Novel Synthesis of Oxacycloalkenylidene Complexes and their Annulation to an Acyl Hydroquinone Derivative[1]

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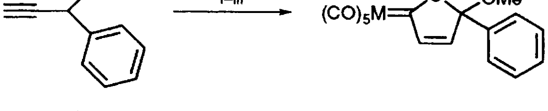
2-Oxacyclopentenylidene complexes of chromium and tungsten are formed in a one pot reaction from lithiated prop-2-ynylic ether and the metal carbonyl; the chromium complex undergoes annulation by tolan to give an acyl hydroquinone skeleton.

Fischer-type carbene complexes have been recognized as valuable reagents in organic synthesis, particularly for cycloaddition reactions and stereoselective C–C bond formation.[2] Compounds with various substitution patterns within the carbene ligand are routinely available.[3] While oxacycloalkylidene complexes are accessible from different procedures,[4–9] only one report refers to their endocyclic α,β-unsaturated congeners.[9] Here we describe a facile one pot synthesis of this type of compound which appeared to us to be an attractive candidate for carbene annulation reactions.



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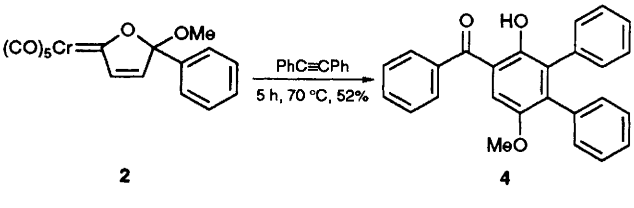
M = Cr: 2, 44%
W: 3, 56%

Scheme 1 *Reagents and conditions*: i, Bu^{n}Li, tetrahydrofuran, −78 °C; ii, M(CO)$_6$, room temp.; iii, SiO$_2$–H$_2$O



2

4

Scheme 2

The lithiated prop-2-ynylic ether derived from 1[†] reacts with hexacarbonyl chromium or tungsten to give the ketal functionalized-2-oxacyclopentenylidene complexes 2 and 3 after quenching with wet silica gel. The structure elucidation of these dark-red 2 and black 3 compounds is based on their coupled ^{13}C NMR spectra, selective irradiation experiments on either 4-H or 5-H and the ^{13}C, ^{183}W-coupling observed for 5-C in the tungsten complex 3.[‡] A mechanistic rationale to the formation of 2 and 3 starts from a lithio allene, present in equilibrium with the lithio propyne. Its addition to the metal carbonyl generates an acyl metallate which undergoes cyclization and after protonation affords the oxacycloalkenylidene complex (Scheme 1).

We were interested in whether the ketal structure in chromium complex 2 might serve as a protected benzoyl group, and thus tested for a rare example of carbene annulation leading to an acceptor-substituted hydroquin-

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[†] Prepared from acetylene, *n*-butyllithium, benzaldehyde and methyl iodide in 68% yield following a modified literature procedure.[10]

[‡] Pentacarbonyl(3-methoxy-3-phenyl-2-oxacyclopent-4-enylidene)-tungsten(0) 3: Fourier transform infrared (FT-IR) (PE): ν(CO)/cm^{-1} 2073, 1966, 1944. High resolution mass spectrometry (HR-MS) (EI): found 495.9910, calcd. 495.9910 for $C_{16}H_{10}O_7{}^{182}W$. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.40 (s, 3H, OMe), 7.03 (d, *J* 5.27 Hz, 1H, 4-H), 7.12 (d, *J* 5.27 Hz, 1H, 5-H), 7.42–7.46 (m, 5H, C$_6$H$_5$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 52.87 [q, $^1J(^{13}C,^1H)$ 144.1 Hz, 1C, OMe], 125.89 [dm, $^1J(^{13}C,^1H)$ 160.2 Hz, 2C, *meta* CH], 126.10 (m, 1C, 3-C), 128.97 [dd, $^1J(^{13}C,^1H)$ 157.7 Hz, $^2J(^{13}C,^1H)$ 6.0 Hz, 2C, *ortho* CH], 129.94 [dm, $^1J(^{13}C,^1H)$ 163.4 Hz, 1C, *para* C], 133.27 (m, 1C, *ipso* C), 144.77 [dd, ddd, $^1J(^{13}C,^1H)$ 178.9 Hz, $^2J(^{13}C,^1H)$ 3.4 Hz, $^2J(^{13}C,^{183}W)$ 12.7 Hz, 1C, 5-C], 145.88 [dd, $^1J(^{13}C,^1H)$ 178.0 Hz, $^2J(^{13}C,^1H)$ 4.2 Hz, 1C, 4-C], 196.66 [s, d, $^1J(^{13}C,^{183}W)$ 127.2 Hz, 4C, *cis* CO], 205.39 [s, d, $^1J(^{13}C,^{183}W)$ 115.3 Hz, 1C, *trans* CO], 295.87 [dd,ddd, $^2J(^{13}C,^1H)$ 14.4 Hz, $^3J(^{13}C,^1H)$ 8.5 Hz, $^1J(^{13}C,^{183}W)$ 104.1 Hz, 1C, 1-C].

one.[11] Upon reaction with tolan, the acyl benzannulation product **4**§ is obtained in 52% yield (Scheme 2). We speculate that the reaction sequence is induced by ring opening of the cyclic ketal followed by methyl migration to generate an alkoxy(*Z*-acylethenyl)carbene ligand. Similar to the annulation of fluorovinyl carbene ligands[11b] no $Cr(CO)_3$ complex could be detected. The combination of endocyclic unsaturation and ketal functionalization makes the oxacycloalkenylidene complexes promising reagents for further synthetic elaboration.

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§ 1-Benzoyl-2-hydroxy-5-methoxy-3,4-diphenylbenzene **4**: FT-IR (KBr): ν/cm^{-1} 3500 (s), 3059 (w), 2930 (s), 2861 (m), 1658 (s), 1450 (s), 1327 (s). HR-MS (EI): found 380.1410, calcd. 380.1412 for $C_{26}H_{20}O_3$. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.78 (s, 3H, OMe), 6.47 (s, 1H, 6-CH), 7.19–7.29 (m, 6H, 3- and 4-, *ortho*- and *para*-CH), 7.32–7.39 (m, 6H, 1-, 3-, and 4-*meta*-CH), 7.47–7.49 (m, 1H, 1-*para*-CH), 7.71 (d, *J* 7.7 Hz, 2H, 1-*ortho*-CH). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 59.74 (1C, OMe), 116.31 (1C, 6-CH), 124.88 (2C), 127.35 (1C), 127.90 (1C), 128.06 (2C), 128.24 (2C), 128.29 (1C, 1-C), 128.70 (2C), 128.85 (1C), 129.78 (2C), 130.12 (2C), 130.20 (1C, 3-C), 130.99 (1C, 4-C), 131.22 (1C, 1-*ipso*-C), 141.13 (2C), 145.90 (1C, 2-C), 151.08 (1C, 5-C), 172.98 (1C, C=O).

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