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# SET pathway in tributylstannyllithium addition to alkynyl Fischer carbene complexes

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## Abstract

The reaction of tributyltin lithium with Fischer type alkynyl carbene complexes has been studied. The reaction proceeds via a nucleophilic pathway to produce the conjugate addition product, and a single electron transfer pathway to afford cyclopentannulated derivatives derived from two units of the alkyne complex. Structure of the latter was confirmed by crystal structure determination of a representative complex.

*Keywords:* Fischer carbene; Single-electron transfer; Tributylstannyllithium; Conjugate addition

## 1. Introduction

Since their discovery by Fischer and Maasböl in 1964 [1], Fischer carbene complexes emerged as valuable building blocks in organic synthesis [2]. The α,β-unsaturated Fischer carbene complexes play a key role in Dötz benzannulation [3] and many other cyclization reactions. Michael addition of carbon nucleophiles to such unsaturated carbene complexes has been well studied [4], but similar examples for metal-based nucleophiles remain scarce. Addition of tin anion to the triple bond of an alkynyl Fischer carbene complex can serve as a convenient route to make complexes tethered with vinyl tin which can in turn be used in tin–lithium exchange reaction [5] or Stille type coupling reactions [6]. We report herein our preliminary results on the addition of tri-*n*-butyltin lithium to a set of alkynyl Fischer carbene complexes. Rather than the conjugate addition product, a cyclopentadiene complex was obtained as the major product by a single electron transfer pathway.

## 2. Results and discussion

Tributyltin lithium was prepared by the addition of butyllithium to hexabutylditin in THF at 0 °C [7]. This THF solution of tributyltin lithium was added to an ethereal solution of tungsten alkynyl complexes **1** at 0 °C. After stirring for 15 min and quenching with water, a new tungsten-containing product **3** was isolated along with the conjugate addition product **2** by chromatography (Scheme 1).

Conjugate addition product **2** was isolated as inseparable mixture of two isomers. The ratio of the *E*:*Z* isomer was determined from the integration of two well separated $-OCH_2-$ proton signals. The signal for *E*-isomer is shielded compared to that of *Z*-isomer. Assignment was made in analogy with isostructural sulfur adducts [8]. The $^{13}C$ NMR signals of carbene carbon

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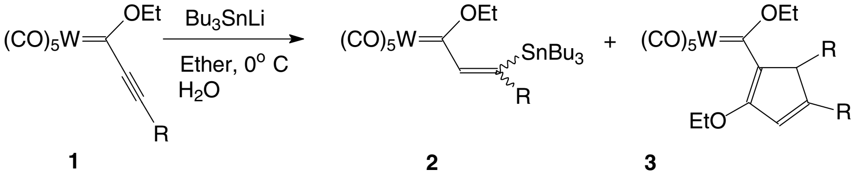


| | | | E:Z |
|---|---|---|---|
| **1a** | R= Phenyl | **2a** | 35:65 |
| **1b** | R= p-Tolyl | **2b** | 45:55 |
| **1c** | R= o-Tolyl | **2c** | 40:60 |
| **1d** | R= p-Chlorophenyl | **2d** | 58:42 |

| Starting material | Michael Adduct | Yield (%) | Annulated product | Yield (%) |
|---|---|---|---|---|
| **1a** | **2a** | 21 | **3a** | 59 |
| **1b** | **2b** | 22 | **3b** | 62 |
| **1c** | **2c** | 21 | **3c** | 60 |
| **1d** | **2d** | 23 | **3d** | 61 |

Scheme 1.

were similarly assigned: 313.3 ppm for *E*-isomer and 310.5 ppm for *Z*-isomer (for compound **2a**).

In the proton NMR spectra of compounds **3a**–**d**, two distinct sets of $–OCH_2CH_3$ signals were observed. There were two well separated clear triplets integrating for three protons each in the upfield region corresponding to the methyl groups. For one $–OCH_2–$ group, two sets of multiplets (one proton each) were observed in the region 4.4–4.7 ppm. The other $–OCH_2–$ group displayed one set of two proton multiplet at 4.59–4.67 ppm. While the data suggested that the product might have resulted from combination of two molecules of carbene complex, they were inadequate for an unambiguous structural assignment. Therefore, diffraction-grade crystals of compound **3** were grown from a solution of dichloromethane–hexane and the structure was established by X-ray diffraction analysis (Fig. 1). Crystallographic and data collection parameters and selected bond lengths and angles for complex **3a** are given in Tables 1 and 2.

