A study of the reactivity and structure of cyclic α,β-unsaturated Fischer-type carbene complexes

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Abstract

Cycloaddition reactions with α,β-unsaturated carbene complexes of the Fischer-type bearing the carbene carbon atom and the double bond incorporated in the same ring are described. Pentacarbonyl(2*H*-benzopyran-2-ylidene)chromium(0) complexes (**2a–c**) and pentacarbonyl(4-methoxy-3,3-dimethyl-2-oxacyclopentylidene)-chromium(0) (**3**) show a rather low reactivity towards 1,3-dipoles and 1,3-dienes. The reactions with diazomethane are regioselective but not chemoselective; compounds **2** and **3** show two sites of attack: the α,β carbon–carbon and the carbon–metal double bond. The crystal and molecular structures of **2a** and **3** have been elucidated by single crystal X-ray analysis. Crystals of **2a** are monoclinic, space group $P2_1/c$, $a=7.614(3)$, $b=14.033(3)$, $c=12.766(3)$ Å, $\beta=95.24°$, $V=1358.3(7)$ Å^3, $Z=4$; crystals of **3** are triclinic, space group $P\bar{1}$, $a=6.553(1)$, $b=9.408(1)$, $c=10.620(1)$ Å, $\alpha=92.70(1)$, $\beta=92.30(1)$, $\gamma=92.12(1)°$, $V=653.0(1)$ Å^3, $Z=2$. Final agreement indices for **2a** and **3** are $R=0.034$ and 0.033, respectively. Vibrational properties of the $Cr(CO)_5$ moiety were interpreted by FT-IR and FT-Raman spectroscopy. Electronic spectra and π electron distribution were interpreted by resonance Raman spectroscopy.

Key words: Crystal structures; Cycloaddition reactions; Chromium complexes; Carbonyl complexes; Fischer carbene complexes; Spectroscopy

Introduction

α,β-Alkenylcarbene complexes of the Fischer-type stabilized by an oxygen atom have been widely used to make more elaborate carbene complexes through reactions proceeding on the carbene ligand. In particular, Michael additions and cycloaddition reactions have been well exploited even in the intramolecular version [1]. Alkenyl alkoxy carbene complexes can be considered analogous to acrylate derivatives according to isolobal analogy [2], one important difference being that, by backbonding from the chromium to the five carbonyl ligands, the chromium pentacarbonyl moiety can delocalize a negative charge much better than a single oxygen atom.

The olefinic double bond of alkenyl carbene complexes must therefore be considered an activated double bond, as demonstrated by the high reactivity shown by these complexes, for example as dienophiles in [4+2] cycloaddition reactions [1c]. When we began to concentrate on these problems, we were surprised to find that no 1,3-dipolar cycloaddition reactions were reported using alkenyl alkoxy carbene complexes as dipolarophiles.

In a recent note, we reported that 1,3-dipolar cycloaddition reactions of diazoalkanes on 5-methylene-(2-oxacyclopentylidene)pentacarbonyl chromium(0) complexes are very fast and regioselective but not

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chemoselective unless trimethylsilyldiazomethane is used [3].

As a development of the above results, and as part of a research programme concerning the study of cycloaddition reactions on olefins activated by non-conventional electron-withdrawing groups [4], we thought it would be interesting to extent our study of the reactivity of α,β-unsaturated carbene complexes by exploiting cycloaddition reactions with carbene complexes bearing the double bond incorporated in a ring and having the general formula **1** (Fig. 1). Very few examples of cyclic alkenyl alkoxy carbene complexes are reported in the literature [5]. We studied the cycloaddition reaction of diazoalkanes with pentacarbonyl(2*H*-benzopyran-2-ylidene)chromium complexes (**2a–c**) and with pentacarbonyl(4-methoxy-3,3-dimethyl-2-oxacyclopentylidene)chromium (**3**) (Fig. 2) [6]. In principle, geometric constraints due to the ring could affect the reactivity of the double bond in cycloaddition reactions by varying its conjugation with the $Cr(CO)_5$ group. Moreover, the use of substrates **2** and **3** as dienophiles or dipolarophiles would have given an entry to condensed polycyclic ring systems, and we expected that the presence of the strongly electron-withdrawing $Cr(CO)_5$ group could activate the double bond of complexes **2a–c** and **3** towards cycloaddition reactions.

Recently it has been shown that the $Cr(CO)_5$ group activates pyranylidene complexes towards the inverse-electron-demand Diels–Alder reaction [5c].

Additional interest in studying pentacarbonyl(2*H*-benzopyran-2-ylidene)chromium complexes (**2**) is related to the fact that such compounds can be considered precursors of coumarin derivatives, into which they can be transformed by oxidation. In the latter class of compounds, attempts at building a carbocyclic or an heterocyclic ring on the double bond in the 3,4 position have been pursued [7] since the resulting polycyclic compounds often show interesting biological properties, e.g. aflatossins, warfarins, angelicin and cumestans [8]. However, coumarin itself fails to react with butadiene and isoprene, and only reacts with 2,3-dimethyl-1,3-butadiene under severe conditions (260 °C, 40 h, yield 22%) [9].

