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Carbene ligands as anthracyclinone synthons

VII *. Quinone ketal functionalized carbonyl carbene complexes: synthesis, structure and carbene annulation

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Abstract

The addition of lithiated quinone bis-ketals obtained via anodic oxidation of 2-bromo-1,4-dimethoxy-benzene or -naphthalene and subsequent metal–halogen exchange to hexacarbonyl-chromium or -tungsten leads to pentacarbonyl quinone bis-ketal metallates. Alkylation of these compounds with $[Et_3O][BF_4]$ in methylene chloride is accompanied by rearomatization to give 1,4-dimethoxyarylcarbene complexes. In protic media the naphthoquinone bis-ketal metallates undergo a novel rearrangement/decarbonylation/elimination reaction to give pentacarbonyl monoketal dihydronaphthalidene complexes, which represent a new type of low-valent transition metal carbene complexes in which the stabilizing heteroatom is not bound directly to the carbene carbon. The X-ray analysis of the chromium complex indicates a conjugation of the metal–carbene bond and the vinyl-like enol ether substituent. Alkylation of the benzoquinone bis-ketal metallate using $[Me_3O][BF_4]$ in a two-phase system leads to a pentacarbonyl bis-ketal carbene complex, which combines the quinone oxidation state in the carbene ligand with a zerovalent chromium center. Decarbonylation affords a tetracarbonyl carbene chelate with an extremely long chromium–oxygen bond which is responsible for a ready ring-opening of the chelate structure upon reaction with alkynes. This feature is taken advantage of in a regiospecific carbene annulation by 2-pentyne leading to a bis-ketal hydroquinone complex.

Some time after the discovery of stable transition metal carbonyl carbene complexes [2] during which their coordination chemistry was intensively studied in

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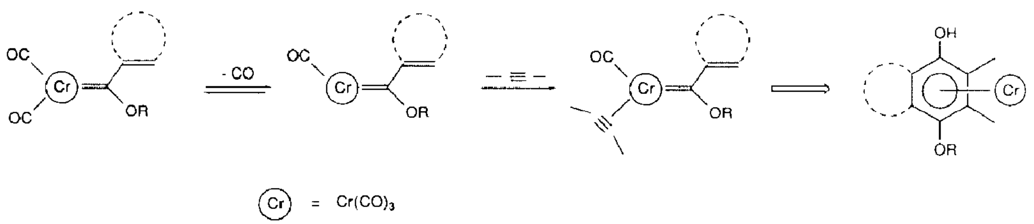
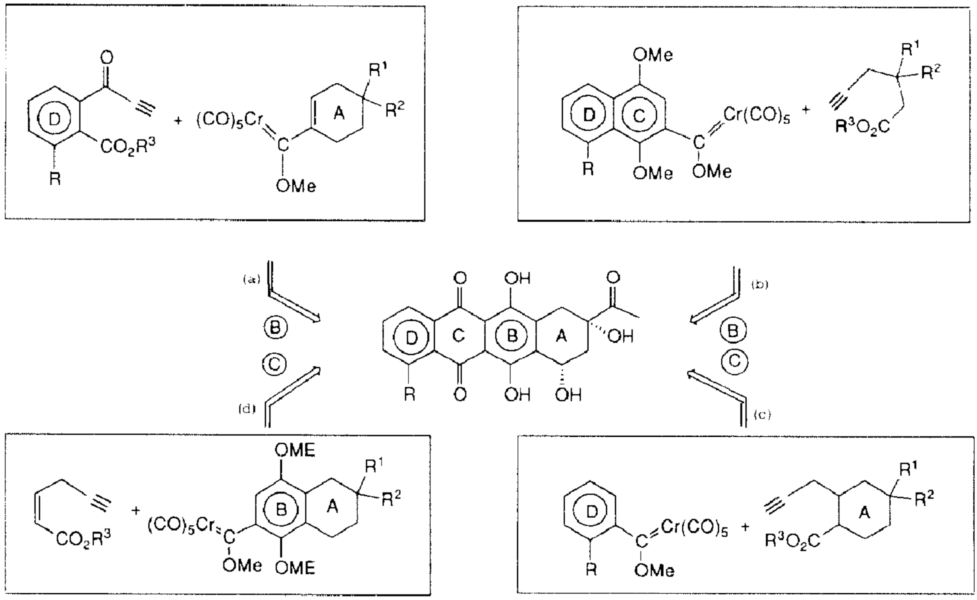
* For part VI see ref. 1.



Scheme 1

E.O. Fischer's laboratory we realized the enormous potential of this novel class of compounds in synthetic organic chemistry [3]. Important applications are concerned with cycloaddition reactions which are based on a carbene transfer to olefins [4], alkynes [5], isocyanides [6] and imines [7]. Among them, the reaction with alkynes provides quite an unprecedented type of reaction which involves a coupling of 3 different ligands: alkyne, carbene and carbonyl ligands, within the coordination sphere of a low valent metal to form a six-membered aromatic ring.

The carbene annulation using chromium(0) as a template is compatible with a wide range of α,β-unsaturated carbene ligands containing vinyl [8], aryl [9] or heteroaryl [10] groups, and the alkyne incorporation is regioselective [11]. Since it provides a direct access to functionalized hydroquinones we have applied it to natural product synthesis [12], and later this strategy has been used also by other groups [13]. Recently we have focused on the synthesis of anthracyclinones which form the aglycon of the antitumor-active anthracyclines [14]. These compounds contain a linear array of four ring systems; in the most important anthracyclinone, daunomycinone, the central rings represent an adjacent quinone/hydroquinone structure. They are an ideal target for the carbene annulation reaction because either the hydroquinone ring C or the quinone ring B may be formed from a carbonyl



Scheme 2. Carbene complex strategies towards daunomycinone.

Table 1

IR and ^1H NMR data of quinone bis-ketals III–VII

	IR [a]	^1H NMR [b]				
	ν(C=O)	1-,1-OCH_3	4-,4-OCH_3	H3	H5,H6	H7,H8
III [c]		3.30(S,6)	3.20(S,6)	6.53(D,1)	5.90(D,1) [d] 6.17(DD,1) [e]	
IV		3.24(S,6)	2.93(S,6)	7.07(S,1)		7.54(M,4)
V	2043 w 1910 vs,br	3.37(S,6)	3.04(S,6)	7.32(M,1)	5.62(M,1) 6.41(M,1)	
VI	2043 w 1909 vs,br	3.35(S,6)	2.84(S,6)	7.76(S,1)		7.54(M,4)
VII	2053 w 1910 vs,br	3.35(S,6)	2.85(S,6)	7.78(S,1)		7.59(M,4)

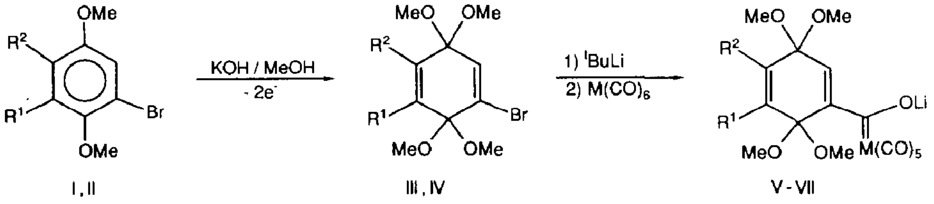
[a] In methylene chloride (cm^{-1}). [b] In acetone-d_6, rel. i. TMS in δ (ppm)). [c] In carbon tetrachloride. [d] H6. [e] H5.

complex containing an unsaturated carbene ligand and from an alkyne as outlined in Scheme 2. So far routes (a), (b) and (c) have been exploited in syntheses of daunomycinone derivatives [1,15].

