New Organometallic Derivatives of 1,6-Methano[10]annulene

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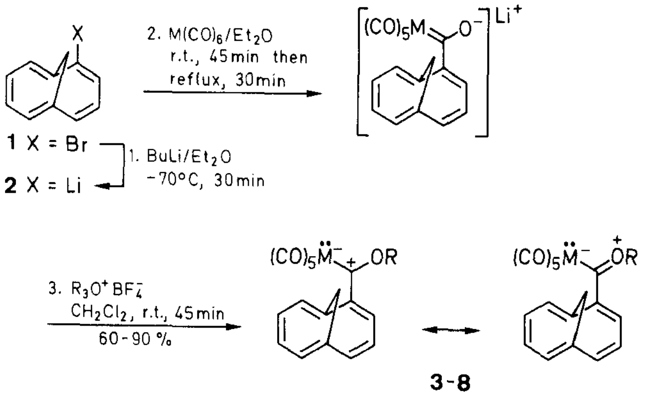
The reverse addition of 2-lithio-1,6-methano[10]annulene (2-lithio-1,6-methanocyclodecapentaene) to some group VI metal carbonyl compounds followed by alkylation with Meerwein salts gave the E. O. Fischer transition metal complexes in good to excellent yields. Cyclization of the chromium complex with diphenylacetylene is achieved in moderate yield.

2-Lithio-1,6-methano[10]annulene (2-lithio-1,6-methanocyclodecapentaene) (**2**) may be prepared in high yield by the action of butyllithium at −60 °C on 2-bromo-1,6-methano[10]annulene (**1**) in diethyl ether. The addition of **2** to a stirred suspension of a group VI transition metal carbonyl compounds in diethyl ether followed by alkylation using either trimethyl- or triethyloxonium tetrafluoroborate in dichloromethane forms the E.O. Fischer transition metal carbene complex.[1,2,3] The tungsten complexes (**3** and **4**) are easily purified using column chromatography followed by recrystallisation from hexane. The chromium complex **5** may be purified in a similarly manner, whilst **6** requires additional purification by preparative TLC. The compounds **7** and **8** could not be obtained in a sufficienty pure state due to their continued rapid decomposition (Table).



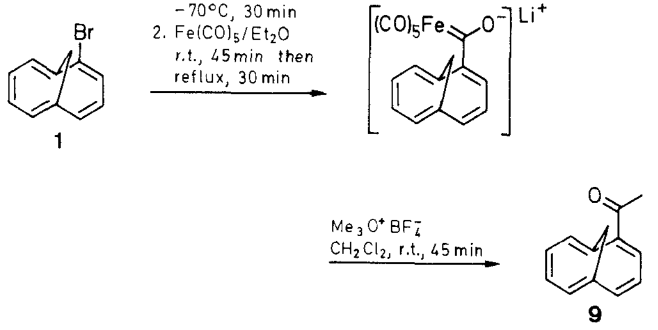
Product	M	R	Product	M	R
3	W	OMe	6	Cr	OEt
4	W	OEt	7	Mo	OMe
5	Cr	OMe	8	Mo	OEt

Compounds **3** and **4** are stable in the solid state at room temperature over a period of months while **5** slowly decays over the same period. Compound **6** totally decomposes within days while **7** and **8** under the same conditions decomposes within hours. Hence the order of stability of the complexes may be summarized as **3** = **4** > **5** > **6** >> **7** > **8**.

It is known that the [methoxy(phenyl)carbene]chromium(0) complex shows a dynamic equilibrium in its ^{1}H-NMR spectrum:[4,5,6] the ^{1}H-NMR spectra of the prepared complexes shows a similar phenomenon. Low temperature ^{1}H-NMR at 213 K in deuterochloroform shows 2 signals for the methoxy group in **5**, namely at $\delta = 4.97$ and 2.65 which corresponds to *cis/trans* isomerism of the system around the partial double bond character of the carbon-oxygen bond. Integration of the signals show that neither isomer is predominant as the integrals are equivalent.

Proof that the carbene carbon atom is positively polarized is shown by ^{13}C-NMR, where the signal has the expected chemical shift in excess of $\delta = 200$ which is in the correct region for a carbocation (see Table).

Attempted repetition of the reaction with iron pentacarbonyl led to the isolation of 2-acetyl-1,6-methano[10]annulene (**9**) in 22 % yield (Collmans Reaction).[7] In this case, initial alkylation occurred at iron, rather than on the carbon atom, followed by reductive elimination. A ketonic carbonyl group is observed at $\nu = 1720\ \text{cm}^{-1}$ in the IR. The poor yield is due to the lability of the carbon-iron bond.