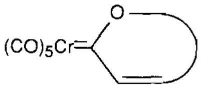

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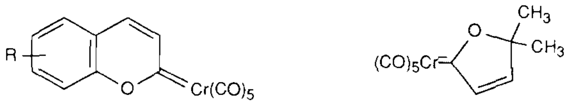
Fig. 1.



2a-d

3

a : R = H
b : R = 6-Br
c : R = 7-OCH_3
d : R = 6-OCH_3

Fig. 2.

As a dipolarophile, coumarin gives variable yields in products of 1,3-dipolar cycloaddition reactions with azomethine (28%), nitrile imine (63%) and 3,5-dichloro-2,4,6-trimethylbenzonitrileoxide (80%) [10], but it has been reported to be completely unreactive towards diazomethane*. Finally, coumarin derivatives have been shown to be reactive in cycloaddition reactions if an electron-withdrawing substituent is present in position 3 or 4 of the ring [11] and [8]. In the latter case, and particularly with diazomethane, stable primary products can be isolated only exceptionally.

Experimental

Instrumentation and materials

All melting points were obtained using a Büchi apparatus and are uncorrected. Spectroscopic measurements were made using the following instrumentation: ^1H NMR, Varian XL300 (300 MHz), XL200 (200 MHz), Bruker FT300 (300 MHz), WP 80 ST (80 MHz). All of the NMR spectra were taken in $CDCl_3$ unless otherwise specified, and the samples filtered on Millex-SR 0.5 μm filters (Millipore Waters) before measurement. IR spectra were recorded using Perkin Elmer 298 and Perkin Elmer FT-IR 1725X1 spectrophotometers. Mass spectra were taken with a Varian MAT 311-A spectrophotometer equipped with a combined EI-FI-FD ion source. All of the chromatographic purifications were accomplished by means of flash column chromatography with silica gel 60 (230–400 mesh). The *N,N*-dimethylformamide used for reactions was dried by filtration on an Al_2O_3 (90 active, neutral, activity I) pad just before use. Diethyl ether was freshly distilled over sodium–lead alloy (Fluka) with benzophenone under nitrogen atmosphere just before use. Pentacarbonyl(methoxymethylcarbene)chromium(0) was synthesized according to a previously published procedure [12]. The physical, analytical and spectroscopic data of complexes **2b–d** are reported in Table 1.

Synthesis of complexes 2a and 2d

Complex **2a** was synthesized according to a published procedure [13]; the same was used to synthesize complex **2d** with a 42% yield.

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*No reaction was observed when we left a solution of coumarin **5a** and CH_2N_2 in diethyl ether at room temperature for several days.

TABLE 1. Physical, analytical and spectroscopic data of complexes **2b–d**

Compound	m.p.[a] (°C)	Analytical data (%) found (calc.)		IR data ν(CO) (cm^{-1})	^{1}H NMR data δ (ppm)	^{13}C NMR data δ (ppm)
		C	H			
2b	130	42.43 (41.89)	1.30 (1.25)	2060, 2000–1870	7.0 (d, 1H, J_{vic}=9 Hz, Ar–CH=) 7.7–7.8 (m, 3H, H arom) 8.15 (d, 1H, J_{vic}=9 Hz, =CH–C=Cr)	300.2 (C=Cr), 224.8 (CO *trans*), 216.8 (CO *cis*), 161.8, 138.7, 135.1, 131.0, 124.0, 123.2, 119
2c	138	51.89 (51.13)	2.40 (2.27)	2060, 1990, 1970–1870	3.9 (s, 3H, –OCH$_3$) 7.0 (d, 1H, J_{meta}=2.9 Hz, H *ortho* to OMe) 7.15 (d, 1H, J_{vic}=8.95 Hz, Ar–CH=) 7.28 (dd, 1H, J_{meta}=2.9 Hz, J_{ortho}=9.2 Hz, H *ortho* to OMe) 7.8 (d, 1H, J_{ortho}=9.2 Hz, H *meta* to OMe) 8.17 (d, 1H, J_{vic}=8.95, =CH–C=Cr)	293.0 (C=Cr), 224.7 (CO *trans*), 217.5 (CO *cis*), 165.3, 163.7, 136.2, 130.0, 127.8, 117.2, 116.1, 99.9, 56.2
2d	99–101	51.03 (51.13)	2.32 (2.27)	2060, 1980, 1970–1900	3.98 (s, 3H, –OCH$_3$) 7.02 (dd, 1H, J_{meta}=2.5 Hz, J_{ortho}=8.8 Hz, H *ortho* to OMe) 7.10 (d, 1H, J_{ortho}=8.8 Hz, H *meta* to OMe) 7.25 (d, 1H, J_{meta}=2.5 Hz, H *ortho* to OMe) 7.55 (d, 1H, J_{vic}=8.8 Hz, Ar–CH=) 8.05 (d, 1H, J_{vic}=8.8 Hz, =CH–C=Cr)	293.4 (C=Cr), 224.8 (CO *trans*), 217.3 (CO *cis*), 159.6, 157.4, 138.1, 127.1, 122.5, 122.5, 119.1, 108.2, 56.0

[a]All the complexes were crystallized from pentane/CH$_2$Cl$_2$.