In persuing route (b) we became interested whether we could incorporate a redox equivalent of ring C into the carbene ligand. Thus we have studied carbonyl complexes containing quinone ketal carbene ligands. More generally, these compounds are expected to reveal also interesting redox properties since they combine the quinone oxidation state in the carbene ligand with a low-valent metal center.

Pentacarbonyl quinone bisketal acyl metallates

Quinone ketals are accessible from 1,4-dialkoxy arenes via anodic oxidation [16,17]. We have used a divided cell cooled to −7 °C and equipped with platinum electrodes in methanolic potassium hydroxide. Starting from 2-bromo-1,4-dimethoxy-benzene (I) or -naphthalene (II) we have isolated the bis-ketals III and IV in excellent yields. Metal–halogen exchange using t-butyllithium in ether at −78 °C affords the lithiated bis-ketals which add to hexacarbonyl-chromium or -tungsten suspended in ether at −60 °C to give the lithio bis-ketal metallates V–VII.



	R^1	R^2	M
I, III, V	H	H	Cr
II, IV, VI	CH = CH - CH = CH		Cr
VII	CH = CH - CH = CH		W

Scheme 3

Table 2

^{13}C NMR data of quinone bis-ketals IV–VII (in acetone-d_6, rel. i. TMS in δ (ppm))

	CO	C2	C3	C9,C10	C5–8	C1,C4	1-,1-,4-,4-OCH_3
IV		138.0 135.1		138.5 138.3	130.2 130.0 127.5 127.2	98.5 97.4	51.6 51.4
V	217.0 [a] 210.3 [b] 197.7 [c]	153.8	144.9	[d]	[d]	99.2 [d]	49.5 49.1 [e]
VI	221.8 [a] 210.1 [b] 197.8 [c]	153.9	141.8	137.8 129.9 129.4 127.3 126.4 126.2		100.5 95.9	51.2 [e] 50.4
VII	210.2 [a] 202.3 [b] [d]	149.5	137.9	134.9 129.8 129.3 128.5 126.3 [d]		100.2 95.8	51.3 50.4

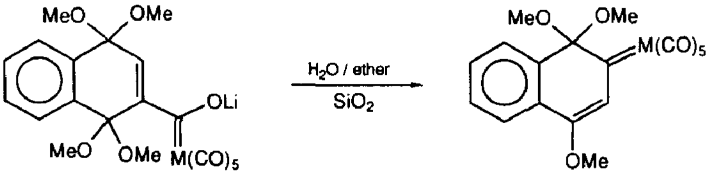
[a] CO_{trans}. [b] CO_{cis}. [c] CO_{acyl}. [d] Cannot be assigned unequivocally. [e] Broad.

Precipitation by addition of pentane yields an ochre (V, VI) or orange (VII) solid which is dried in vacuo and characterized by IR and NMR spectra (Tables 1 and 2).

Pentacarbonyl monoketal dihydronaphthylidene complexes

The quinone bis-ketal acyl metallates may react with electrophiles in different ways depending on the substitution pattern in the acyl ligand and the reaction conditions. Upon treatment with aqueous ether at room temperature the naphthoquinone-derived complexes VI and VII form a deep-blue emulsion. After chromatographic work-up on silica gel golden crystals of pentacarbonyl dihydronaphthalidene complexes VIII and IX are obtained [18] which again give deep-blue solutions in organic solvents. This type of compounds the formation of which formally involves a combined rearrangement/decarbonylation/elimination process is one of the rare examples of carbonyl carbene complexes in which a stabilizing heteroatom is not bound directly to the carbene carbon atom and which are stable above room temperature. Obviously the metal carbene structure is stabilized by the vinyl-like enol ether functionality, by the incorporation into a rigid six-membered ring and by the annulated arene ring. In contrast only decomposition products have been observed from the benzoquinone bis-ketal acyl metallate V when it is exposed to aqueous ether and silica gel under identical conditions.

The mechanism of this unprecedented decarbonylation/rearrangement/elimination reaction is not obvious. Nor can be decided on the basis of available spectroscopic and structural data whether the metal ends up bonded to the former C2 or C3 carbon atom of the symmetric quinone bis-ketal unit. One possible



VI , VII

VIII , IX

VI , VIII : M = Cr
VII, IX : M = W

Scheme 4

mechanism involving a 1,3-metal migration is outlined below. We assume that the reaction sequence is initiated by a protonation to generate a hydroxycarbene complex. These compounds are known to undergo a facile decarbonylation [19]. Coordination of the metal to the C=C bond could induce a metal migration to the quinone bis-ketal ring followed by the formation of a new metal carbene structure and elimination of methoxide. The dihydronaphthylidene complexes have been characterized by IR and NMR spectra (Tables 3 and 4).

The molecular structure of the chromium dihydronaphthylidene complex VIII has been determined by X-ray diffraction (Tab. 12). As is evident from Fig. 1, the structure of VIII shows no unexpected features in comparison with classical Fischer

Table 3

IR and NMR data of dihydronaphthylidene complexes VIII and IX

	IR[a]	^{1}H NMR[b]				
	ν(C=O)	H3	H5,H8	H6,H7	4-OCH_3	1-,1-OCH_3
VIII	2047 m 1988 w 1962 vs 1926 s	8.91(S,1)	8.05(M,2)	7.62(M,2)	4.45(S,3)	2.78(S,6)
IX	2058 m 1995 w 1960 vs 1925 s	8.85(S,1)	7.92(M,4)		4.42(S,3)	2.82(S,6)

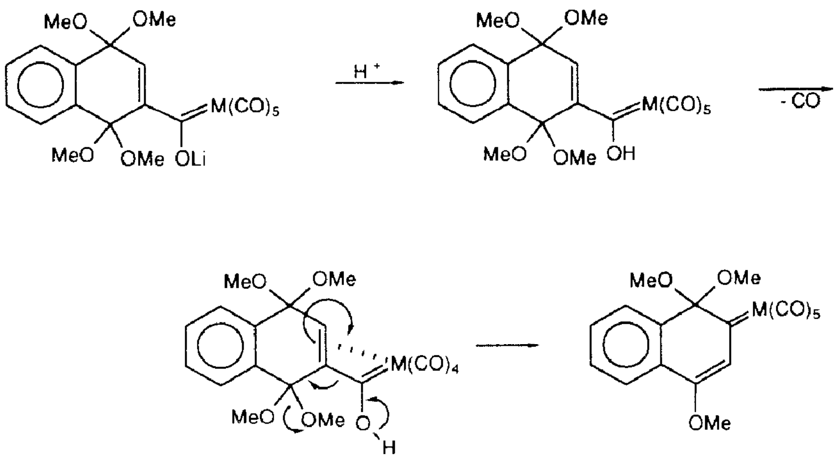
[a] In pentane (cm^{-1}). [b] In acetone-d_6, rel. i. TMS in δ (ppm).

Table 4

^{13}C NMR data of mono-ketal dihydronaphthylidene complex VIII [a] (in acetone-d_6, rel. i. TMS in δ (ppm))

CO_{trans}	CO_{cis}	C3,C4	C9,C10	C5–C8	4-OCH_3	1-,1-OCH_3
219.4	212.7	152.2 147.3	134.2 134.1	131.5 130.1 130.0 127.6	58.8	51.1

[a] Signals for $C_{carbene}$ and C1 could not be observed.