The [3 + 2 + 1] cycloaddition of transition metal carbenes is a well-known reaction, which has potential for the syntheses of new systems, especially as the 3 position in the parent 1,6-methano[10]annulene is tedious to functionalize, allowing future access to new antibiotics and vitamins.[8-14] When one equivalent of **5** is heated with diphenylacetylene in dibutyl ether for 4 hours, upon removal of the solvent a red compounds is isolated. This compound **10** contained no chromium and was liable to further oxidation. In order to characterize this new system, **10** was oxidized using dilute nitric acid in acetic acid to the quinone **11**.[15]

The formation of the new system is due to the incorporation of the alkyne and one carbon monoxide ligand into the chromium containing substrate. Subsequent liability of the new system to oxidation causes the chromium ligand to be lost as chromium oxide.

Table. Compounds 3–8 Prepared

Product	Yield (%)	mp[a] (°C)	Molecular[b] Formula	IR (KBr)[c] ν_{CO} (cm^{-1})	UV/Vis[d] (MeOH) λ_{max}(nm)(log ε)	^{1}H-NMR (CDCl$_3$/TMS)[e] δ, *J* (Hz)	^{13}C-NMR (CDCl$_3$)[e] δ	MS (100 eV)[f] *m/z* (%)
3	90	66	$C_{18}H_{12}O_6W$ (508.1)	2085, 1995, 1840	235 (5.12), 340 (4.70), 390 (4.19)	−0.4 (d, 1H, ^2J = 10.6, H-11a), −0.25 (d, 1H, ^2J = 10.6, H-11b, 4.4 (s, 3H, OCH$_3$), 7.02–7.32 (m, 5H$_{arom}$), 7.4–7.5 (m, 2H$_{arom}$)	204.28	510 (18.2), 396 (100)
4	85	55–57	$C_{19}H_{14}O_6W$ (522.2)	2080, 1990, 1940	235 (5.10), 340 (4.33), 390 (4.17)	−0.4 (d, 1H, ^2J = 9.3, H-11a), −0.25 (d, 1H, ^2J = 9.3, H-11b), 1.55 (t, 3H, *J* = 6.3, CH$_3$), 4.72 (br, 2H, CH$_2$), 7.04–7.3 (m, 5H$_{arom}$), 7.45–7.55 (m, 2H$_{arom}$)	210.88	522 (M$^+$, 14.4), 141 (100)
5	85	70	$C_{18}H_{12}O_6Cr$ (376.3)	2085, 1990, 1950	250 (5.02), 340 (4.14), 400 (4.22)	−0.25 (d, 2H, H-11a, b), 3.52 (br, 3H, OCH$_3$), 6.7–7.6 (m, 7H$_{arom}$)	216.20	376 (M$^+$, 2.3), 52 (100)
6	85	oil	$C_{19}H_{14}O_6Cr$ (390.3)	2060, 2000, 1940	250 (4.98), 330 (4.24), 390 (5.63)	−0.35 (br, 2H, H-11a, b), 1.25 (br, 3H, CH$_3$), 3.45 (br, 3H, OCH$_2$), 6.75–7.5 (br, 7H$_{arom}$)	224.97	390 (M$^+$, 2.5), 52 (100)
7	70	81	$C_{18}H_{12}O_6Mo$ (420.2)	2070, 1990, 1940	245 (5.06), 330 (4.22), 390 (4.15)	−0.4 (d, 1H, ^2J = 10.6, H-11a), −0.25 (d, 1H, ^2J = 10.6, H-11b), 4.6 (br, 3H, CH$_3$), 7.02–7.50 (m, 5H$_{arom}$)	214.05	422 (M$^+$, 6.2), 282 (100)
8	60	oil	$C_{19}H_{14}O_6Mo$ (434.3)	2070, 1990, 1940	250 (5.02), 340 (4.24), 400 (4.22)	−0.4 (d, 1H, ^2J = 9.3, H-11a), −0.25 (d, ^2J = 9.3, H-11b), 1.55 (t, 3H, *J* = 9.3, CH$_3$), 4.72 (br, 2H, CH$_2$), 7.04–7.30 (m, 5H$_{arom}$), 7.45–7.55 (m, 2H$_{arom}$)	222.41	436 (M$^+$, 11.9), 237 (100)

[a] Uncorrected, measured with a Reichert (Wien) hot stage apparatus equipped with a microscope.

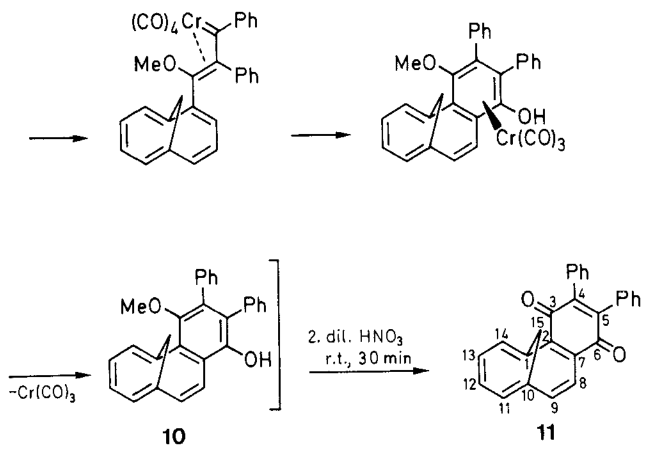
[b] Microanalyses were carried out on automatic Heraus CHN G-R-S Microanalyser or Heraus CHN-O-Rapid. Satisfactory microanalysis obtained (**3**–**6**): (±0.27, H ±0.28, or HRMS (**7**, **8**) ±0.0014.