Synthesis of complex 2b

DMF (30 ml) and Al$_2$O$_3$ (90 active, neutral, activity I) (2 g) were added to a mixture of pentacarbonyl(methoxymethylcarbene)chromium(0) (5 g, 20 mmol) and salicylaldehyde (5 g, 25 mmol). The mixture was stirred at room temperature for 28 h, and then additional Al$_2$O$_3$ was added to adsorb all the mixture. Water was added, and the mixture was filtered on a sintered glass filter. The Al$_2$O$_3$ was washed with CH$_2$Cl$_2$, and then with CH$_3$OH. The CH$_3$OH was removed under reduced pressure and the residue was dissolved in CH$_2$Cl$_2$; the two organic solutions were combined, washed with water, dried over Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (eluent, hexane/CH$_2$Cl$_2$ 9:1), giving a yield of 3.65 g of **2b** (46%). M.p. 130 °C (pentane/CH$_2$Cl$_2$).

Synthesis of complex 2c

DMF (10 ml) was added to a mixture of pentacarbonyl(methoxymethylcarbene)chromium(0) (1.02 g, 6.7 mmol) and 4-methoxy-2-hydroxybenzaldehyde (2.01 g, 8 mmol). The solution was cooled to −20 °C and K$_2$CO$_3$ (0.55 g, 4 mmol) was added. The mixture was stirred at −20 °C for 24 h and then diluted with Et$_2$O. The organic layer was washed with water, dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The residue was purified by flash column chromatography (eluent, hexane/CH$_2$Cl$_2$ 8:2), giving a yield of 0.72 g of **2c** (30%) and 0.752 g of **4c** (5.6%).

Oxidation of complexes 2a–c to compounds 5a–c with bromine

Bromine (2 equiv., 1 M solution in CH$_2$Cl$_2$) was added dropwise at room temperature over 10–30 min to a solution of **2a–c** in CHCl$_3$ or in CH$_2$Cl$_2$. Water was then added, the organic layer separated, and the aqueous layer again extracted with CHCl$_3$ or CH$_2$Cl$_2$. The combined organic layers were dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The residue was purified by crystallization. **5a**: yield 92%, m.p. 60 °C (i-Pr$_2$O) (lit: 70 °C [14]); **5b**: yield 66%, m.p. 158–159 °C (EtOH) (lit: 160–161 °C [15]); **5c**: yield 93%, m.p. 113–114 °C (MeOH) (lit: 117–118 °C [14]).

Synthesis of compound 8

A solution of diethyl ether (4 ml), previously saturated with gaseous HBr (1 g in 20 ml of Et$_2$O), was added at −20 °C to a solution of complex **2c** (100 mg, 0.28 mmol) in Et$_2$O (2 ml). The mixture was stirred at −20 °C for 1 h, and then at room temperature for 24 h. A green hygroscopic solid was filtered off and dissolved in ethanol. To this solution, 70% HClO$_4$ was added and the resulting salt was filtered to yield **8**, 60%. M.p. 168–170 °C (EtOH). IR (nujol), ν (cm^{-1}): 3092, 3046, 1619, 1596, 1518, 884, 857, 756, 724. ^{1}H NMR (DMSO-d$_6$), δ (ppm): 3.7 (s, 3H, OCH$_3$), 5.8 (d, 1H, C*H*=CH-CH=O–), 5.9 (dd, 1H, CH=C*H*–CH=O–), 6.65 (d, 1H, C*H*=O–), 6.7–7 (m, 3H, arom). *m/z* (FAB$^+$): 161 (M^+).

TABLE 2. Reaction conditions and yields of the reactions of **2a–c** with diazomethane

Starting material	Temp. (°C)	Time (h)	Product **9** (%)	Product **10** (%)
2a	−20	6	40	
2b	−78 −20	1 3	44	1
2c	−20 0	42 6	34	10

Reaction of complexes 2a–c with diazomethane: synthesis of complexes 9a–c and 10a–c

Diethyl ether (50 ml) cooled to −78 °C was saturated with CH_2H_2 generated by adding 10 M NaOH (10 ml) to a solution of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald, 4.5 g) in Et_2O/methoxyethanol 1:1 (50 ml). A solution of complexes **2a–c** (2.5 mmol) was added at −78 °C to the bright yellow solution of CH_2N_2. Temperature, reaction times and yields of the products obtained are summarized in Table 2. After completion of the reaction, argon was bubbled into the solution for 1 h to remove the residual CH_2N_2. The solvent was then evaporated under reduced pressure, and the residue purified by flash chromatography (eluent, hexane/CH_2Cl_2 8:2). The physical, analytical and spectroscopic data of complexes **9a–c** are reported in Table 3; those of complexes **10a–c** in Table 4.