Scheme 5

type carbene complexes. In particular, the Cr–$C_{carbene}$ bond (Cr–C12, see Tab. 12) is relatively short and in the range usually encountered in chromium carbene complexes with not particularly electron donating substituents at the carbene carbon atom [3]. However, the bond length pattern in the dihydronaphthylidene ring indicates that the metal carbene bond participates in a partly delocalized π-system which extends over atoms C13 and C14 and also includes the methoxy substituent at C14. Particularly indicative in this respect are the short bond C14–O6 (1.333(4) Å) and the large valence angle at O6 (119.5(2)°). Note also that the next bond in the dihydronaphthylidene ring (C14–C15) is much longer, whereas the following C–C bond (C15–C20) again is short due to the fused aromatic ring system. Thus the electron deficit of the carbene carbon atom C12 is partly compensated for by electron donation from the dihydronaphthylidene system. π-Back donation from the metal to the CO group *trans* to the carbene ligand should be comparatively weak; it is instructive to see that the *trans* Cr–CO bond Cr–C1 is by no means shorter than the other Cr–CO bonds, nor is C1–O1 longer than in the other carbonyl ligands

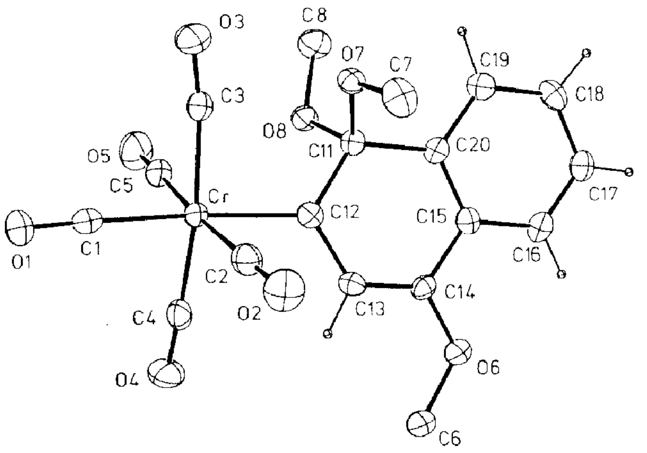


Fig. 1. Molecular structure of VIII in the crystal and atomic numbering used (ORTEP; displacement ellipsoids at the 50% probability level; hydrogen atoms with arbitrary radii; without methyl hydrogens).

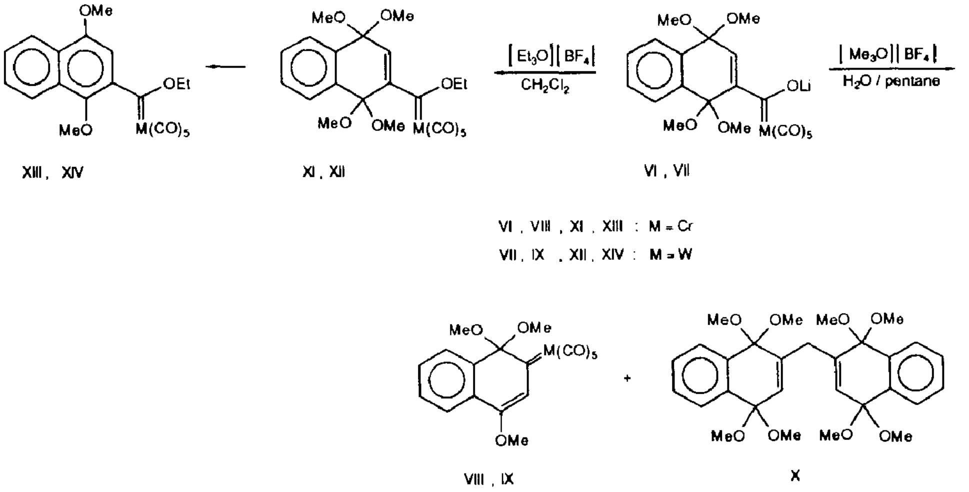
(Tab. 12). It should also be noted that the geminal methoxy groups at C11 show no tendency to coordinate to the metal center, although the neighboring carbonyl group C3–O3 is bent away from the methoxy groups which is certainly due to steric crowding. Surprisingly, despite of the saturated carbon atom C11 and correspondingly long bonds C11–C12 and C11–C20, the entire dihydronaphthylidene ring system is essentially planar.

Pentacarbonyl quinone bis-ketal carbene complexes

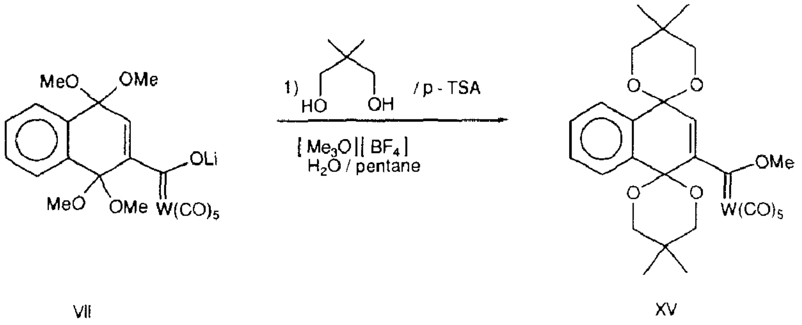
The alkylation of the naphthoquinone bis-ketal acyl metallates VI and VII using trialkyloxoniumtetrafluoroborates [3] is difficult. Following the customary procedure based on a two-phase system ($[Me_3O][BF_4]$ in H_2O/pentane) the chromium compound VI gives the dihydronaphthylidene complex VIII together with the bis-ketal dimer X. Alkylation in homogeneous solution ($[Et_3O][BF_4]$ in methylene chloride) affords the desired bis-ketal carbene complexes XI and XII in good yields, but these compounds turned out to be very labile with respect to aromatization. They can be isolated by rapid recrystallization; however, after column chromatography even at low temperature the pentacarbonyl[(1,4-dimethoxy-2-naphthyl)ethoxycarbene) complexes XIII and XIV are obtained.

To enhance the stability of bis-ketal carbene complexes we have extended our studies to cyclic ketal structures. Since six-membered ketals are less prone to protolysis than their five-membered homologues [20] we have focused on neopentyldioxy ketals. In the presence of catalytic amounts of *p*-toluene sulfonic acid the acyl wolframate VII undergoes a reketalization upon reaction with 2,2-dimethyl-1,3-propanediol. Subsequent alkylation with $[Me_3O][BF_4]$ affords the naphthoquinone bis-ketal carbene complex XV in moderate yield.

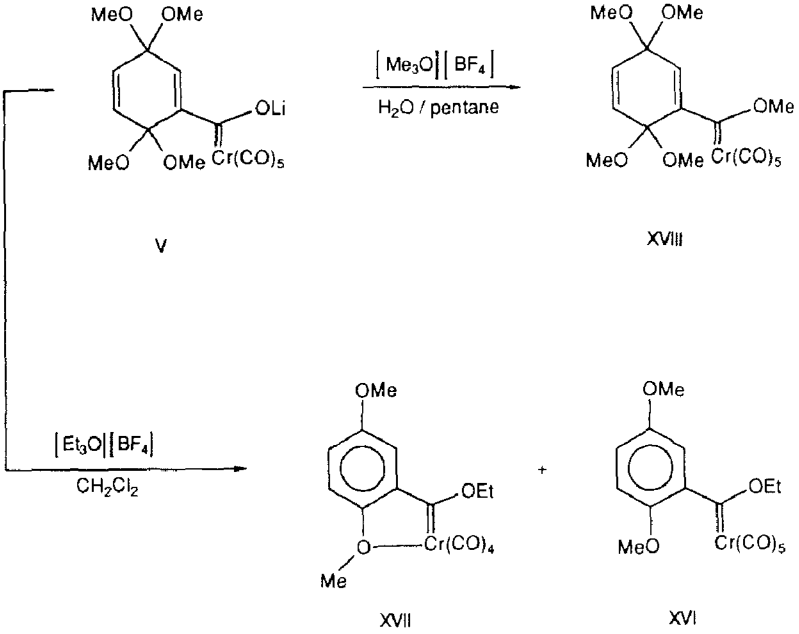
The homogeneous alkylation of the benzoquinone bis-ketal acyl chromate V results in aromatization leading both to the pentacarbonyl(1,4-dimethoxy-2-phenylcarbene) complex XVI and its decarbonylation product, the tetracarbonyl carbene chelate XVII [21]. The two-phase procedure carried out with $[Me_3O][BF_4]$ in