The molecular structure does not have any unusual feature. In the crystal lattice, however, several short contacts are observed. Prominent intermolecular interactions consist of (Ar)-H/π (2.862, 2.899 Å), $CH_3$/π (2.734 Å) and (M) CO–H (Ar) (2.687 Å) (relevant diagrams are included in Supporting Information).

Product ratio remains the same when experiments were carried out at 0 or −15 or −78 °C. Changing reaction time does not appreciably alter the product ratio [9]. Moreover, we prepared tributyltin lithium by addition of LDA to a solution of tributyltin hydride in THF [7]. Using the $Bu_3SnLi$ reagent so prepared, the reaction led to similar product distribution. The less reactive amino carbene complex was recovered unaltered under the same reaction conditions (see Scheme 2).

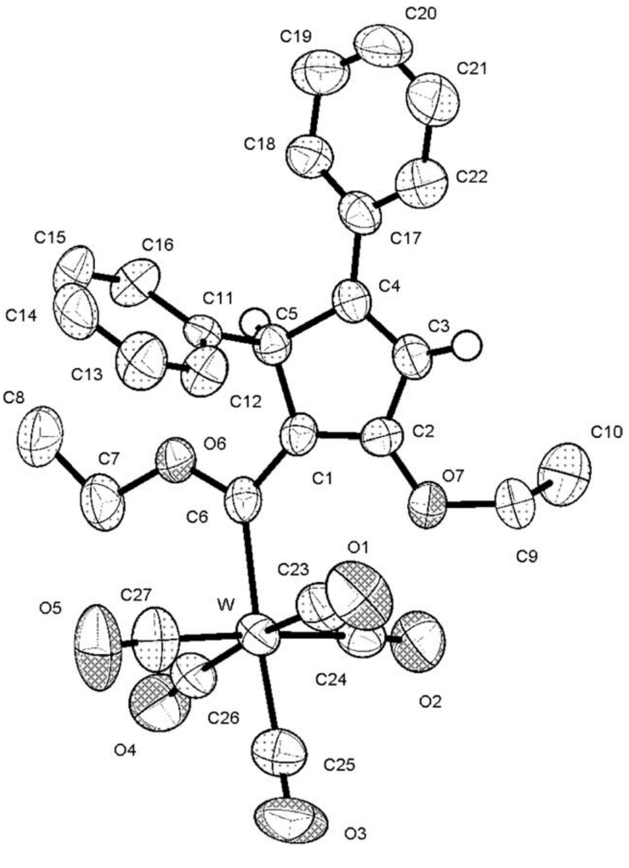


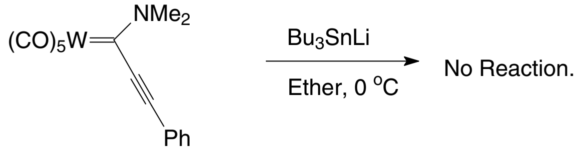
Fig. 1. ORTEP diagram of complex **3a** (50% thermal ellipsoid).

Table 1
Crystal data and structure refinement for compound **3a**

| | |
|---|---|
| Empirical formula | $C_{27}H_{22}O_7W$ |
| Formula weight | 642.30 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system, space group | Orthorhombic, $Pna2_1$ |
| Unit cell dimensions | |
| *a* (Å) | 19.516(19) |
| *b* (Å) | 10.226(10) |
| *c* (Å) | 12.788(12) |
| Volume (Å$^3$) | 2552(4) |
| *Z* | 4 |
| Calculated density (Mg/m$^3$) | 1.672 |
| Absorption coefficient (mm$^{-1}$) | 4.569 |
| *F*(000) | 1256 |
| Crystal size (mm) | 0.14 × 0.09 × 0.09 |
| $\Theta$ range for data collection (°) | 2.09–28.34 |
| Limiting indices | $-25 \leqslant h \leqslant 26$,<br>$-13 \leqslant k \leqslant 13$,<br>$-15 \leqslant l \leqslant 16$ |
| Reflections collected/unique | 18651/5322 [*R*(int) = 0.0444] |
| Completeness to $\theta = 28.34$ | 94.8% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 5322/1/318 |
| Goodness-of-fit on $F^2$ | 1.125 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1 = 0.0485$, $wR_2 = 0.1001$ |
| *R* indices (all data) | $R_1 = 0.0673$, $wR_2 = 0.1065$ |
| Absolute structure parameter | 0.513(16) |
| Largest diff. peak and hole (e Å$^{-3}$) | 1.701 and −0.421 |

