Reactions of Complex Ligands, LXVI[◇]

Diastereomerically Pure 2-Ethynylcyclopropanecarboxylic Acid Derivatives and (2-Ethynylcyclopropyl)methoxycarbene Complexes of Chromium and Tungsten

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Ethynylcyclopropanecarboxylic acid esters **2c/2t** were prepared from phenylbutenyne **1** and ethyl diazoacetate. Pure diastereomers were obtained by chromatography and converted into the corresponding acyl chlorides **4c/4t**. Reaction with $K_2[M(CO)_5]$ (M = Cr, W) affords alkynylcyclopropylcarbene complexes of chromium **7c/7t** and tungsten **8c/8t**. An X-ray structure analysis of **7t** reveals a distorted cyclopropane skeleton.

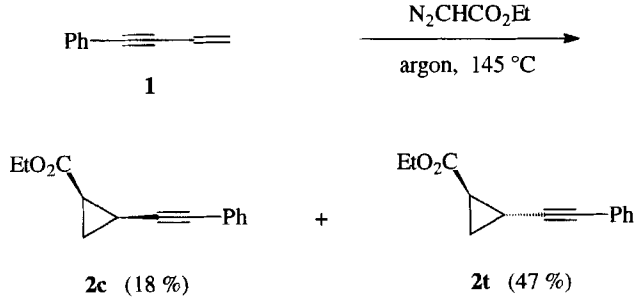
During the past twenty years Fischer-type carbene complexes have become very useful reagents in organic synthesis[2]. Moreover, cyclopropyl derivatives and especially ethynylcyclopropanes are valuable synthons in organic synthesis[3] and have received increasing interest as functional groups in transition metal carbene and carbyne[4] chemistry. Cyclopropylcarbene complexes undergo cycloaddition reactions with alkynes to form five- and seven-membered rings[5], and the cyclopropyl group is known as donor substituent in vinylcarbene complexes[6]. We were interested in exploiting the properties of the cyclopropane ring in chromium-mediated carbon-carbon bond formation, and we now report on a convenient route to novel diastereomerically pure *cis*- and *trans*-2-ethynylcyclopropanecarboxylic acid derivatives **2**–**4**[7] which were subsequently converted into the methoxycarbene complexes of chromium **7** and tungsten **8** as their organometallic analogues. Further, the crystal structure of pentacarbonyl{methoxy[*trans*-2-(phenylethynyl)cyclopropyl]carbene}chromium(0) (**7t**) is reported.

2-Ethynylcyclopropanecarboxylic Acid Derivatives

The addition of ethyl diazoacetate to butenyne **1** occurs predominantly at the carbon-carbon double bond and provides access to both *cis* and *trans* esters **2c/2t** in moderate yields based on easily available starting materials (Scheme 1). The diastereomers were separated by column chromatography on silica gel and isolated as colourless oils in a ratio of **2c/2t** = 1:2.7.

The relative configuration at C-1 and C-2 in the three-membered ring can be deduced unambiguously from their ^{1}H-NMR data by the analysis of the vicinal coupling constants of the cyclopropyl protons. The $^3J_{trans}$ values are distinctly smaller than the $^3J_{cis}$ coupling constants, e.g. $^3J_{cis}$ = 8.41 Hz in **2c** compared with $^3J_{trans}$ = 4.11 in **2t**. Due to diastereotopic hydrogen atoms in the oxymethylene group two doublets of quadruplets are observed for the methylene protons in the *cis* ester **2c**. A similar discrimination within the oxymethylene group of the *trans* isomer **2t** could not be corroborated. The cyclopropanecarboxylic acid derivatives **2**–**4** are configurationally stable under the conditions required for the conversion of the esters **2c/2t** into the acyl chlorides **4c/4t**. The hydrolysis of either ester proceeded with retention of configuration and thus afforded the diastereomerically pure carboxylic acids **3c/3t** which were isolated as colourless crystals after recrystallisation from hexane. Similarly, their chlorination using thionyl chloride occurs without isomerisation as well.