Scheme 6



Scheme 7



Scheme 8

Table 5

IR data of bis-ketal and hydroquinoid carbene complexes XI–XIII and XV–XVII (in pentane, $\nu(C{=}O)$ frequencies in cm^{-1})

	A_1	B_1	A_1	E	B_2
XI	2056m		1948vs,br		
XII	2070w		1952s,sh	1945vs	
XIII	2066s	1988m	1962vs,sh	1948vs	
XV	2070s	1984m	1955vs,sh	1947vs	
XVI	2064s	1988m	1956vs,sh	1949vs	
XVII	2020s	1929vs	1940s		1868s
XVIII	2064s	1994m	1955vs	1942vs	

Table 6

^{1}H NMR data of bis-ketal and hydroquinoid carbene complexes XII–XVIII and sideproduct X (in acetone-d_6, rel. i. TMS in δ (ppm))

	H3	H5–8	OCH_3	CH_2	CH_3
X	8.09(S,2)	7.56(M,8)	3.29(S,12) 2.97(S,12)	3.73(S,2)	
XII	6.46(S,1)	7.56(M,4)	3.27(S,6) 3.12(S,6)	5.14(Q,2) [a]	1.73(T,3)
XIII	6.88(S,1)	8.23(M,2) 7.65(M,2)	4.08(S,3) 3.98(S,3)	4.85(Q,2) [a]	1.65(T,3)
XIV	7.18(S,1)	8.23(M,2) 7.62(M,2)	4.05(S,3) 3.95(S,3)	5.13(Q,2) [a]	1.68(T,3)
XVI	6.47(M,1)	6.98(M,2) [b]	3.82(S,3) 3.78(S,3)	4.48(Q,2) [a]	1.53(T,3)
XVII	7.18(M,3) [c]		4.33(S,3) 3.78(S,3)	5.27(Q,2) [a]	1.78(T,3)
XVIII	6.07(M,3) [c]		3.33(S,6) 3.27(S,6) 4.73(S,3) [d]		
XVIII [e]	5.96(D,1)	6.03(DD,1) 5.60(DD,1) [f]	3.15(S,6) 3.08(S,6) 4.01(S,3) [d]		

[a] OCH_2. [b] H5,H6. [c] H3,H5,H6. [d] $OCH_{3\,\mathrm{carbene}}$. [e] In benzene-$d_6$. [f] ${}^3J$(H5,H6) 10.2 Hz; ${}^3J$(H3,H5) 2.0 Hz.

H_2O/pentane at 0 °C, however, affords the bis-ketal carbene complexes XVIII; rapid column chromatography at low temperature (to avoid decarbonylation) followed by crystallization from ether/pentane gives bright red needles. The quinone bis-ketal carbene complexes are expected to have interesting redox properties since they combine the quinone oxidation state in the carbene ligand with a zerovalent metal center.

The spectroscopic data of the hydroquinoid and bis-ketal carbene complexes are summarized in Tables 5–7.

Table 7

^{13}C NMR data of bis-ketal and hydroquinoid carbene complexes XVI–XVIII (in aceton-d_6, rel. i. TMS in δ (ppm))

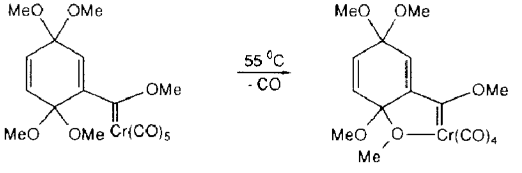
	C_{carbene}	CO	C1,C4	C2	C3,C5,C6	OCH_2	1-,4-OCH_3	CH_3
XVI	351.9	225.6 [a] 216.5 [b]	153.5	141.9	113.8 112.1 106.3	76.0	55.2 54.9	14.0
XVII	333.2	232.2 [a] 215.4 [b]	161.5 155.9	134.2	121.4 [c]	78.5	66.8 56.4	15.5
XVIII	355.5	225.4 [a] 216.2 [b]	96.4 92.5	153.5	130.7 126.1 114.3		67.7 [d] 48.8 48.6	

[a] CO_{trans}. [b] CO_{cis}. [c] Further signals cannot be assigned unequivocally. [d] $OCH_{3(\mathrm{carbene})}$.

Tetracarbonyl quinone bis-ketal carbene complexes

Pentacarbonyl arylcarbene complexes containing an *ortho*-donor substituent in the aryl ring undergo a facile decarbonylation to give five-membered metal carbene chelates [21–23]. A similar chelation reaction is observed for the quinone bisketal carbene complex XVIII. Slight warming in refluxing t-butyl methyl ether induces a quantitative intramolecular substitution of a *cis*-CO ligand by a ketal methoxy group. Low-temperature chromatography affords black metallic shining crystals of XIX which are reasonably soluble only in more polar organic solvents.

The tetracarbonyl chelate structure of XIX is obvious from IR and NMR data (Tables 8 and 9). The ν(C=O) frequencies are characteristic for carbene chelate complexes. However, the ^{1}H NMR spectrum when recorded at ambient temperature shows only 2 sharp singlets of equal intensity for the bis-ketal methoxy groups; moreover, the signals for the 1-,1-methoxy substituents are deshielded only slightly in comparison with the parent pentacarbonyl complex XVIII. This indicates that under these conditions both methoxy substituents in 1-position are on average magnetically equivalent. Obviously an exchange of these groups with respect to the coordination to the chromium occurs which is rapid on the NMR time scale. The



XVIII XIX

Scheme 9

Table 8

IR and ^{1}H NMR data of quinone bis-ketal carbene chelate complex XIX

IR [a]	^{1}H NMR [b]				
ν(C=O)	1-,1-OCH$_3$	4-,4-OCH$_3$	OCH$_{3(\text{carbene})}$	H3	H5,H6
2019 s 1952 s 1938 vs 1865 vs	3.36(S,6)	3.30(S,6)	4.80(S,3)	6.33(M,1)	6.37(M,2)

[a] In hexane (cm^{-1}). [b] In acetone-d_6, rel. i. TMS in δ (ppm), 23° C.

Table 9

^{13}C NMR data of quinone bis-ketal carbene chelate complex XIX (in acetone-d_6, rel. i. TMS in δ (ppm), 23° C)

C$_{\text{carbene}}$	CO	C2	C3	C5,C6	C1,C4	OCH$_{3(\text{carbene})}$	OCH$_3$
341.5	233.1 [a]	145.1	133.8	125.4	100.0	68.8	56.5 [c]
	232.2 [b]			119.6	94.4		50.3 [d]

[a] CO$_{trans}$. [b] CO$_{cis}$. [c] 1-,1-OCH$_3$. [d] 4-,4-OCH$_3$.