Reaction of complex 3 with diazomethane: synthesis of compound 11

Diethyl ether (50 ml) cooled at −78 °C was saturated with CH_2N_2 generated by adding 10 M NaOH (2.8 ml) to a solution of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald, 6 g) in Et_2O/methoxyethanol 1:1 (30 ml). A solution of complex **3** (0.65 g, 2.26 mmol) in diethyl ether was added at −78 °C to the bright yellow solution of CH_2N_2. The reaction was completed after 1 h and argon was bubbled into the reaction solution to remove the residual CH_2N_2. The solvent was evaporated under reduced pressure and the residue was

TABLE 3. Physical, analytical and spectroscopic data of complexes **9a–c**

Compound	m.p. (°C)	IR data ν(CO) (cm^{-1})	^1H NMR data δ (ppm)	^{13}C NMR data[c] δ (ppm)
9a	100–102[a]	2070, 1990, 1970–1900	3.5 (m, 1H, Ar–CH) 4.7 (d, 1H, J_{gem} = 1.2 Hz, =CH*H*) 4.8 (m, 2H, −N=N−CH_2−) 5.0 (m, 1H, CH−C=CH_2) 5.1 (d, 1H, J_{gem} = 1.2 Hz, =CH*H*) 6.8–7.3 (m, 4H, arom)	
9b	119–123[b]	2060, 2000–1860	3.5 (ddd, 1H, J_{vic} = 7.5 Hz, J_{vic} = 7.8 Hz, J_{vic} = 4.15 Hz, Ar−CH−) 4.65 (ddd, 1H, J_{gem} = 16.3 Hz, J_{vic} = 4.15 Hz, $J_{1\text{-}5}$ = 1.5 Hz, HC*H*−N=N−) 4.81 (ddd, 1H, J_{gem} = 16.3 Hz, J_{vic} = 7.5 Hz, $J_{1\text{-}5}$ = 2.3 Hz, *H*CH−N=N−) 4.84 (d, 1H, J_{gem} = 2 Hz, =CH*H*) 5.06 (dt, broad, 1H, J_{vic} = 7.8 Hz, $J_{1\text{-}5}$ = 1.5–2.5 Hz, CH−C=CH_2) 5.10 (d, 1H, J_{gem} = 2 Hz, =C*H*H) 6.81 (d, 1H, J_{ortho} = 8.7, H *ortho* to Br) 7.20 (d, 1H, J_{meta} = 2.2 Hz, H *ortho* to Br) 7.30 (dd, 1H, J_{ortho} = 8.75 Hz, J_{meta} = 2.2 Hz, H *meta* to Br)	221.2 (CO), 213.8 (CO), 147.6, 132.4, 131.3, 120.4, 118.9, 115.0, 105.4, 98.9, 90.0, 83.9, 83.0
9c	105–107[a]	2075, 2000–1850	3.46 (dt, 1H, J_{vic} = 7.3 Hz, J_{vic} = 5.3 Hz, Ar−CH−) 3.76 (s, 3H, −OCH_3) 4.72 (dd, 2H, J_{vic} = 5.3 Hz, $J_{1\text{-}5}$ = 2 Hz, −CH_2−N=N−) 4.80 (d, 1H, J_{gem} = 1.7 Hz, =CH*H*) 4.97 (dt, 1H, J_{vic} = 7.3 Hz, $J_{1\text{-}5}$ = 2 Hz, CH−C=CH_2) 5.06 (d, 1H, J_{gem} = 1.7 Hz, =C*H*H) 6.41 (d, 1H, J_{meta} = 2.5 Hz, H *ortho* to OMe) 6.58 (dd, 1H, J_{ortho} = 8.6 Hz, J_{meta} = 2.5 Hz, H *ortho* to OMe) 6.86 (d, 1H, J_{ortho} = 8.6 Hz, H *meta* to OMe)	

[a] Crystallized from pentane. [b] Crystallized from hexane/CH_2Cl_2. [c] ^{13}C NMR spectra were not recorded for compounds **9a**, **c**.