Table 2
Selected bond lengths (Å) and bond angles (°) for compound **3a**

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1.375(10) | C(25)–W–C(6) | 174.9(4) |
| C(2)–C(3) | 1.420(11) | C(27)–W–C(26) | 90.2(4) |
| C(3)–C(4) | 1.347(11) | C(1)–C(6)–W | 127.6(5) |
| C(4)–C(5) | 1.532(10) | O(6)–C(6)–W | 128.1(5) |
| C(5)–C(1) | 1.528(10) | O(6)–C(6)–C(1) | 103.8(6) |
| C(1)–C(6) | 1.443(11) | C(1)–C(5)–C(4) | 103.0(6) |
| W–C(6) | 2.215(8) | C(4)–C(3)–C(2) | 110.1(7) |

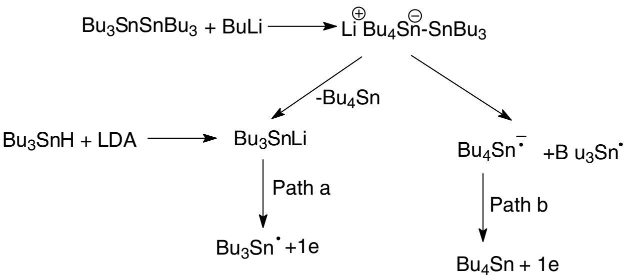


Scheme 2.

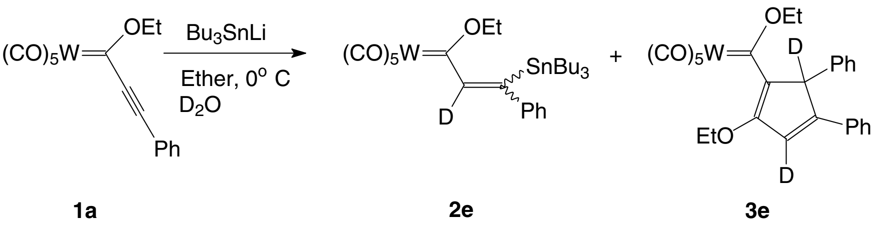
To establish the mechanism of the process, the reaction was repeated as above, but using $D_2O$ as the quenching agent. The deuterium was located at the sites shown in Scheme 3. For compound **2e** integration of the peak corresponding to =CH [singlet at 8.10 ppm (for *Z*-isomer) and singlet in the region 7.11–7.14 ppm for *E* isomer] was substantially reduced. Corresponding carbon signal at 159.9 ppm displayed a multiplet typical of a C–D coupling. Similarly, for compound **3e** the integration of two singlets at 6.97 ppm (=CH) and 5.08 ppm (CHPh) has substantially diminished. In $^{13}$C NMR spectrum, corresponding carbon resonances at 55.5 and 120.6 ppm appear as multiplets.

Trialkyltin anion is known to be an excellent one-electron donor towards alkyl halides [10]. In the reaction of a cyclizable alkyl halide with trialkyltin anion, a cyclized product was observed which supports the radical involvement in the reaction. However, to the best of our knowledge, such type of phenomenon has not been observed yet for the reactions when the electrophile is a Michael acceptor.