Scheme 1. Preparation of ethyl *cis*- and *trans*-2-ethynylcyclopropanecarboxylate from ethyl diazoacetate and 4-phenyl-1-buten-3-yne (**1**)



2c (18 %) **2t** (47 %)

(2-Ethynylcyclopropyl)methoxycarbene Complexes

The preparation of Fischer carbene complexes from carboxylic acid chlorides is an alternative strategy to the well-known Fischer procedure[8]. It is best performed in a one-

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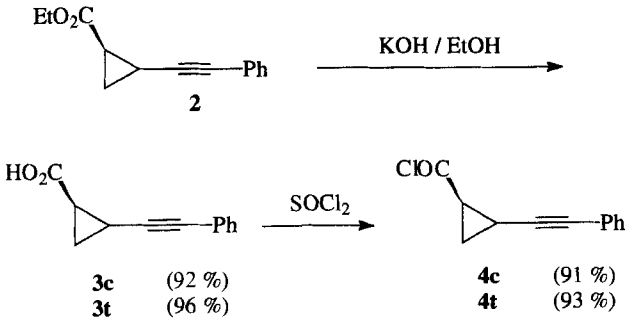
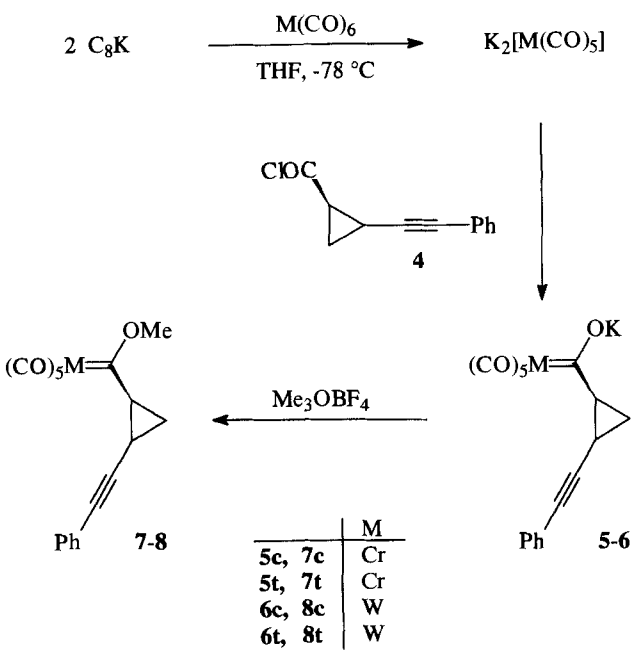
Scheme 2. Preparation of *cis*- and *trans*-2-ethynylcyclopropanecarboxylic acids and acyl chlorides



pot reaction using graphite-potassium laminate as reducing reagent for the hexacarbonylmetal substrate[9]. Upon addition of the acyl chloride isomers **4c/4t** to the pentacarbonylmetalate dianions the acylmetalates **5c/5t** and **6c/6t** were formed, which underwent alkylation with trimethyloxonium tetrafluoroborate to give complexes **7c/7t** and **8c/8t** in 72–82% yield (Scheme 3).

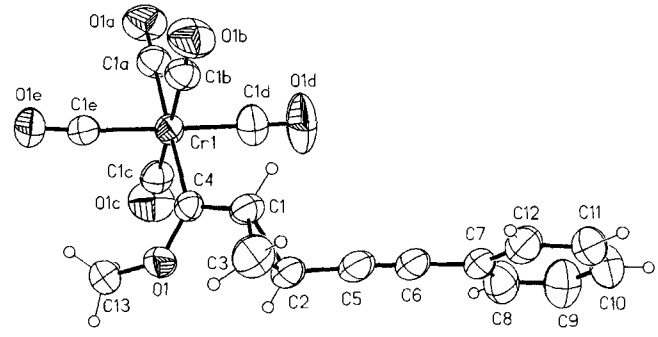
Scheme 3. Synthesis of pentacarbonylcarbene complexes **7c/7t** and **8c/8t**



The potassium pentacarbonylacylmetalates **5–6** could be isolated and stored for weeks at 0 °C without decomposition. The relative configuration of the pure carbene complex diastereomers was determined on the basis of their ^{1}H-NMR spectra and independently established by an X-ray crystal structure analysis of **7t** (Figure 1).