TABLE 4. Physical, analytical and spectroscopic data of complexes **10a–c**

Compound	m.p. (°C)	Analytical data (%) found (calc.)			IR data ν(CO) (cm^{-1})	*m/z*	^{1}H NMR data δ (ppm)	^{13}C NMR data δ (ppm)
		C	H	N				
10a	144[a]	50.91 (50.80)	2.95 (2.66)	6.91 (7.41)	2065, 1990, 1970–1900	378 (M^+) 350 ($M^+ - $CO) 322 ($M^+ - $2CO) 294 ($M^+ - $3CO) 266 ($M^+ - $4CO) 238 ($M^+ - $5CO)	2.50 (s, 3H, $-$CH$_3$) 3.82 (dd, 1H, J_{vic} = 10 Hz, J_{vic} = 11 Hz, Ar–C*H*–CH$_2$–) 4.12 (dd, 1H, J_{gem} = 16 Hz, J_{vic} = 11 Hz, Ar–CH–HC*H*–) 5.04 (dd, 1H, J_{gem} = 16 Hz, J_{vic} = 10 Hz, Ar–CH–*H*CH–) 7.00–7.08 (m, 4H, arom)	221.3 (CO), 214.4 (CO), 157.8, 152.8, 151.3, 128.7, 127.7, 125.2, 121.3, 116.9, 81.7, 33.9, 16.2
10b	119–123[b]	42.04 (42.04)	2.02 (1.98)	5.97 (6.13)	2060, 2000–1860	456, 458 (M^+) 428, 430 ($M^+ - $CO) 400, 402 ($M^+ - $2CO) 372, 374 (l O) 344, 346 (l O) 316, 318 (l O)	2.50 (d, 3H, $J_{1\text{–}6}$ = 1.5 Hz) 3.80 (ddq, 1H, J_{vic} = 11.5 Hz, J_{vic} = 10 Hz, $J_{1\text{–}6}$ = 1.5 Hz, Ar–CH) 4.10 (dd, 1H, J_{vic} = 11.5 Hz, J_{gem} = 16 Hz, Ar–CH–HC*H*–) 5.02 (dd, 1H, J_{vic} = 9 Hz, J_{gem} = 16 Hz, Ar–CH–*H*CH–) 7.00 (d, 1H, J_{ortho} = 9 Hz, H *ortho* to Br) 7.18 (d, 1H, J_{meta} = 1.5 Hz, H *ortho* to Br) 7.35–7.40 (dd, 1H, J_{ortho} = 9 Hz, J_{meta} = 1.5 Hz, H *meta* to Br)	221.0 (CO), 215.3 (CO), 152.0, 150.3, 141.1, 131.6, 130.5, 123.2, 118.5, 117.5, 81.5, 33.8, 16.2
10c	132[a]	49.76 (50.01)	2.72 (2.96)	7.03 (6.84)	2073, 2000–1850	408 (M^+) 380 ($M^+ - $CO) 352 ($M^+ - $2CO) 324 ($M^+ - $3CO) 296 ($M^+ - $4CO) 268 ($M^+ - $5CO)	2.50 (s, 3H, $-$CH$_3$) 3.73 (dd, 1H, J_{vic} = 10 Hz, J_{vic} = 11 Hz, Ar–C*H*–CH$_2$–) 3.79 (s, 3H, $-$OCH$_3$) 4.05 (dd, 1H, J_{vic} = 11 Hz, J_{gem} = 16 Hz, Ar–CH–HC*H*–) 4.99 (dd, 1H, J_{vic} = 10 Hz, J_{gem} = 16 Hz, Ar–CH–*H*CH–) 6.65 (d, 1H, J_{meta} = 2.5 Hz, H *ortho* to OMe) 6.70 (dd, 1H, J_{meta} = 2.5 Hz, J_{ortho} = 8.3 Hz, H *ortho* to OMe) 6.93 (d, 1H, J_{ortho} = 8.3 Hz, H *meta* to OMe)	222.0 (CO), 216.5 (CO), 160.0, 152.1, 142.2, 128.2, 113.3, 111.6, 102.3, 82.2, 82.0, 55.7, 33.5, 16.2

[a] Crystallized from n-pentane. [b] Crystallized from n-hexane/CH$_2$Cl$_2$.

purified by flash column chromatography (eluent, light petroleum/CH_2Cl_2 7:3). Compound **11** was recovered as a yellow–ochre solid in 32% yield. M.p. 80–83 °C. IR (nujol), ν (cm^{-1}): 2073, 2009, 1954, 1908, 1674, 659. ^1H NMR, δ (ppm): 1.15 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 2.62 (m, 1H, $(CH_3)_2C-CH-CH_2$), 4.56 (m, 4H, $H_2C=C$ and $N=N-CH_2$), 5.58 (d, 1H, $N=N-CH$). *m/z*: 344 (M^+), 316, 288, 260, 232, 204, 174.

Reaction of complex 3 with cyclopentadiene: synthesis of compound 12

A solution of complex **3** (0.23 g, 0.8 mmol) and cyclopentadiene (10 ml) in benzene (20 ml) was left at room temperature for 20 h and then at 40–45 °C for 5 h. The solvent was distilled under reduced pressure and the residue was purified by flash column chromatography (eluent, diisopropyl ether/n-pentane 1:22). The first fraction (65 mg, yellow solid) and the second one (44 mg, yellow oil) resulted to be the two *endo* and *exo* isomers of the cycloadduct **12**, even if, on the basis of the ^1H NMR spectra, we could not assign exactly the stereochemistry of the two isomers. Spectroscopic data for the first fraction: IR (nujol), ν (cm^{-1}): 2060, 1985, 1980, 1970–1870 (CO): ^1H NMR, δ (ppm): 0.82–0.90 (1H, broad d, $J=9.4$ Hz, $-CHH-$), 1.22–1.42 (1H, m, $-CHH-$), 1.42 (3H, s, CH_3), 1.58 (3H, s, CH_3), 1.84 (1H, broad d, $J=7.4$ Hz, $-CHC(CH_3)_2$), 2.80 (1H, m, $-CH-CH_2$), 3.7 (1H, m, $-CH-CH_2-$), 4.0 (1H, broad d, $J=7.1$ Hz, $-CH-C=Cr$), 6.25 (1H, m, $-CH=CH-$), 6.35 (1H, m, $-CH=CH-$). Spectroscopic data for the second fraction: IR (neat), ν (cm^{-1}): 2060, 1985, 1975–1880 (CO); ^1H NMR, δ (ppm): 1.22–1.6 (2H, m, $-CH_2$), 1.38 (3H, s, CH_3), 1.51 (3H, s, CH_3), 2.51 (1H, dd, $J_1=8.2$, $J_2=3.6$ Hz, $CHC(CH_3)_2$), 2.91 (1H, m, $CH-CH_2$), 3.86 (1H, m, $CH-CH_2$), 4.65 (1H, dd, $J=8.2$, $J=4.7$ Hz, $CH-C=Cr$), 6.0–6.25 (2H, m, $-CH=CH-$).