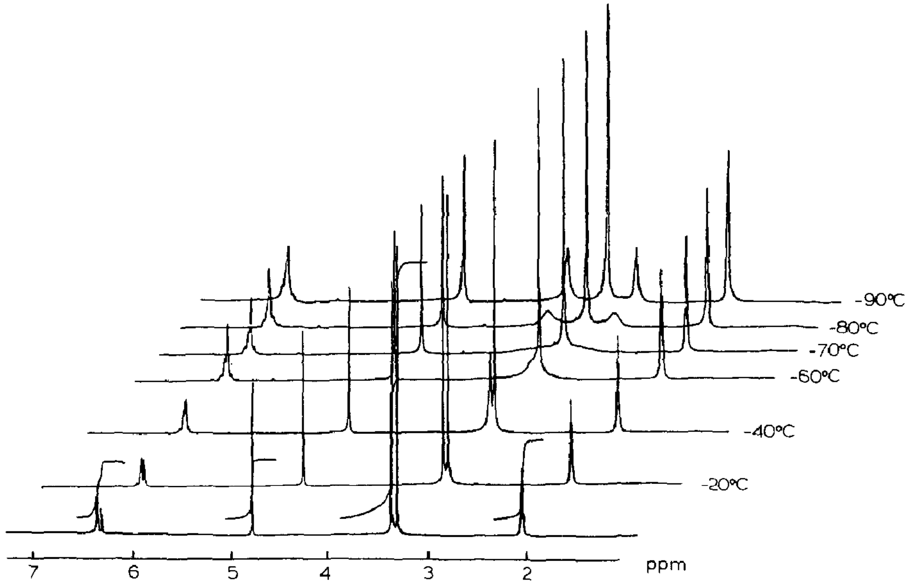


Fig. 2. Temperature dependent ^{1}H NMR spectra of XIX.

fluxional behaviour of the geminal 1-methoxy groups has been demonstrated by variable temperature ^{1}H NMR spectroscopy [24]. Upon cooling the sample the low-field signal begins to broaden and below $-70\,^\circ$C splits into 2 separate lines (Fig. 2). From the coalescence which occurs at $-73(\pm 2)\,^\circ$C with $\Delta\nu$ 178 Hz the activation enthalpy for the chelation exchange process can be estimated to be ca. 9 kcal/mol.

In the solid state the chelation exchange process in XIX is frozen out. The X-ray structure determination established two geminal methoxy groups (O31–C31 and O32–C32) which are in sufficiently close spatial proximity to compete directly for the sixth coordination site at the metal center; however, only one of them is coordinated to the metal (Fig. 3, Tab. 13, Cr...O32 3.332(2) Å). The five-membered ring formed upon complexation of O31 to the chromium center has an approximate envelope conformation, the angle of fold between the planes Cr, C1, C2, C3 and Cr, O31, C3 being 44.3° (see also Tab. 13). Again, as already observed in the mono-ketal complex VIII, the non-aromatic nature of the quinone-bis-ketal ligand in XIX does not seem to induce a significant deviation from planarity of the six-membered ring. The small deviations of planarity observed, however, rather seem to be induced by the complexation of O31 to chromium (see Fig. 4). Thus the observed molecular conformation of XIX is chiral in the solid state (Fig. 4), and XIX indeed crystallizes in a non-centrosymmetric space group. In other words, in the solid state molecules of equal chirality group together to form single crystals. For the single crystal examined in this investigation, the data set and the refined molecular structure as shown in Fig. 3 and 4, had the same chirality, as could be verified by Flack's x-refinement (see Experimental Part and ref. 26). It should be remembered, however, that approximately equal amounts of single crystals of opposite chirality are formed upon crystallization. Tab. 13 lists important distances and angles of XIX. Again, they are in line with a plethora of other methoxy substituted chromium carbene complexes of the Fischer type [3].

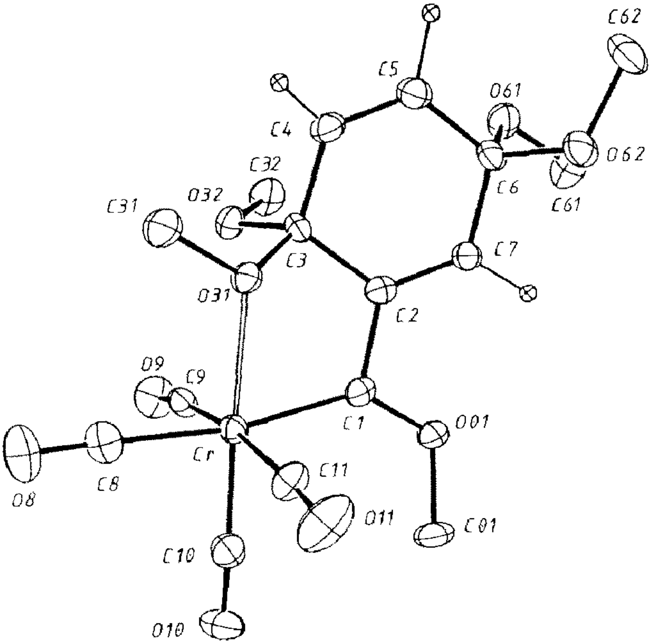


Fig. 3. Molecular structure of XIX (without methyl hydrogens).

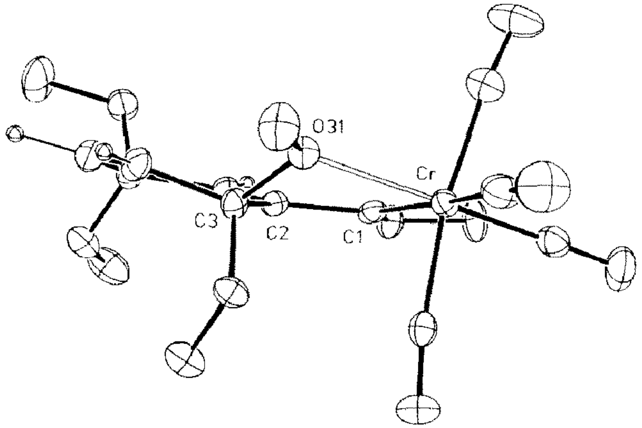


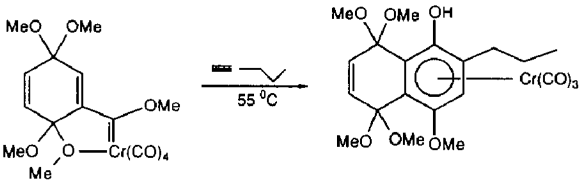
Fig. 4. "Side-on" view of XIX showing the distortions from planarity of the quinone-bisketal ring induced by the coordination of one methoxy group to the metal center.

Table 10

IR and ^1H NMR data of hydroquinone complex XX

IR [a]	^1H NMR [b]				
ν(C=O)	4-OCH_3	H5,5–8,8-OCH_3	H3	H6,H7	CH_2/CH_3
1938 vs	3.65(S,3)	3.79(S,br,6)	5.61(S,1)	6.88(M,2)	1.32(M,4)
1855 vs,br		3.74(S,6)			0.87(M,3)

[a] In KBr (cm^{-1}). [b] In acetone-d_6, rel. i. TMS in δ (ppm).



XIX XX

Scheme 10

Carbene annulation of the quinone bis-ketal carbene complex

The facile decarbonylation of the pentacarbonyl complex XVII and the extremely long chromium-oxygen bond in the carbene chelate XIX encouraged us to study the carbene annulation of these compounds upon reaction with alkynes [25]. On slight warming in t-butyl methyl ether the chelate complex XIX reacts with 1-pentyne to give the hydroquinone bis-ketal complex XX. This compound is only slightly soluble in non-polar organic solvents; it precipitates from the reaction mixture and must be purified by recrystallization; chromatography on silica gel results in partial decomplexation. The spectroscopic data of the tricarbonyl chromium complex XX are summarized in Table 10.

Experimental

All reactions and workup procedures were carried out under an atmosphere of dry inert gas (nitrogen or argon). Solvents and adsorbents (silica gel, Merck type 60, 0.06–0.2 mm) were dried using standard methods and saturated with nitrogen. Products were isolated and purified by recrystallization or by column chromatography.