The molecular structure of **7t** demonstrates the *trans* configuration of the cyclopropane skeleton which is attached both to the chromium carbene acceptor and the alkyne π system. As observed in a series of vicinal-disubstituted cyclopropanes[10] the C1–C2 bond [155.0(3) pm] is significantly longer than the other two carbon-carbon bonds within the three-membered ring [C1–C3: 151.1(4); C2–C3: 148.6(4) pm]. In comparison with the parent cyclopropane (C–C: 150.9 pm), the C2–C3 bond is slightly shortened[11] revealing the acceptor properties of the carbene moiety bound to the opposite side[12].

Figure 1. Molecular structure of **7t**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [pm] and angles [°]: Cr(1)–C(4) 202.9(2), C(1)–C(4) 147.6(4), C(4)–O(1) 131.6(3), C(1)–C(2) 155.0(3), C(2)–C(3) 148.6(4), C(1)–C(3) 151.1(4), C(2)–C(5) 144.2(4), C(5)–C(6) 118.8(4); Cr(1)–C(4)–C(1) 121.3(2), Cr(1)–C(4)–O(1) 131.8(2), C(1)–C(4)–O(1) 106.9(2), C(5)–C(6)–C(7) 178.2(3)



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Experimental

All operations except the preparation of compounds **3** and **4** were performed under argon. Solvents were dried by distillation from sodium-potassium alloy and sodium hydride; petroleum ether 40–60 °C. – ^{1}H and ^{13}C NMR: Bruker AM 400. Chemical shifts refer to those of residual solvent signal based on $\delta_{TMS} = 0.00$. – FT-IR: Nicolet Magna 550. – MS: Kratos MS 50 and Hewlett Packard 5972. – Melting points: Büchi SMP 20, uncorrected. – Refractive indices: Zeiss-Abbe refractometer. – Elemental analyses: Heraeus CHN-O-Rapid. – The butenyne **1** was prepared as described by Sonogashira[13]. The mixture of *cis* and *trans* esters **2c/2t** was prepared by a procedure of Yoshimoto[7] using 145 °C as reaction temperature. Pure diastereomers were obtained by column chromatography (silica gel, petroleum ether/diethyl ether, 5:1).

Ethyl cis-2-(Phenylethynyl)cyclopropanecarboxylate (**2c**): R_f = 0.5 (petroleum ether/diethyl ether, 5:1), colourless oil, n_D^{20} = 1.5557. – IR (film): $\tilde{\nu}$ = 2981 cm^{-1}, 2229 (C≡C), 1734 (C=O), 1598, 1382, 1187, 1027, 757, 692. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.24 Hz, 3H; CH_3), 1.29 (ddd, $^3J_{cis}$ = 8.61, 7.82, ^2J = 4.70 Hz, 1H; 3-H), 1.54 (ddd, $^3J_{trans}$ = 6.85, 6.26, ^2J = 4.70 Hz, 1H; 3-H), 1.99 (td, $^3J_{cis}$ = 8.61, $^3J_{trans}$ = 6.85 Hz, 1H; 2-H), 2.03 (ddd, $^3J_{cis}$ = 8.41, 7.82, $^3J_{trans}$ = 6.26 Hz, 1H; 1-H), 4.18 (dq, ^2J = 12.52, ^3J = 7.24 Hz, 1H; OCH_2), 4.21 (dq, ^2J = 12.52, ^3J = 7.24 Hz, 1H; OCH_2), 7.23–7.27 (m, 3H; Ph), 7.34–7.39 (m, 2H; Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7 (C-2), 14.1 (CH_3), 14.3 (C-3), 21.4 (C-1), 60.5 (OCH_2), 79.2 (C≡C), 87.1 (C≡C), 123.2 (*ipso*-C), 127.5 (*m*-C), 127.9 (*o*-C), 131.4 (*p*-C), 169.8 (C=O). – MS (70 eV), *m/z* (%): 214 (40) [M^+], 185 (12) [$M^+ - C_2H_5$], 169 (15) [$M^+ - OC_2H_5$], 141 (100) [$M^+ - COOC_2H_5$], 115 (75) [$C_9H_7^+$], 77 (8) [$C_6H_5^+$]. – $C_{14}H_{14}O_2$ (214.3): calcd. C 78.48, H 6.59; found C 78.26, H 6.45.