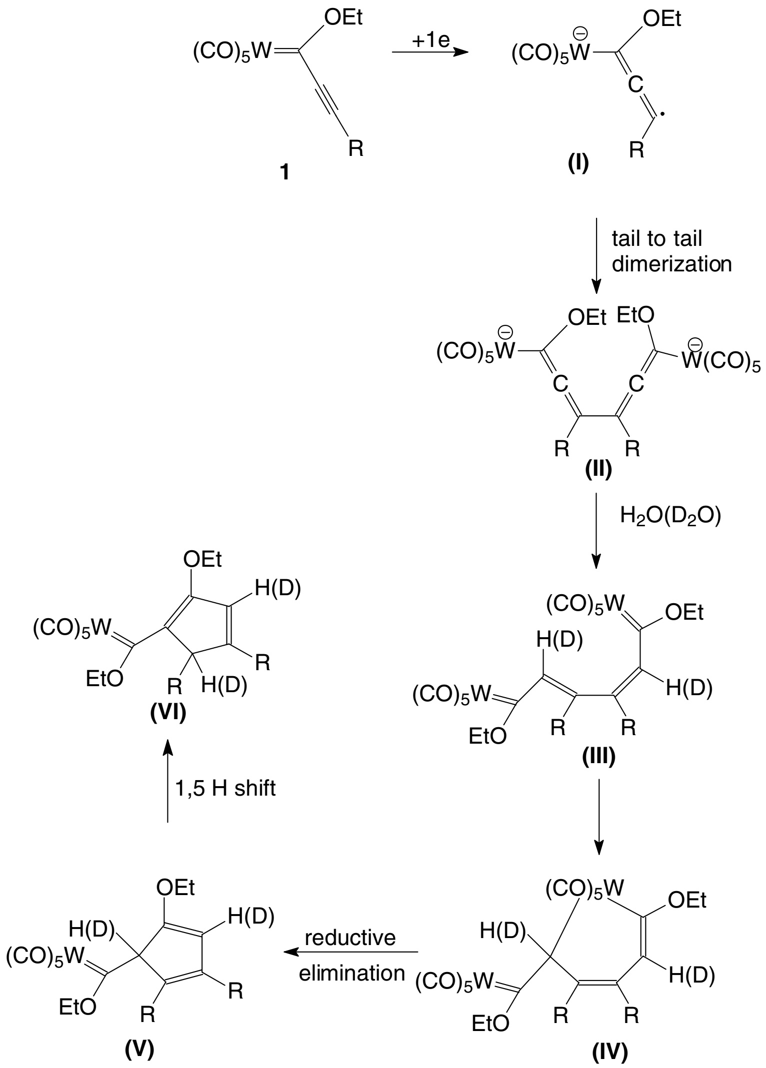
While the products **2a–d** were formed by the anticipated conjugated addition of tin anion on the activated alkyne bond, formation of products **3a–d** can be explained readily by a SET mechanism. A tin-centered anion radical can be generated either from the reaction of hexabutylditin with butyllithium (path *b*) or electron-transfer could occur from tributyltinlithium (path *a*) prepared from $Bu_3SnH$ and LDA, as shown in Scheme 4. Identical products were obtained in comparable yield with both of these procedures. It seems likely, therefore, that path *a* is the likely electron transfer pathway in this reaction. The single electron adds to the alkyne and



Scheme 4.



Scheme 3.



Scheme 5.

triggers the transformation cascade (Scheme 5). When the present work was under way, similar single-electron addition to unsaturated carbene complexes were reported where potassium metal on graphite [11] or samarium iodide [12] was used as single electron reductant.

As depicted in Scheme 5, the first step is a tail-to-tail dimerization. It was followed by a formal electrocyclization after addition of water and reductive elimination afforded the cyclic structure. Position of the hydrogens on the ring was ascertained by deuterium incorporation experiment as discussed before.

## 3. Conclusion

In summary, we have described a reaction pattern of tributyltin lithium with highly polarized alkynyl Fischer carbene complexes. On the basis of the results of the reactions of **1a**–**1d** with tributyltin anion it appears that $Bu_3Sn^-$ serves both as a nucleophile as well as a good single electron donor. The latter attribute produces cyclic products triggered by tail-to-tail dimerization of two carbene complexes. Result of deuterium incorporation experiment is consistent with the proposed mechanism.

## 4. Experimental

All reactions were carried out under an atmosphere of argon. Tetrahydrofuran and ether were distilled under argon from sodium and benzophenone. Acetylenes were prepared from the corresponding aldehyde, following reported procedure [13]. Compound **1a**–**d** were synthesized following reported procedures [14]. All chemicals were purchased from commercial suppliers (Aldrich, Strem, Merck) and used as received. Infrared spectra were recorded on a Shimadzu FTIR-8400 spectrometer and absorptions are expressed in $cm^{-1}$. The $^1H$ and $^{13}C$ NMR spectra were obtained on a Bruker AC200 spectrometer and DRX-500 spectrometer. Elemental analyses were performed by the microanalysis group at NCL using a Carlo-Ebra 1100 automatic analyzer. Melting points were recorded on a Thermonik Campbell melting point apparatus and are uncorrected.