A third fraction was eluted (eluent, diethyl ether/light petroleum 1:1), thus recovering the unreacted complex **3** (60 mg). The conversion of complex **3** into **12** was then 52%.

X-ray single crystal structure determination of 2a and 3

A crystal of complex **2a** was mounted in the air; a crystal of **3** was mounted in a glass capillary and sealed under nitrogen. Reduced cells were obtained using TRACER [16]. Crystal data and the details associated with data collection and structure refinement for compounds **2a** and **3** are given in Table 5. The data were collected at room temperature (295 K). The diffracted intensities were corrected for Lorentz, polarization and background effects. For **2a**, an empirical absorption correction was applied based on Ψ-scans of three suitable reflections having χ values close to 90° (Ψ 0–360°, every 10°) [17]; absorption effects for **3** could be ignored.

The structures were solved by means of a combination of heavy-atom and difference Fourier methods, and refined by full-matrix least-squares, minimizing the function $\Sigma w \Delta F^2$. For compound **2a**, the weights assigned to individual observations were $w=0.7816/[\sigma^2(F_o)+0.0348F_o^2]$ where $\sigma^2(F_o)$ is the standard deviation for each reflection as derived from counting statistics. During the refinement of **3**, unit weights were used since they gave a satisfactory analysis of variance and the best agreement factors.

Refinements were at first isotropically, and then anisotropic thermal displacement parameters were assigned to all non-hydrogen atoms. All of the hydrogen atoms were located from difference Fourier maps and introduced in the final stages of refinement as fixed atom contributions (isotropic U fixed at 0.06 and 0.08 Å^2 for **2a** and **3**, respectively). The scattering factors for neutral non-hydrogen atoms, hydrogen atoms and anomalous dispersion corrections for scattering factors were taken from ref. 18a–c. Among low-angle reflections, no correction for secondary extinction was deemed necessary. The final difference map showed no unusual features, with no significant peaks above the general background. All of the calculations were performed using SHELX-76 [19]. Final non-hydrogen atomic coordinates for compounds **2a** and **3** are listed in Tables 6 and 7, respectively.

FT-IR, Raman and resonance Raman spectra of 2a, 2d and 3

FT-IR spectra were obtained on n-heptane solutions and KBr pellets of all the examined compounds, using an FTS-40 Digilab spectrophotometer.

Electronic spectra of the n-hexane solutions of the compounds were recorded on a Perkin Elmer, Lambda series spectrophotometer.

FT-Raman spectra were recorded on powdered samples, using a Bruker IFS 66 spectrophotometer equipped with a Bruker FRA 106 accessory and an Nd-YAG laser (1064 nm).

Resonance Raman (RR) spectra were obtained on n-hexane solutions of the compounds by means of a JASCO TRS-300 spectrophotometer. For excitation, the 568.2 nm line of a Kr ion laser was used for compounds **2a** and **2d**, and the 457.9 nm line of an Ar ion laser for compound **3**.

Results and discussion

The only type **2** cyclic complex known when we began this work was compound **2a**, prepared by Aumann and Heinen from salicylaldehyde, pentacarbonyl(methoxymethylcarbene)chromium(0) and triethylam-

TABLE 5. Summary of crystallographic data and data collection parameters for **2a** and **3**

	Compound **2a**	Compound **3**
Formula	$C_{14}H_6CrO_6$	$C_{11}H_8CrO_6$
Formula weight	322.2	288.2
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	7.614(3)	6.553(1)
b (Å)	14.033(3)	9.408(1)
c (Å)	12.766(3)	10.620(1)
α (°)		92.70(1)
β (°)	95.24(2)	92.30(1)
γ (°)		92.12(1)
V (Å^3)	1358.3(7)	653.0(1)
Z	4	2
$F(000)$	648	292
ρ_c (g cm^{-3})	1.576	1.466
λ radiation (Mo Kα) Å	0.71073	0.71069
Diffractometer	Enraf-Nonius CAD4	Philips PW 1100
μ (Mo Kα) (cm^{-1})	8.43	8.67
Transmission factor: max.–min.	1.00–0.96	1.00–0.87
Crystal size (mm)	0.13 × 0.15 × 0.22	0.24 × 0.35 × 0.46
θ Range (°)	3–25	3–23
Collected octants	$\pm 9/+16/+15$	$\pm 7/\pm 10/+11$
No. significant reflections ($I > 3\sigma(I)$)	1071	1255
Ratio: N_{obs}/N_{var}	5.6	7.8
R^a	0.034	0.033
R_w	0.044	0.033

$^aR = \Sigma\Delta F/\Sigma F_o$. $^bR_w = [\Sigma w\Delta F^2/\Sigma wF_o^2]^{1/2}$.