Ethyl trans-2-(Phenylethynyl)cyclopropanecarboxylate (**2t**): R_f = 0.68 (petroleum ether/diethyl ether, 5:1), colourless oil, n_D^{20} = 1.5550. – IR (film): $\tilde{\nu}$ = 2982 cm^{-1}, 2233 (C≡C), 1724 (C=O), 1599, 1406, 1325, 1195, 1035, 756, 692. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, ^3J = 7.04 Hz, 3H; CH_3), 1.27 (m_c, 1H; 3-H), 1.45 (ddd, $^3J_{cis}$ = 9.00, $^3J_{trans}$ = 5.09, ^2J = 4.11 Hz, 1H; 3-H), 2.00 (ddd, $^3J_{cis}$ = 8.41, $^3J_{trans}$ = 5.09, 4.11 Hz, 1H; 1-H), 2.03 (ddd, $^3J_{cis}$ = 9.00, $^3J_{trans}$ = 6.26, 4.11 Hz, 1H; 2-H), 4.14 (q, ^3J = 7.04 Hz, 2H; OCH_2), 7.23–7.29 (m, 3H; Ph), 7.33–7.38 (m, 2H; Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.7 (C-2), 13.9 (CH_3), 16.8 (C-3), 22.8 (C-1), 60.7 (OCH_2), 77.5 (C≡C), 89.2 (C≡C), 122.9 (*ipso*-C), 127.7 (*p*-C), 128.0 (*m*-C), 131.4 (*o*-C), 172.0 (C=O). – MS (70 eV), *m/z* (%): 214 (40) [M^+], 185 (12) [$M^+ - C_2H_5$], 169 (15) [$M^+ - OC_2H_5$], 141 (100) [$M^+ - COOC_2H_5$], 115 (75) [$C_9H_7^+$], 77 (8) [$C_6H_5^+$]. – $C_{14}H_{14}O_2$ (214.3): calcd. C 78.48, H 6.59; found C 78.32, H 6.68.

General Procedure for the Preparation of 2-(Phenylethynyl)cyclopropanecarboxylic Acids **3**: To a solution of 9.42 g (168 mmol) of potassium hydroxide in 150 ml of 95% ethanol, 12 g (56 mmol) of pure ester **2c** or **2t** was added, and the mixture was refluxed for 2 h. The ethanol was removed, 190 ml of water was added to the solid, and the solution was extracted with 90 ml of ether. The ether extract was discarded and the aqueous phase acidified to pH 1–2 with hydrochloric acid. The aqueous phase was extracted several times with ether, and the combined ether layers were dried with magnesium sulfate. Removal of ether and recrystallisation yielded the pure acids **3c/3t**.

cis-2-(Phenylethynyl)cyclopropanecarboxylic Acid (**3c**): Yield 9.65 g (52 mmol, 92%), m.p. 91 °C (hexane). – IR (KBr): $\tilde{\nu}$ = 3200–2700 cm^{-1} (OH), 1710 (C=O), 2224 (C≡C), 1228, 758, 695. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.36 (td, $^3J_{cis}$ = 8.22, ^2J = 4.69 Hz, 1H; 3-H), 1.53 (td, $^3J_{trans}$ = 6.55, ^2J = 4.69 Hz, 1H; 3-H), 2.04 (td, $^3J_{cis}$ = 8.22, $^3J_{trans}$ = 6.26 Hz, 1H; 2-H), 2.09 (td, $^3J_{cis}$ = 8.51, $^3J_{trans}$ = 6.84 Hz, 1H; 1-H), 7.18–7.25 (m, 3H, Ph), 7.32–7.37 (m, 2H, Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1 (C-2), 15.4 (C-3), 21.3 (C-1), 80.1 (C≡C), 86.5 (C≡C), 123.2 (*ipso*-C), 127.8 (*p*-C), 128.1 (*m*-C), 131.7 (*o*-C), 176.8 (C=O). – MS (70 eV), *m/z* (%): 186 (91) [M^+], 141 (100) [$M^+ - COOH$], 115 (82) [$C_9H_7^+$], 77 (6) [$C_6H_5^+$]. – $C_{12}H_{10}O_2$ (186.2): calcd. C 77.40, H 5.41; found C 77.06, H 5.55.