### *4.1. General procedure for preparation of compound **2** and **3***

Tributyltin lithium was prepared following a reported procedure [7]. A solution of hexabutylditin (0.66 mmol) in anhydrous THF (3 ml) under argon was cooled to 0 °C and *n*-BuLi (0.6 mmol) was added dropwise. The solution was stirred at 0 °C for 15 min to obtain a pale yellow solution of $Bu_3SnLi$ (0.6 mmol). It was transferred dropwise to the solution of alkynyl carbene **1** (0.5 mmol) in ether (4 ml) at 0 °C. After 15 min, the reaction mixture was quenched with water and extracted with ether. The ether layer was dried over sodium sulfate and concentrated under vacuum. The crude product was purified by flash column chromatography using dichloromethane in petroleum ether as eluant. Elution with dichloromethane–petroleum ether (10:90) afforded compound **2** and compound **3** was obtained when the eluant was dichloromethane–petroleum ether (25:75).

*Complex* ***2a***. Red liquid, 21%. IR ($CHCl_3$): 1940, 2065 ($\nu_{CO}$). $^1H$ NMR ($CDCl_3$, 200 MHz): Mixture of isomers (*E*:*Z* = 35:65): $\delta$ 8.10 (s, *Z* =C*H*), 7.39–7.21 (m, 3H, Ar*H*), 7.14–7.11 (m, 1 Ar*H* and *E* =C*H*), 6.83 (d, *J* = 8 Hz, 1H, Ar*H*), 5.08 (q, *J* = 8 Hz, *Z* C*H*$_2$), 4.48 (q, *J* = 8 Hz, *E* C*H*$_2$), 1.68 (t, *J* = 8 Hz, *Z* C*H*$_3$), 1.45–1.24 (m, 12H, C*H*$_2$), 1.03–0.74 (m, 15H of $SnBu_3$ and *E* C*H*$_3$). $^{13}C$ NMR ($CDCl_3$, 50.3 MHz): $\delta$ 313.3, 310.5, 204.1, 197.6, 159.9, 156.9, 146.5, 128.6, 128.3, 127.3, 126.7, 125.4, 80.3, 79.3, 29.2, 27.6, 15.6, 13.8, 12.6, 10.7. Anal. Calc. for $C_{28}H_{38}O_6SnW$: C, 43.48; H, 4.91. Found: C, 43.52; H, 4.96%.

*Complex* ***3a***. Red solid, 59% (Dec. Point 105–107 °C). IR ($CHCl_3$): 1923, 2057 ($\nu_{CO}$). $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 7.50–7.48 (m, 2H, Ar*H*), 7.28 (d, *J* = 5 Hz, 3H, Ar*H*), 7.17–7.14 (m, 2H, Ar*H*), 7.09 (d, *J* = 10Hz, 3H, Ar*H*), 6.97 (s, 1H, =C*H*), 5.08 (s, 1H, C*H*), 4.67–4.59 (m, 3H, C*H*$_2$), 4.45–4.42 (m, 1H, C*H*$_2$), 1.70 (t, *J* = 7.5 Hz, 3H, C*H*$_3$), 1.32 (t, *J* = 7.5 Hz, 3H, C*H*$_3$). $^{13}C$ NMR ($CDCl_3$, 125.1 MHz): $\delta$ 280.1, 204.6, 199.4, 175.6, 162.4, 140.3, 138.9, 133.4, 130.0, 128.9, 128.5, 128.2, 127.7, 126.8, 120.6, 77.0, 68.9, 55.5, 15.4, 15.0. Anal. Calc. for $C_{27}H_{22}O_7W$: C, 50.46; H, 3.42. Found: C, 50.52; H, 3.47%.