IR spectra: Perkin–Elmer 283B and Nicolet FT–IR 5DX. NMR spectra: JEOL PMX 60, JEOL FX 90 Q, JEOL FX 270. Mass spectra: Varian MAT 311 A.

Pentacarbonyl[ethoxy(1,4-dimethoxy-2-naphthyl)carbene] complexes (XIII, XIV), pentacarbonyl[ethoxy(1,4-dimethoxy-2-phenyl)carbene]chromium (XVI) and tetracarbonyl[ethoxy(1,4-dimethoxy-2-phenyl)carbene-*C*,*O*]chromium (XVII) were synthesized according to published procedures [18,21].

2-Bromo-1,1,4,4-tetramethoxycyclohexa-2,5-diene (III) and 2-bromo-1,4-dihydro-1,1,4,4-tetramethoxynaphthalene (IV)

A solution of 50 mmol 2-bromo-1,4-dimethoxyarene (I or II) in 200 ml of 3% methanolic potassium hydroxide was electrolyzed for 16 h at $-7\,^\circ$C using a divided cell equipped with a platinum gauze cathode and a platinum sheet anode (power supply: Wenking SMP 72; current density: 10.9 mA/cm^2). After evaporation of the solvent a yellow oily solid was obtained which was extracted with 200 ml of pentane. The organic layer was washed with saturated brine, dried over Na_2SO_4, and the solvent was removed in vacuo. Crystallization from ether/pentane yielded white crystals (III: m.p. 62 °C [17], yield: 87%; $C_{10}H_{15}BrO_4$ (279.1), $M^+ = 278$ (mass spectrum, based on ^{79}Br); IV: m.p. 65–66 °C, yield: 95%; $C_{14}H_{17}BrO_4$ (329.2), $M^+ = 328$ (mass spectrum, based on ^{79}Br).

Table 11

Crystal structure data for VIII and XIX

	VIII	XIX
formula	$C_{18}H_{14}CrO_8$	$C_{16}H_{18}CrO_9$
Mr	410.30	406.31
crystal system	triclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)
a, Å	7.262(1)	11.691(1)
b, Å	11.151(2)	11.970(1)
c, Å	12.138(3)	12.760(1)
α, deg.	89.78(2)	90.
β, deg.	104.50(2)	90.
γ, deg.	112.48(1)	90.
V, Å^3	874.7	1785.7
Z	2	4
d_{calc}, g/cm^3	1.558	1.511
μ(Mo-K_α), cm^{-1}	6.8	6.7
$F(000)$, e	420	840
scan	ω	ω
scan width (deg. in ω)	0.8	1.0
$(\sin\theta/\lambda)_{max}$	0.572	0.594
hkl-range	+8, ±12, ±13	+13, ±13, ±15
refl. measd.	2740	4631
refl. unique	2740	2758
R_{int}	–	0.029
refl. obs. $[F_0 \geq 4.0\sigma(F_0)]$	2356	2645
H-atoms (found/calcd.)	14/–	15/3
parameters ref.	244	250
R [a]	0.040	0.028
wR [b]	0.046	0.032
x [c]	–	0.00(2)
$\Delta\rho_{fin}$ (max/min), e/Å^3	±0.41	0.40/–0.37

[a] $R = \Sigma(\|F_0| - |F_c\|)/\Sigma|F_0|$. [b] $wR = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2]^{1/2}$; $w = 1/\sigma^2(F_0)$. Function minimized: $\Sigma w(|F_0| - |F_c|)^2$. [c] Flack's x parameter, see ref. 26.

Lithium(pentacarbonylacylchromates) (V, VI) and -tungstate (VII)

A solution of 30 mmol t-butyllithium (15% in hexane) was added dropwise to a solution of 15 mmol bromide III or IV in 60 ml of ether at –75 °C. The orange suspension was stirred at this temperature for 10 h and then added dropwise to 15 mmol $Cr(CO)_6$ or $W(CO)_6$ suspended in 150 ml of ether. During 4 h the mixture was warmed to room temperature. The solvent was removed in vacuo, and the residue was washed with pentane and dried to give ochre (V, VI) or orange (VII) solids of acylmetallates V (5.75 g, 90%), VI (6.57 g, 92%) and VII (8.67 g, 95%) which are directly used for the synthesis of carbene complexes VIII, IX and XI–XVIII.

Pentacarbonyl(1,2-dihydro-1,1,4-trimethoxy-2-naphthylidene)-chromium (VIII) and -tungsten (IX)

5 mmol acylmetallate VI or VII were stirred in 200 ml H_2O/ether (1/1) at ambient temperature for 1 h while a colour change occurred from yellow to blue.

Table 12

Selected distances (Å) and angles (°) for VIII with standard deviations in units of the last significant figure in parentheses (see Fig. 1 for the atomic numbering)

Cr–C12	2.045(3)	Cr–C1	1.897(4)
Cr–C2	1.906(4)	Cr–C3	1.927(4)
Cr–C4	1.889(4)	Cr–C5	1.915(4)
C1–O1	1.142(4)	C2–O2	1.144(4)
C3–O3	1.134(4)	C4–O4	1.143(4)
C5–O5	1.142(4)	C12–C13	1.410(4)
C13–C14	1.376(4)	C14–C15	1.460(4)
C15–C20	1.403(4)	C11–C20	1.532(4)
C11–C12	1.541(4)	C14–O6	1.333(4)
O6–C6	1.439(4)	C11–O7	1.415(4)
O7–C7	1.429(4)	C11–O8	1.420(4)
O8–C8	1.426(4)		
Cr–C12–C13	121.4(2)	Cr–C12–C11	122.8(2)
C11–C12–C13	115.8(3)	C12–Cr–C1	175.9(1)
C12–Cr–C2	83.7(1)	C12–Cr–C3	95.4(1)
C12–Cr–C4	90.4(1)	C12–Cr–C5	91.4(1)
C14–O6–C6	119.5(2)	C11–O7–C7	114.1(2)
C11–O8–C8	118.1(2)		
Dihedral angle	C11,C12,C13,C14,C15,C20/Cr,C1,C3,C4,C12		24.5

Table 13

Selected distances (Å) and angles (°) for XIX (see Fig. 2 for the atomic numbering)

Cr–C1	1.978(3)	Cr–O31	2.226(2)
Cr–C8	1.895(3)	Cr–C9	1.899(3)
Cr–C10	1.822(3)	Cr–C11	1.918(3)
C8–O8	1.153(3)	C9–O9	1.147(3)
C10–O10	1.167(4)	C11–O11	1.135(3)
C1–C2	1.497(4)	C1–O01	1.321(3)
O01–C01	1.442(3)	C2–C3	1.505(4)
C3–C4	1.505(4)	C4–C5	1.323(4)
C5–C6	1.501(4)	C6–C7	1.499(4)
C2–C7	1.328(4)	C3–O31	1.441(3)
O31–C31	1.452(3)	C3–O32	1.431(3)
O32–C32	1.424(3)		
C1–Cr–O31	76.9(1)	C1–Cr–C8	169.6(1)
C1–Cr–C9	89.0(1)	C1–Cr–C10	100.5(1)
C1–Cr–C11	92.0(1)	Cr–C1–C2	116.0(2)
Cr–C1–O01	136.1(2)	C2–C1–O01	108.0(2)
C1–O01–C01	118.6(2)	C1–C2–C3	114.7(2)
C2–C3–O31	103.6(2)	C3–O31–Cr	109.6(1)
C3–O31–C31	117.0(2)	Cr–O31–C31	119.7(2)
C2–C3–O32	114.3(2)	C2–C3–C4	113.1(2)
C4–C3–O31	114.0(2)	C4–C3–O32	107.6(2)
O31–C3–O32	104.0(2)	C3–O32–C32	115.5(2)
Torsion angle	Cr–C1–C2–C3		−9.2
Dihedral angle	Cr,C1,C2,C3/Cr,O31,C3		44.3