trans-2-(Phenylethynyl)cyclopropanecarboxylic Acid (**3t**): Yield 10.06 g (54 mmol, 96%), m.p. 92 °C (hexane). – IR (KBr): $\tilde{\nu}$ = 3200–2800 cm^{-1} (OH), 2228 (C≡C), 1686 (C=O), 1456, 1325, 1234, 760, 692. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.36 (ddd, $^3J_{cis}$ = 8.50, $^3J_{trans}$ = 6.20, ^2J = 4.20 Hz, 1H; 3-H), 1.52 (ddd, $^3J_{cis}$ = 9.00, $^3J_{trans}$ = 5.40, ^2J = 4.20 Hz, 1H; 3-H), 2.03 (ddd, $^3J_{cis}$ = 8.50, $^3J_{trans}$ = 5.40, 4.00 Hz, 1H; 2-H), 2.13 (ddd, $^3J_{cis}$ = 9.00, $^3J_{trans}$ = 6.20, 4.00 Hz, 1H; 1-H), 7.25–7.29 (m, 3H, Ph), 7.33–7.39 (m, 2H, Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.9 (C-2), 17.8 (C-3), 22.9 (C-1), 78.1 (C≡C), 88.7 (C≡C), 122.8 (*ipso*-C), 128.1 (*p*-C), 128.3 (*m*-C), 131.7 (*o*-C), 178.9 (C=O). – MS (70 eV), *m/z* (%): 186 (88) [M^+], 141 (100) [$M^+ - COOH$], 115 (80) [$C_9H_7^+$], 77 (8) [$C_6H_5^+$]. – $C_{12}H_{10}O_2$ (186.2): calcd. C 77.40, H 5.41; found C 77.53, H 5.38.

General Procedure for the Preparation of 2-(Phenylethynyl)cyclopropanecarbonyl Chlorides **4**: 25.83 g (217 mmol) of thionyl chloride was added to 8.44 g (45 mmol) of pure carboxylic acid **3c** or **3t** and the solution stirred until the gas evolution had ceased. Additional warming at reflux for 1 h and removal of excess thionyl chloride in vacuo yielded the crude chlorides **4c** or **4t** as brown oils, which were purified by Kugelrohr distillation.

cis-2-(Phenylethynyl)cyclopropanecarbonyl Chloride (**4c**): Yield 8.39 g (41 mmol, 91%), colourless oil, n_D^{20} = 1.5885. – IR (film): $\tilde{\nu}$ = 2235 cm^{-1} (C≡C), 1782 (C=O), 1492, 1365, 932, 757, 691, 667. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.53 (ddd, $^3J_{cis}$ = 8.70, 7.70, ^2J = 5.10 Hz, 1H; 3-H), 1.70 (ddd, $^3J_{trans}$ = 7.20, 6.00, ^2J = 5.10 Hz, 1H; 3-H), 2.31 (m_c, 1H; 2-H), 2.61 (td, $^3J_{cis}$ = 7.90, $^3J_{trans}$ = 6.00 Hz, 1H; 1-H), 7.23–7.29 (m, 3H; Ph), 7.37–7.42 (m, 2H; Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5 (C-2), 18.5 (C-3), 31.9 (C-1), 81.3 (C≡C), 84.7 (C≡C), 122.5 (*ipso*-C), 128.1 (*p*-C), 128.2 (*m*-C), 131.6 (*o*-C), 169.9 (C=O). – MS (70 eV), *m/z* (rel. ^{35}Cl, %): 204 (8) [M^+], 169 (73) [$M^+ - Cl$], 141 (100) [$M^+ - COCl$], 115 (83) [$C_9H_7^+$]. – $C_{12}H_9ClO$ (204.7): calcd. C 70.43, H 4.43; found C 70.14, H 4.50.