*Complex* ***2b***. Red liquid, 22%. IR ($CHCl_3$): 1938, 2065 ($\nu_{CO}$). $^1H$ NMR ($CDCl_3$, 200 MHz): Mixture of isomers (*E*:*Z* = 45:55):$\delta$ 8.11 (s, *Z* =C*H*), 7.19–7.03 (m, 3 Ar*H* and *E* =C*H*), 6.72 (d, *J* = 8 Hz, 1H, Ar*H*), 5.07 (q, *J* = 8 Hz, *Z* C*H*$_2$), 4.49 (q, *J* = 8 Hz, *E* C*H*$_2$), 2.37 and 2.31 (s, 3H, C*H*$_3$), 1.68 (t, *J* = 8 Hz, *Z* C*H*$_3$), 1.48–1.24 (m, 12H, C*H*$_2$), 1.02–0.82 (m, 15H of $SnBu_3$ and *E* C*H*$_3$). $^{13}C$ NMR ($CDCl_3$, 50.3 MHz): $\delta$ 309.7, 301.5, 204.1, 197.6, 159.7, 157.5, 154.0, 143.4, 137.4, 129.3, 128.9, 126.9, 125.6, 80.2, 79.3, 29.1, 27.6, 21.4, 15.7, 13.8, 12.6, 10.6. Anal. Calc. for $C_{29}H_{40}O_6SnW$: C, 44.80; H, 5.08. Found: C, 44.83; H, 5.12%.

*Complex* ***3b***. Red solid, 62% (Dec. Point 109–110 °C). IR ($CHCl_3$): 1923, 2056 ($\nu_{CO}$). $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 7.41 (d, *J* = 10 Hz, 2H, Ar*H*), 7.08 (d, *J* = 10 Hz, 3H, Ar*H*), 6.96 (t, *J* = 10 Hz, 3H, Ar*H*), 6.92 (s, 1H, =C*H*), 5.03 (s, 1H, C*H*), 4.67–4.57 (m, 3H, C*H*$_2$), 4.44–4.42 (m, 1H, C*H*$_2$), 2.29 (s, 3H, C*H*$_3$), 2.22 (s, 3H, C*H*$_3$), 1.69 (t, *J* = 7.5 Hz, 3H, C*H*$_3$), 1.34 (t, *J* = 7.5 Hz, 3H, C*H*$_3$). $^{13}C$ NMR ($CDCl_3$, 125.1 MHz): $\delta$ 278.6, 204.7, 199.4, 176.1, 162.9, 140.5, 140.2, 136.1, 135.9, 130.6, 129.7, 129.2, 127.7, 119.5, 76.7, 68.8, 55.0, 21.6, 21.3, 15.5, 15.0. Anal.Calc. for $C_{29}H_{26}O_7W$: C, 51.94; H, 3.88. Found: C, 51.99; H, 3.92%.

*Complex* ***2c***. Red liquid, 21%. IR ($CHCl_3$): 1940, 2065 ($\nu_{CO}$). $^1H$ NMR ($CDCl_3$, 200 MHz): Mixture of isomers (*E*:*Z* = 40:60): $\delta$ 8.02 (s, *Z* =C*H*), 7.19–7.10 (m, 3 Ar*H* and *E* =C*H*), 6.82 (d, *J* = 8 Hz, 1H, Ar*H*), 5.08 (q, *J* = 8 Hz, *Z* C*H*$_2$), 4.48 (q, *J* = 8 Hz, *E* C*H*$_2$), 2.37 and 2.29 (s, 3H, C*H*$_3$), 1.70 (t, *J* = 8 Hz, *Z* C*H*$_3$), 1.44–1.24 (m, 12H, C*H*$_2$), 1.02–0.83 (m, 15H of $SnBu_3$ and *E* C*H*$_3$). $^{13}C$ NMR ($CDCl_3$, 50.3 MHz): $\delta$ 309.6, 301.4, 204.0, 197.6, 159.7, 157.5, 153.8, 143.4, 137.4, 130.1, 128.9, 126.7, 125.5, 80.4, 79.4, 29.2, 27.4, 21.4, 15.7, 13.8, 12.5, 10.8. Anal. Calc. for $C_{29}H_{40}O_6SnW$: C, 44.80; H, 5.08. Found: C, 44.85; H, 5.13%.