Table 14

Fractional atomic coordinates and equivalent isotropic displacement parameters for the non-H-atoms of VIII ($U_{eq} = (U_1U_2U_3)^{1/3}$, where U_i are the eigenvalues of the U_{ij} matrix)

Atom	x/a	y/b	z/c	$U_{eq.}$
Cr	0.4207(1)	0.0834(1)	0.2187(1)	0.019
O1	0.2111(5)	−0.2042(2)	0.1298(2)	0.037
O2	0.0856(4)	0.0734(3)	0.3320(2)	0.035
O3	0.1926(4)	0.1273(2)	−0.0157(2)	0.034
O4	0.6455(4)	−0.0036(3)	0.4282(2)	0.035
O5	0.7792(5)	0.1215(3)	0.1148(2)	0.040
O6	0.7833(4)	0.4557(2)	0.5780(2)	0.024
O7	0.4177(3)	0.3742(2)	0.1301(2)	0.019
O8	0.7434(3)	0.3782(2)	0.1673(2)	0.020
C1	0.2886(6)	−0.0954(3)	0.1606(3)	0.026
C2	0.2065(6)	0.0730(3)	0.2872(3)	0.025
C3	0.2796(6)	0.1192(3)	0.0737(3)	0.023
C4	0.5626(6)	0.0324(3)	0.3508(3)	0.024
C5	0.6464(6)	0.1098(3)	0.1538(3)	0.027
C6	0.7608(5)	0.3510(3)	0.6500(3)	0.025
C7	0.2484(5)	0.3768(4)	0.1686(3)	0.028
C8	0.7837(5)	0.4522(4)	0.0736(3)	0.028
C11	0.5956(5)	0.3899(3)	0.2195(3)	0.019
C12	0.5534(5)	0.2726(3)	0.2909(3)	0.018
C13	0.6147(5)	0.3032(3)	0.4105(3)	0.021
C14	0.7120(5)	0.4281(3)	0.4647(3)	0.018
C15	0.7435(5)	0.5439(3)	0.4032(3)	0.019
C16	0.8274(5)	0.6691(3)	0.4613(3)	0.024
C17	0.8446(5)	0.7763(3)	0.4019(3)	0.024
C18	0.7753(5)	0.7592(3)	0.2832(3)	0.024
C19	0.6922(5)	0.6355(3)	0.2244(3)	0.023
C20	0.6788(5)	0.5262(3)	0.2833(3)	0.018

The organic layer was separated and evaporated to give a blue oil. Chromatography on silica gel at −30 °C using methylene chloride/pentane as eluent gave golden plates.

VIII: Yield: 1.33 g (65%); m.p. 100 °C. Found: C, 53.17; H, 3.68; $M^+ = 410$ (mass spectrum). $C_{18}H_{14}CrO_8$ (410.3) calcd.: C, 52.69; H, 3.44%.

IX: Yield: 1.84 g (68%). Found: C, 40.70; H, 3.10; $M^+ = 542$ (mass spectrum, based on ^{184}W). $C_{10}H_{14}O_8W$ (542.2) calcd.: C, 39.88; H, 2.60%.

Pentacarbonyl[ethoxy(1,4-dihydro-1,1,4,4-tetramethoxy-2-naphthyl)carbene]-chromium (XI) and -tungsten (XII)

7.5 mmol $[Et_3O][BF_4]$ were added to a solution of 5 mmol VI or VII in 75 ml methylene chloride kept at −20 °C. The solution was stirred for 1 h and the solvent was removed in vacuo at 0 °C. After addition of 100 ml of precooled ether the solution was filtered rapidly over a 4 cm layer of basic aluminum oxide. Evaporation of the solvent at −20 °C in vacuo gave a green XI or deep-red oil XII both of which could not be purified by chromatography on silica gel owing to decomposition.

XI: Yield not determined. $M^+ = 498$ (mass spectrum). $C_{22}H_{22}CrO_{10}$ (498.4).

Table 15

Fractional atomic coordinates and equivalent isotropic displacement parameters for the non-H-atoms of XIX

Atom	x/a	y/b	z/c	$U_{eq.}$
Cr	−0.2038(1)	−0.0600(1)	−0.4593(1)	0.018
O8	−0.3873(2)	0.0254(2)	−0.3099(2)	0.042
O9	−0.3079(2)	0.0831(2)	−0.6314(2)	0.033
O10	−0.3773(2)	−0.2196(2)	−0.5439(2)	0.037
O11	−0.1410(2)	−0.2487(2)	−0.3095(2)	0.040
O01	−0.0429(2)	−0.1722(2)	−0.6176(1)	0.022
O31	−0.0703(2)	0.0574(2)	−0.4015(1)	0.020
O32	−0.0761(2)	0.1726(1)	−0.5420(1)	0.022
O61	0.2547(2)	0.1032(2)	−0.6726(1)	0.026
O62	0.3176(1)	−0.0223(2)	−0.5431(2)	0.027
C1	−0.0719(2)	−0.0920(2)	−0.5516(2)	0.018
C2	0.0237(2)	−0.0089(2)	−0.5485(2)	0.019
C3	−0.0023(2)	0.0962(2)	−0.4884(2)	0.019
C4	0.1034(2)	0.1594(2)	−0.4564(2)	0.022
C5	0.2046(3)	0.1412(2)	−0.4995(2)	0.024
C6	0.2268(2)	0.0487(2)	−0.5762(2)	0.021
C7	0.1271(2)	−0.0294(2)	−0.5871(2)	0.020
C8	−0.3149(3)	−0.0060(3)	−0.3638(2)	0.029
C9	−0.2640(2)	0.0351(2)	−0.5648(2)	0.022
C10	−0.3079(3)	−0.1594(2)	−0.5103(2)	0.026
C11	−0.1597(3)	−0.1750(2)	−0.3627(2)	0.026
C01	−0.1154(3)	−0.2693(3)	−0.6253(2)	0.028
C31	−0.0989(3)	0.1387(3)	−0.3211(2)	0.032
C32	−0.0388(3)	0.2060(2)	−0.6436(2)	0.029
C61	0.2807(3)	0.0312(3)	−0.7588(2)	0.037
C62	0.4277(3)	0.0288(3)	−0.5351(3)	0.037

XII: Yield: 1.51 g (48%). $M^+ = 630$ (mass spectrum, based on ^{184}W). $C_{22}H_{22}O_{10}W$ (630.3).

Pentacarbonyl[methoxy(1,4-dihydro-1,1,4,4-bis-2′,2′-dimethylpropan-1′,3′-diyldioxy-2-naphthyl)carbene]tungsten (XV)

10 mmol 2,2-dimethyl-1,3-propanediol and 0.02 g *p*-toluenesulfonic acid were added to a solution of 5 mmol acyl tungstate VII in 60 ml of methylene chloride. The solution was stirred at ambient temperature for 6 h. After addition of 15 mmol $[Me_3O][BF_4]$ a colour change occurred from brown to red and after 2 h the solvent was removed. Chromatography on silica gel using methylene chloride/pentane (1/1) as eluent gave a red solid. Yield: 1.46 g (42%). $M^+ = 696$ (mass spectrum). $C_{27}H_{28}O_{10}W$ (696.4).