trans-2-(Phenylethynyl)cyclopropanecarbonyl Chloride (**4t**): Yield 8.66 g (42 mmol, 93%), colourless oil, n_D^{20} = 1.5906. – IR (film): $\tilde{\nu}$ = 2237 cm^{-1} (C≡C), 1778 (C=O), 1493, 1386, 1018, 756, 708. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.56 (ddd, $^3J_{cis}$ = 8.30, $^3J_{trans}$ = 6.90, ^2J = 4.70 Hz, 1H; 3-H), 1.76 (ddd, $^3J_{cis}$ = 9.30, $^3J_{trans}$ = 5.30, ^2J = 4.70 Hz, 1H; 3-H), 2.38 (ddd, $^3J_{cis}$ = 9.30, $^3J_{trans}$ = 6.90, 3.80 Hz, 1H; 2-H), 2.52 (ddd, $^3J_{cis}$ = 8.30, $^3J_{trans}$ = 5.30, 3.80 Hz, 1H; 1-H), 7.25–7.31 (m, 3H; Ph), 7.35–7.40 (m, 2H; Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.0 (C-2), 20.3 (C-3), 32.8 (C-1), 79.3 (C≡C), 87.1 (C≡C), 122.3 (*ipso*-C), 128.2 (*p*-C), 128.3 (*m*-C), 131.6 (*o*-C), 172.6 (C=O). – MS (70 eV), *m/z* (rel. ^{35}Cl, %): 204 (10) [M^+], 169 (73) [$M^+ - Cl$], 141 (100) [$M^+ - COCl$], 115 (83) [$C_9H_7^+$]. – $C_{12}H_9ClO$ (204.7): calcd. C 70.43, H 4.43; found C 70.29, H 4.40.

General Procedure for the Preparation of [2-(Phenylethynyl)cyclopropyl]carbene Complexes **7**, **8**: 5 mmol of hexacarbonyl metal (M = Cr, W) was added at −78 °C to a suspension of 1.49 g (11 mmol) of graphite/potassium in 75 ml of dry THF. After 3 h at −78 °C the temp. was raised for 15 min to 0 °C, and then the mixture was recooled to −78 °C. After addition of 1.02 g (5 mmol) of the pure acyl chloride **4c** or **4t** and stirring for 2 h at −40 °C, 0.81 g (5.5 mmol) of trimethyloxonium tetrafluoroborate was added, and the mixture was warmed to room temp. The graphite was filtered off and the solvent removed in vacuo. Chromatography (75 g of silica gel, 21 × 4 cm, −10 °C, petroleum ether/dichloromethane, 5:1) of the orange residue yielded yellow to orange solids.

Pentacarbonyl{methoxy[cis-2-(phenylethynyl)cyclopropyl]carbene}chromium(0) (**7c**): Yield 1.35 g (72%), R_f = 0.41, yellow solid. – IR (hexane): $\tilde{\nu}$ = 2064 cm^{-1} (m, A_1^1; C=O), 1985 (w, B_1; C=O), 1960 (s, A_1^2; C=O), 1946 (s, E; C=O). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.35 (ddd, $^3J_{cis}$ = 8.30, 7.00, ^2J = 4.49 Hz, 1H; 3-H), 2.01 (ddd, $^3J_{trans}$ = 6.95, 6.27, ^2J = 4.49 Hz, 1H; 3-H), 2.49 (td, $^3J_{cis}$ = 8.49, $^3J_{trans}$ = 6.91, 1H; 2-H), 3.82 (ddd, $^3J_{cis}$ = 8.49, 7.00, $^3J_{trans}$ = 6.63 Hz, 1H; 1-H), 4.77 (s, 3H; OCH_3), 7.25–7.29 (m, 3H; Ph), 7.30–7.34 (m, 2H; Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9 (C-2), 19.7 (C-3), 46.8 (C-1), 66.4 (OCH_3), 80.8 (C≡C), 86.3 (C≡C), 123.0 (*ipso*-C), 128.0 (*p*-C), 128.3 (*m*-C), 131.5 (*o*-C), 216.5 (*cis*-C=O), 223.5 (*trans*-C=O), 349.5 (Cr=C). – MS (70 eV), *m/z* (%): 376 (1.2) [M^+], 236 (87) [$M^+ - 5\ CO$], 184 (38) [$M^+ - Cr(CO)_5$], 141 (72) [$M^+ - PhC{\equiv}CC_3H_4^+$], 51 (100) [$C_4H_3^+$]. – $C_{18}H_{12}CrO_6$ (376.3): calcd. C 57.46, H 3.21; found C 57.17, H 3.21.