[c] Recorded on a Perkin-Elmer 325 grating Infrared Spectrophotometer.

[d] Measured on a Carl-Zeiss DMR-4 UV Spectrophotometer.

[e] ^{1}H-NMR and ^{13}C-NMR obtained on a Bruker WM-250 Spectrophotometer.

[f] Recorded on a Varian MAT 311 A Spectrophotometer with reference to the respective main isotope i.e. ^{52}Cr, ^{98}Mo, ^{184}W.



Carbene Complexe 3; Typical Procedure:

To a stirred solution of 2-bromo-1,6-methano[10]annulene (**1**, 1 g/4.5 mmol) at −70 °C in dry Et_2O (100 mL) is added dropwise 2.5 M BuLi in hexane (2 mL, 5 mmol). After stirring for 30 min at this temperature, the solution is transferred by inverse addition to a stirred suspension of $W(CO)_6$ (1.76 g, 5 mmol) in dry argon sat. Et_2O (100 mL) at r.t.. On completion of addition, the brown/red suspension is stirred for 45 min and then refluxed for 30 min. Upon cooling, the solvent is removed under reduced pressure and dry argon sat. CH_2Cl_2 (150 mL) is added to the residue to which a solution of trimethyloxonium tetrafluoroborate (0.74 g, 5 mmol) in absolute CH_2Cl_2 (50 mL) is added. The mixture is stirred for 45 min, then the solvent is removed under reduced pressure leaving a bright red solid which is purified by column chromatography (silica gel) with hexane as eluent followed by recrystallisation from hexane to give the pure product (Table).

4,5-Diphenyltricyclo[8.4.1.0^{2,7}]pentadeca-1(15),2(7),4,9,11,13-hexaene-3,6-dione (11):

A solution of **5** (0.5 g, 1.3 mmol) and diphenylacetylene (0.24 g, 1.3 mmol) in dibutyl ether (15 mL) under an argon atmosphere is warmed to 45 °C for 4 h. The solution is allowed to cool and the solvent removed under reduced pressure to leave a red oil which is immediately dissolved in AcOH (20 mL) and conc. HNO_3 (2 mL) is added to the mixture. The resulting red solution is stirred for 30 min. then carefully neutralized using sat. Na_2CO_3 solution and finally extracted using Et_2O (4 × 25 mL). The organic phases were combined, dried (anhydrous $MgSO_4$), and the solvent removed under reduced pressure leaving an orange semi-solid which is purified using preparative TLC with hexane/EtOAc (1 : 1) as eluent to give the pure compound; yield: 0.19 g (39 %).

$C_{27}H_{18}O_2$	calc.	C 86.61	H 4.85
(374.4)	found	86.40	4.70

IR (KBr): ν = 1660, 1500, 1450, 1325, 1320, 1270, 1260, 1200, 1150, 810, 790, 750, 710, 700, 690, 600, 595 cm^{-1}.

^1H-NMR (250 MHz, $CDCl_3$/TMS): δ = 0.0–0.5 (br d, 2 H, H-16), 7.0–7.55 [m (partially solvent obscured), aromatic], 8.35 (d, 2 H, J = 10.4 Hz), 8.62 (d, 1 H, J = 10.4 Hz), 8.95 (d, 1 H, J = 10.4 Hz).

^{13}C-NMR (62.89 MHz, $CDCl_3$): δ = 35.16 (t, C 11), 112.29 (s, C 1), 118.55 (s, C 6), 126.01, 127.67, 129.57, 130.00, 136.18, 141.28 (d, C 4/5/7/8/9/10), 130.41, 130.48 (d, 2 × Ph), 133.78, 134.02 (s, (C 2/3), 144.61 (s, C 5′/6′), 186.73, 186.83 (s, C 1′/4′).

MS (100 eV 210 °C): m/z (%) = 375 (m^+, 7.3), 374 (16.6), 373 (37.8), 372 (20.5), 371 (9.3), 345 (8.0), 344 (6.6), 316 (7.3), 315 (21.2), 313 (17.2), 302 (9.9), 239 (15.9), 178 (15.9), 139 (53.64), 138 (8.6), 105 (10.6), 77 (6.0), 55 (3.3), 43 (2.7).

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