Pentacarbonyl[methoxy(1,1,4,4-tetramethoxy-2,5-cyclohexadienyl)carbene]chromium (XVIII)

15 mmol $[Me_3O][BF_4]$ and 100 ml pentane were added to a solution of 15 mmol acyl chromate V in 100 ml of ice-water. The aqueous phase was repeatedly extracted with pentane. The organic phase was dried over Na_2SO_4 and chromatographed on silica gel at −30 °C using methylene chloride/pentane as eluent. Elution of the

main red band with methylene chloride followed by recrystallization at −78 °C from ether/pentane gave bright-red needles (m.p. 47 °C). Yield: 3.80 g (58%). Found: C, 47.27; H, 4.17; Cr, 11.82%. $M^+ = 434$ (mass spectrum). $C_{17}H_{18}CrO_{10}$ (434.3) calc.: C, 47.01; H, 4.18; Cr, 11.97%.

Tetracarbonyl[methoxy(1,1,4,4-tetramethoxy-2,5-cyclohexadienyl)carbene-C,O]chromium (XIX)

5 mmol pentacarbonyl complex XVIII were warmed in 10 ml of refluxing t-butyl methyl ether for 4 h. Evaporation of the solvent and recrystallization from methylene chloride at −78 °C gave black metallic crystals (m.p. 100 °C). Yield: 1.99 g (98%). Found: C, 47.13; H, 4.73; Cr, 12.60; O, 34.67%. $M^+ = 406$ (mass spectrum). $C_{16}H_{18}CrO_9$ (406.3) calc.: C, 47.30; H, 4.46; Cr, 12.80; O, 35.44%.

Tricarbonyl[1–4 : 9–10-η^6-(2-n-propyl-4,5,5,8,8-pentamethoxy-5,8-dihydro-1-naphthol)]chromium (XX)

A solution of 5 mmol carbene chelate XIX and 5.5 mmol 1-pentyne in 20 ml of t-butyl methyl ether was kept at 55 °C for 0.5 h. The annulation product was precipitated by addition of pentane. Recrystallization from methylene chloride/pentane gave brown microcrystals. Yield: 1.35 g (57%). $M^+ = 474$ (mass spectrum). $C_{21}H_{26}CrO_9$ (474.4).

X-ray structure determinations of VIII and XIX

Suitable crystals of VIII (from ether/pentane) and XIX (from methylene chloride) were sealed at dry ice temperature under argon into glass capillaries and examined directly on the diffractometer (Syntex-P2$_1$, Mo-K_α radiation, λ 0.71069 Å, graphite monochromator, T −35 °C). Crystal data and important numbers pertinent to data collection and structure refinement are collected in Tab. 11.

Exact cell constants were obtained by least-squares methods from the setting angles of 15 high-angle reflexions from various parts of reciprocal space carefully centered on the diffractometer. Reduced cell calculations did not indicate higher cell symmetry for both compounds. Both structures were solved by standard Patterson methods and completed by Fourier syntheses. Refinement was done with anisotropic displacement parameters for all non-hydrogen atoms. The latter were kept constant with U_{iso} 0.05 Å^2. The methyl groups of XIX were treated as rigid groups. For XIX it was shown by Flack's x-refinement that the data set and the refined coordinates had the same chirality [26]. Figures 1, 3 and 4 show the molecular structures. Tables 12 and 13 list important distances and angles, Tables 14 and 15 the atomic coordinates. Complete lists of atomic and displacement parameters and observed and calculated structure factors have been deposited [27]. Programs used include SHELX-76 [28] (Fourier syntheses and refinement), GFMLX [29] (x-refinement). ORTEP-II [30] (molecular plots) as well as locally written routines [31].

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References

1 K.H. Dötz and M. Popall, Chem. Ber., 121 (1988) 665.

2 E.O. Fischer and A. Maasböl, Angew. Chem. Int. Ed. Engl., 3 (1964) 580.

3 Reviews: K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert and K. Weiss, Transition Metal Carbene Complexes, Verlag Chemie, Weinheim, 1983; K.H. Dötz, Angew. Chem. Int. Ed. Engl., 23 (1984) 587.

4 K.H. Dötz and E.O. Fischer, Chem. Ber., 105 (1972) 1356.

5 K.H. Dötz, Angew. Chem. Int. Ed. Engl., 14 (1975) 644.

6 R. Aumann and H. Heinen, Chem. Ber., 119 (1986) 2289.

7 M.A. McGuire and L.S. Hegedus, J. Am. Chem. Soc., 104 (1982) 5538.

8 K.H. Dötz and W. Kuhn, J. Organomet. Chem., 252 (1983) C78.

9 K.H. Dötz and R. Dietz, Chem. Ber., 110 (1977) 1555.

10 K.H. Dötz and R. Dietz, Chem. Ber., 111 (1978) 2517.

11 K.H. Dötz, J. Mühlemeier, U. Schubert and O. Orama, J. Organomet. Chem., 247 (1983) 187; W.D. Wulff, P.-C. Tang and J.S. McCallum, J. Am. Chem. Soc., 103 (1981) 7677.

12 K.H. Dötz, I. Pruskil and J. Mühlemeier, Chem. Ber., 115 (1982) 1278; K.H. Dötz and W. Kuhn, Angew. Chem. Int. Ed. Engl., 22 (1983) 732.

13 M.F. Semmelhack, J.J. Bozell, T. Sato, W. Wulff, E. Spiess and A. Zask, J. Am. Chem. Soc., 104 (1982) 5850; W.D. Wulff and P.-C. Tang, J. Am. Chem. Soc., 106 (1984) 434; A. Yamashita, J. Am. Chem. Soc., 107 (1985) 5823; R.C. Cambie, P.S. Rutledge, M. Tercel and P.D. Woodgate, J. Organomet. Chem., 315 (1986) 171.

14 Reviews: F. Arcamone, Doxorubicin Anticancer Antibiotics, Academic Press, New York, 1981; H.S. El Khadem (ed.), Anthracycline Antibiotics, Academic Press, New York, 1982.

15 K.H. Dötz and M. Popall, Angew. Chem. Int. Ed. Engl., 26 (1987) 1158; W.D. Wulff and Y.-C. Xu, J. Am. Chem. Soc., 110 (1988) 2312; W.D. Wulff and P.-C. Tang, J. Am. Chem. Soc., 106 (1984) 434.

16 B. Belleau and N.L. Weinberg, J. Am. Chem. Soc., 85 (1963) 2525.

17 J.S. Swenton, D.K. Jackson, M.J. Manning and P.W. Raynolds, J. Am. Chem. Soc., 100 (1978) 6182.

18 K.H. Dötz, M. Popall, G. Müller and K. Ackermann, Angew. Chem. Int. Ed. Engl., 26 (1987) 1158.

19 E.O. Fischer and K. Weiss, Chem. Ber., 109 (1976) 1128.

20 Houben-Weyl, Methoden der organischen Chemie, 6/3, p. 199, Georg Thieme Verlag, Stuttgart, 1965.

21 K.H. Dötz, W. Sturm, M. Popall and J. Riede, J. Organomet. Chem., 277 (1984) 267.

22 Review: K.H. Dötz, M. Popall and G. Müller, J. Organomet. Chem., 334 (1987) 57.

23 K.H. Dötz, H.-G. Erben, W. Staudacher, K. Harms, G. Müller and J. Riede, J. Organomet. Chem., 355 (1988) 177.

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25 Recent review: K.H. Dötz in H. tom Dieck and A. de Meijere (ed.), Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field, Springer Verlag, Berlin, 1988.

26 G. Müller, Acta Cryst. B, 44 (1988) 315, and ref. cited therein.

27 Fachinformationszentrum Karlsruhe GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG); inquiries should be accompanied by the depository number CSD-51951, the names of the authors and the literature citation.

28 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, Cambridge, England, 1976.

29 GFMLX, a highly modified version of ORFLSD, by Hirshfeld, Coppens, Leiserowitz, and Rabinowich, with enantiopole refinement as included by Flack.

30 C.K. Johnson, ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

31 G. Müller, Technische Universität München, unpublished.