Pentacarbonyl{methoxy[trans-2-(phenylethynyl)cyclopropyl]carbene}chromium(0) (**7t**): Yield 1.49 g (79%), R_f = 0.47, orange crystals, m.p. 88 °C (dec.). – IR (hexane): $\tilde{\nu}$ = 2064 cm^{-1} (m, A_1^1; C=O), 1987 (w, B_1; C=O), 1960 (s, A_1^2; C=O), 1948 (s, E; C=O). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.56 (ddd, $^3J_{cis}$ = 7.95, $^3J_{trans}$ = 6.75, ^2J = 3.81 Hz, 1H; 3-H), 1.84 (ddd, $^3J_{cis}$ = 8.90, $^3J_{trans}$ = 5.53, ^2J = 3.81 Hz, 1H; 3-H), 2.31 (ddd, $^3J_{cis}$ = 8.90,

$^3J_{trans}$ = 6.75, 3.91 Hz, 1H; 2-H), 3.78 (ddd, $^3J_{cis}$ = 7.95, $^3J_{trans}$ = 5.53, 3.91 Hz; 1-H), 4.68 (s, 3H; OCH_3), 7.25–7.29 (m, 3H; Ph), 7.33–7.39 (m, 2H; Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.6 (C–2), 24.9 (C-3), 49.9 (C-1), 66.8 (OCH_3), 79.7 (C≡C), 88.9 (C≡C), 122.9 (*ipso*-C), 128.2 (*p*-C), 128.3 (*m*-C), 131.7 (*o*-C), 216.3 (*cis*-C=O), 223.4 (*trans*-C=O), 349.2 (Cr=C). – MS (70 eV), *m/z* (%): 376 (0.5) [M^+], 236 (93) [M^+ – 5 CO], 184 (35) [M^+ – $Cr(CO)_5$], 141 (65) [M^+ – $PhC{\equiv}CC_3H_4^+$], 51 (100) [$C_4H_3^+$]. – $C_{18}H_{12}CrO_6$ (376.3): calcd. C 57.46, H 3.21; found C 57.64, H 3.24.

Pentacarbonyl{methoxy[cis-2-(phenylethynyl)cyclopropyl]carbene}tungsten(0) (**8c**): Yield 2.08 g (82%), R_f = 0.45, yellow solid. – IR (hexane): $\tilde{\nu}$ = 2070 cm^{-1} (m, A_1^1; C=O), 1983 (w, B_1; C=O), 1956 (s, A_1^2; C=O), 1944 (s, E; C=O). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (ddd, $^3J_{cis}$ = 8.30, 7.20, ^2J = 4.49 Hz, 1H, 3-H), 2.00 (ddd, $^3J_{trans}$ = 7.00, 6.50, ^2J = 4.49 Hz, 1H; 3-H), 2.50 (td, $^3J_{cis}$ = 8.49, ^3J = 7.00, 1H; 2-H), 3.81 (ddd, $^3J_{cis}$ = 8.49, 7.20, $^3J_{trans}$ = 6.50 Hz, 1H, 1-H), 4.59 (s, 3H; OCH_3), 7.25–7.29 (m, 3H; Ph), 7.31–7.36 (m, 2H; Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4 (C-2), 19.8 (C-3), 49.7 (C-1), 69.1 (OCH_3), 81.0 (C≡C), 86.3 (C≡C), 123.0 (*ipso*-C), 128.1 (*p*-C), 128.3 (*m*-C), 131.4 (*o*-C), 197.4 (s, d, $^1J_{CW}$ = 127.61 Hz, *cis*-C=O), 203.8 (s, d, $^1J_{CW}$ = 117.91 Hz, *trans*-C=O), 324.4 (s, d, $^1J_{CW}$ = 104.04 Hz, W=C). – MS (70 eV), *m/z* (rel. ^{184}W, %): 508 (0.7) [M^+], 368 (12) [M^+ – 5 CO], 184 (40) [M^+ – $W(CO)_5$], 141 (23) [M^+ – $PhC{\equiv}CC_3H_4^+$], 51 (100) [$C_4H_3^+$]. – $C_{18}H_{12}O_6W$ (508.1): calcd. C 42.55, H 2.38; found C 42.64, H 2.62.