*Complex* ***3c***. Red solid, 60% (Dec. Point 109–111 °C). IR ($CHCl_3$): 1926, 2057 ($\nu_{CO}$). $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 7.16–7.14 (m, 2H, Ar*H*), 7.12–6.95 (m, 4H, Ar*H*), 6.75–6.72 (m, 2H, Ar*H*), 6.57 (s, 1H, =C*H*), 5.21(s, 1H, C*H*), 4.61–4.53 (m, 3H, C*H*$_2$), 4.48–4.46 (m, 1H, C*H*$_2$), 2.18 (s, 3H, C*H*$_3$), 2.14 (s, 3H, C*H*$_3$), 1.67 (t, *J* = 7.5 Hz, 3H, C*H*$_3$), 1.05 (t, *J* = 7.5 Hz, 3H, C*H*$_3$). $^{13}C$ NMR ($CDCl_3$, 125.1 MHz): $\delta$ 280.0, 204.5, 199.4, 176.4, 165.3, 139.4, 136.3, 135.6, 135.0, 130.5, 128.7, 128.4, 126.7, 126.3, 125.4, 125.0, 123.7, 77.0, 69.0, 54.6, 20.4, 20.2, 15.0, 14.9. Anal. Calc. for $C_{29}H_{26}O_7W$: C, 51.94; H, 3.88. Found: C, 51.88; H, 3.91%.

*Complex* ***2d***. Red liquid, 23%. IR($CHCl_3$): 1940, 2065 ($\nu_{CO}$). $^1H$ NMR ($CDCl_3$, 200 MHz): Mixture of isomers (*E*:*Z* = 58:42): $\delta$ 8.03 (s, *Z* =C*H*), 7.37–7.21 (m, 2 Ar*H* and *E* =C*H*), 7.03 (d, *J* = 10 Hz, 1H, Ar*H*), 6.76 (d, *J* = 8 Hz, 1H, Ar*H*), 5.07 (q, *J* = 8 Hz, *Z* C*H*$_2$), 4.51 (q, *J* = 8 Hz, *E* C*H*$_2$), 1.67 (t, *J* = 8 Hz, *Z* –C*H*$_3$), 1.47–1.23 (m, 12H, C*H*$_2$), 0.99–0.82 (m, 15H of $SnBu_3$ and *E* C*H*$_3$). $^{13}C$ NMR ($CDCl_3$, 50.3 MHz): $\delta$ 313.3, 310.5, 204.0, 197.6, 160.0, 154.4, 153.7, 145.0, 144.1, 133.4, 131.2, 128.0, 126.8, 80.3, 79.4, 29.1, 27.5, 15.6, 13.8, 12.5, 10.7. Anal. Calc. for $C_{28}H_{37}O_6SnClW$: C, 41.62; H, 4.58. Found: C, 41.66; H, 4.63%.

Complex **3d** Red solid, 61% (Dec. Point 112–114 °C). IR ($CHCl_3$): 1936, 2058 ($\nu_{CO}$). $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 7.41–6.96 (m, 9H, $=$C*H* and Ar*H*), 5.00(s, 1H, C*H*), 4.66–4.53 (m, 3H, C$H_2$), 4.49–4.41 (m, 1H, C$H_2$), 1.69 (t, $J = 7.5$ Hz, 3H, C$H_3$), 1.35 (t, $J = 7.5$ Hz, 3H, C$H_3$). $^{13}$C NMR ($CDCl_3$, 50.3 MHz): $\delta$ 281.0, 204.1, 199.1, 191.4, 175.1, 160.2, 139.9, 137.3, 132.6, 131.5, 130.0, 129.4, 128.9, 128.4, 127.8, 121.2, 76.6, 69.1, 54.6, 15.5, 15.0. Anal. Calc. for $C_{27}H_{20}O_7Cl_2W$: C, 45.56; H, 2.81. Found: C, 45.61; H, 2.84%.

### 4.2. Preparation of compound 2e and 3e

Compound **1a** (241 mg, 0.5 mmol), hexabutylditin (0.33 ml, 0.66 mmol) and *n*-BuLi (0.4 ml, 0.6 mmol, 1.5 M in hexane) and quenching with $D_2O$ (0.4 ml) afforded mixture of **2e** and **3e**. The mixture was separated by flash column chromatography.