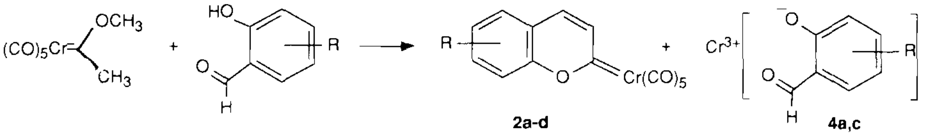
TABLE 6. Fractional atomic coordinates (×10^4) for complex **2a**

Atom	x/a	y/b	z/c
Cr	2484(1)	1636.6(6)	10267.2(7)
O(1)	−17(7)	1328(4)	11968(4)
O(2)	5573(7)	1501(4)	11954(4)
O(3)	4995(6)	1878(4)	8566(4)
O(4)	−548(7)	1805(4)	8559(4)
O(5)	2599(7)	−494(3)	9933(5)
O(6)	2665(5)	3644(3)	9624(3)
C(1)	901(9)	1470(4)	11334(5)
C(2)	4413(9)	1557(4)	11324(5)
C(3)	4080(9)	1804(4)	9223(5)
C(4)	577(9)	1738(4)	9213(5)
C(5)	2547(8)	303(5)	10082(5)
C(6)	2396(7)	3076(4)	10467(4)
C(7)	2069(9)	3584(4)	11395(4)
C(8)	2000(8)	4545(4)	11446(5)
C(9)	2315(7)	5110(4)	10564(4)
C(10)	2278(8)	6121(4)	10533(5)
C(11)	2600(8)	6567(4)	9621(5)
C(12)	2932(9)	6076(5)	8718(6)
C(13)	2963(9)	5095(5)	8737(5)
C(14)	2638(7)	4624(4)	9654(4)

TABLE 7. Fractional atomic coordinates (×10^4) for complex **3**

Atom	x/a	y/b	z/c
Cr	1963.8(12)	1476.5(8)	2134.9(7)
C(1)	3038(7)	1279(5)	503(5)
O(1)	3656(5)	1206(4)	−484(3)
C(2)	4482(8)	963(5)	2901(5)
O(2)	5965(6)	656(4)	3387(4)
C(3)	967(8)	1779(6)	3783(5)
O(3)	419(7)	1968(6)	4767(4)
C(4)	−524(8)	2027(5)	1410(5)
O(4)	−2032(6)	2379(4)	963(4)
C(5)	998(7)	−446(5)	2042(5)
O(5)	425(6)	−1605(4)	1967(4)
O(6)	4096(5)	4151(3)	3109(3)
C(6)	2993(6)	3512(5)	2160(4)
C(7)	4713(8)	5635(5)	2823(5)
C(8)	3733(8)	5755(5)	1576(5)
C(9)	2765(8)	4548(5)	1198(4)
C(10)	3871(11)	6601(6)	3857(5)
C(11)	7005(10)	5713(6)	2867(7)

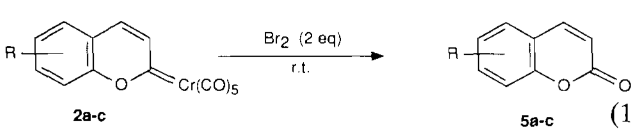
ine in diethyl ether at reflux [13]. The same procedure was used by us to prepare **2d** in 42% yield, but lower yields were obtained in the case of **2b** and **2c** (Scheme 1). Complex **2b** was better synthesized when the reaction was carried out in DMF solution, in the presence of neutral alumina; **2c** was obtained in 30% yield in DMF at −20 °C, using K_2CO_3 as a base. The physical, analytical and spectroscopic data of compounds **2b–d** are reported in Table 1. The preparation of **2c** was always accompanied by the formation of the Cr^{3+} salt of 4-methoxy-2-hydroxybenzaldehyde **4c**. The analogous salt **4a** was also isolated in 12% yield when **2a** was



Reaction conditions : **2a,2d**: Et_3N, Et_2O, reflux, 4h
2b : neutral Al_2O_3, DMF, 20 °C, 28h
2c : K_2CO_3, DMF, -20 °C, 30 min

Scheme 1.

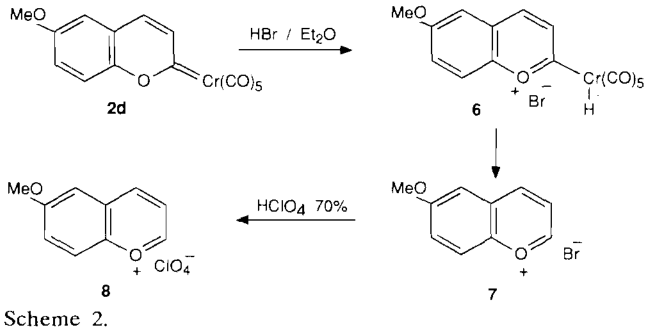
heated at 80 °C for 32 h in commercial 2,3-dimethyl butadiene indicating that complex **2a** would undergo a retrocondensation reaction probably promoted by the water present in the reaction mixture. The structure of **4a** was confirmed by comparison with the spectroscopic data of an authentic sample synthesized as reported in the literature [20].



(1)

The complexes **2a–d** were dark in colour (deep violet or deep red) and very stable even in air (they can be stored at room temperature without any particular precaution for several months, without any detectable decomposition). They also showed a low propensity to be oxidized with the reagents usually used for the oxidation of carbene complexes (Ce^{IV}, DMSO and $O_2/h\nu$), and it was possible to transform complexes **2a–c** into the corresponding coumarin derivatives **5a–c** in quantitative yields only by means of the treatment with two equivalents of bromine in chloroform or dichloromethane (eqn. (1), see 'Experimental').