Pentacarbonyl{methoxy[trans-2-(phenylethynyl)cyclopropyl]carbene}tungsten(0) (**8t**): Yield 2.03 g (80%), R_f = 0.47, orange crystals, m.p. 85°C. – IR (hexane): $\tilde{\nu}$ = 2071 cm^{-1} (m, A_1^1; C=O), 1983 (w, B_1; C=O), 1958 (s, A_1^2; C=O), 1944 (s, E; C=O). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 (ddd, $^3J_{cis}$ = 8.22, $^3J_{trans}$ = 6.90, ^2J = 3.72 Hz, 1H; 3-H), 1.86 (ddd, $^3J_{cis}$ = 9.30, $^3J_{trans}$ = 5.51, ^2J = 3.72 Hz, 1H; 3-H), 2.31 (ddd, $^3J_{cis}$ = 9.30, $^3J_{trans}$ = 6.90, 3.91 Hz, 1H; 2-H), 3.56 (ddd, $^3J_{cis}$ = 8.22, $^3J_{trans}$ = 5.51, 3.91 Hz, 1H; 1-H), 4.51 (s, 3H; OCH_3), 7.25–7.29 (m, 3H; Ph), 7.33–7.38 (m, 2H; Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.5 (C-2), 24.8 (C-3), 53.3 (C-1), 69.4 (OCH_3), 79.7 (C≡C), 89.0 (C≡C), 122.9 (*ipso*-C), 128.2 (*p*-C), 128.3 (*m*-C), 131.7 (*o*-C), 197.3 (s, d, $^1J_{CW}$ = 127.62 Hz, *cis*-C=O), 203.6 (s, d, $^1J_{CW}$ = 117.20 Hz, *trans*-C=O); 323.7 (s, d, $^1J_{CW}$ = 103.12 Hz, W=C). – MS (70 eV), *m/z* (rel. ^{184}W, %): 508 (0.9) [M^+], 368 (10) [M^+ – 5 CO], 184 (45) [M^+ – $W(CO)_5$], 141 (20) [M^+ – $PhC{\equiv}CC_3H_4^+$], 51 (100) [$C_4H_3^+$]. – $C_{18}H_{12}O_6W$ (508.1): calcd. C 42.55, H 2.38; found C 42.71, H 2.44.

Crystallographic Details of **7t**[14]: Formula $C_{18}H_{12}CrO_6$, molecular mass 376.3 monoclinic, space group $P2_1/c$ (no. 14), Z = 4, a = 1581.0(4), b = 1071.3(2), c = 1101.3(3) pm, β = 107.31(2)°, V = 1.781(1) nm^3, $\rho_{calcd.}$ = 1.40 Mg m^{-3}, μ(Mo-K_α) = 0.67 mm^{-1}, crystal dimensions 0.4 × 0.3 × 0.1 mm, 3342 reflections (3155 unique; R_{int} = 0.025) were measured with a Nicolet R3m diffractometer with graphite-monochromated Mo-K_α radiation (λ = 71.073 pm) at room temperature, $2\Theta_{max}$ = 50° ($-18 \leq h \leq 17$, $-12 \leq k \leq 0$, $0 \leq l \leq 13$). The structure was solved by direct methods (SHELXTL-Plus[15]) and refined on F^2 by full-matrix least-squares techniques (SHELXL-93[16]). All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were refined by using a riding model. R values: R_1 = 0.036 [for $I > 2\sigma(I)$], wR_2 = 0.095 for 3155 reflections with 227 parameters. Largest difference peak 0.19 e $nm^{-3} \cdot 10^3$, largest difference hole – 0.25 e $nm^{-3} \cdot 10^3$. A semi-empirical absorption correction on the basis of ψ scans was applied (min./max. transmission: 0.867/0.987).

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