*Complex* ***2e***. Red liquid, 21%. IR ($CHCl_3$): 1940, 2065 ($\nu_{CO}$). $^1$H NMR ($CDCl_3$, 200 MHz): Mixture of isomers (*E*:*Z* = 35:65): $\delta$ 7.39–7.21 (m, 3H, Ar*H*), 7.11–7.14 (m, 1 Ar*H*), 6.83 (d, $J = 8$ Hz, 1H, Ar*H*), 5.08 (q, $J = 8$ Hz, *Z* C$H_2$), 4.48 (q, $J = 8$ Hz, *E* C$H_2$), 1.68 (t, $J = 8$ Hz, *Z* C$H_3$), 1.45–1.24 (m, 12H, C$H_2$), 1.03–0.74 (m, 15H of $SnBu_3$ and *E* C$H_3$). $^{13}$C NMR ($CDCl_3$,50.3 MHz): $\delta$ 313.3,310.5, 204.1, 197.6, 159.9 (m), 156.9, 146.5, 128.6, 128.3, 127.3, 126.7, 125.4, 80.3, 79.3, 29.2, 27.6, 15.6, 13.8, 12.6, 10.7. Anal. Calc. for $C_{28}H_{37}DO_6SnW$: C, 43.42; H, 4.78. Found: C, 43.45; H, 4.81%.

*Complex* ***3e***. Red solid, 59% (Dec. Point 105–107 °C). IR ($CHCl_3$): 1938, 2054 ($\nu_{CO}$). $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.50–7.48 (m, 2H, Ar*H*), 7.28 (d, $J = 5$ Hz, 3H, Ar*H*), 7.17–7.14 (m, 2H, Ar*H*), 7.09 (d, $J = 10$ Hz, 3H, Ar*H*), 4.68–4.59 (m, 3H, C$H_2$), 4.46–4.44 (m, 1H, C$H_2$), 1.71 (t, $J = 7.5$ Hz, 3H, C$H_3$), 1.33 (t, $J = 7.5$ Hz, 3H, C$H_3$). $^{13}$C NMR ($CDCl_3$, 125.1 MHz): $\delta$ 279.7, 204.7, 199.3, 175.7, 162.4, 140.2, 138.8, 133.3, 130.0, 128.9, 128.5, 128.1, 127.7, 126.8, 120.4 (m), 76.8, 68.9, 55.4 (m), 15.4, 15.0. Anal. Calc. for $C_{27}H_{20}D_2O_7W$: C, 50.31; H, 3.10. Found: C, 50.39; H, 3.16%.

### 4.3. X-ray crystal structure analysis for compound 3a

Single crystals of the complex were grown by slow evaporation of the solution in mixture of dichloromethane and hexane. Deep red coloured thin needle of approximate size 0.14 × 0.09 × 0.09 mm, was used for data collection on *Bruker SMART APEX* CCD diffractometer using Mo K$\alpha$ radiation with fine focus tube with 50 kV and 40 mA. Crystal to detector distance 6.05 cm, 512 × 512 pixels/frame, Hemisphere data acquisition. Total scans = 3, total frames = 1271, Oscillation/frame −0.3°, exposure/frame = 50.0 s/frame, maximum detector swing angle = −30.0°, beam center = (260.2, 252.5), in plane spot width = 1.24, SAINT integration, $\theta$ range = 2.09 to 28.34°, completeness to $\theta$ of 28.34° is 94.8%. SADABS correction applied, $C_{27}H_{22}O_7W$, $M = 642.30$. Crystals belong to orthorhombic, space group $Pna2_1$, $a = 19.516(19)$ Å, $b = 10.226(10)$ Å, $c = 12.788(12)$ Å, $V = 2552$ (4) Å$^3$, $Z = 4$, $D_c = 1.672$ mg m$^{-3}$, $\mu$(Mo K$\alpha$) = 4.569 mm$^{-1}$, $T = 293(2)$ K, 18651 reflections measured, 5322 unique [$I > 2\sigma(I)$], *R* value 0.0485, $wR_2 = 0.1001$. All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (ShelxTL) [15] was used for structure solution and full matrix least squares refinement on $F^2$. Hydrogen atoms were included in the refinement as per the riding model. Data collection and refinement parameters are listed in Table 1. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 243228.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.08.016.

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