCDC-783984 contains the supplementary crystallographic data for **5a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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