Interestingly, the treatment of carbene complex **2a** with anhydrous HBr led to the detachment of the $Cr(CO)_5$ moiety, with the production of the pyrilium salt isolated as perchlorate **8** (Scheme 2). Intermediate in the formation of **7** is probably the protonated complex **6**, which is transformed through reductive elimination into the stable pyrilium salt **8** [21]. The reaction of alkoxy and amino Fischer-type carbene complexes with HBr is well documented in the literature and, in these cases, aldehydes are formed through reductive elimination on the intermediate oxonium salt followed by the hydrolysis of the resulting enol ether [1c] and [22].

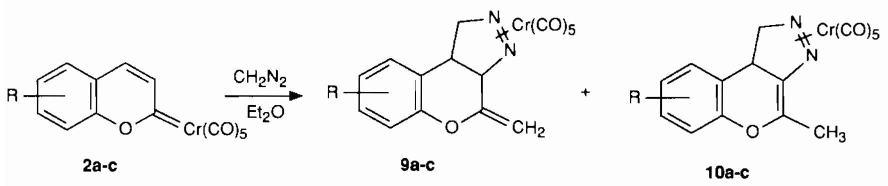


Scheme 2.

The reaction of complexes **2a–c** with CH_2N_2, run between −78 and 0 °C in Et_2O solution, led to products **9a–c** and **10a–c** (Scheme 3). In all cases, an excess of diazomethane was used. Complex **2b** proved to be the most reactive (3 h at −20 °C), followed by **2a** (6 h at −20 °C); **2c** required 6 h at 0 °C to react completely (see Table 2). These are therefore slower than the analogous reactions performed on 5-methylene-(2-oxacyclopentylidene) carbene complexes [3], and they are qualitatively dependent on the nature of the substituent present on the benzene ring.

As expected, compounds **2a–c** show two possible sites of attack: the α,β carbon–carbon and the carbon–metal double bond. As can be seen, cycloadducts **9a–c** arise both from the addition of one equivalent of diazomethane to the double bond α,β to the carbene carbon atom, and the reaction of another equivalent of diazomethane with the carbon–metal double bond, producing the α-methylene double bond [23]; consequently, the addition of diazomethane cannot be achieved chemoselectively. The isomerization of compounds **9** to **10** occurs spontaneously at room temperature and can be followed by TLC.

The reactivity of complexes **2a–c** towards diazomethane parallels that of the Fischer-type carbene complexes bearing a carbon–carbon triple bond [23] or an exocyclic methylene group [3] in the α,β position with respect to the carbene carbon atom. Also in those cases, both a [4+2] 1,3-dipolar cycloaddition reaction on the unsaturated bond and a coupling between the carbene carbon atom and the diazomethane take place, leading to $Cr(CO)_5$ complexed pyrazole or pyrazoline derivatives, respectively. Even in very mild conditions, the transformation of complexes **2a–c** into compounds **9a–c** and **10a–c** reported in Scheme 3 is fast, and therefore no correct determination of the reaction sequence (the cycloaddition and the cleavage of the chromium–carbon bond with the formation of the carbon–carbon double bond) is possible. However, there is some evidence that the $Cr(CO)_5$ group does not actually activate the double bond of complexes **2a–c** towards [4+2] cycloaddition reaction (either 1,3-dipolar



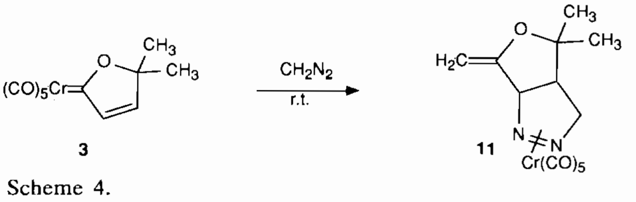
Scheme 3.

or Diels–Alder). In order to obtain more information about the reactivity of complexes **2**, we also studied the reactions of compound **2a** with 2,3-dimethyl-1,3-butadiene and cyclopentadiene as 1,3-dienes, and with 3,5-dichloro-2,4,6-trimethylbenzonitrileoxide and the nitrilimine generated from the corresponding methyl α-chloroglyoxylate phenylhydrazone with triethylamine as 1,3-dipoles. None of these reactions gave the corresponding cycloadducts or any other identifiable product. These results could indicate that, in the case of the reactions of complexes **2a–c** with diazomethane, the formation of the exocyclic double bond is the first reaction to occur, followed by the cycloaddition to the endocyclic double bond. In order to try to gain further insights into these problems and see whether the endocyclic double bond could react independently from the transformation of the carbon–metal double bond, we performed the reaction of compound **2a** with trimethylsilyldiazomethane, which is known to add chemoselectively to carbon–carbon triple bond of alkynylcarbene complexes [23] and to the exocyclic double bond of carbene complexes [3]. No reaction was observed after refluxing a n-hexane solution of trimethylsilyldiazomethane and **2a**; furthermore, it was impossible to achieve any cycloaddition reaction with this reagent, thus confirming the low reactivity of the double bond in complexes **2a–c**. To determine whether variations in the size of the ring in which the double bond is incorporated could have some effect on the reactivity, we studied the reaction of complex **3** [6] with the diazomethane as 1,3-dipole and with some dienes. The reaction of complex **3** with an excess of CH_2N_2 was very rapid (30 min at −78 °C) and gave compound **11** (Scheme 4), in analogy with complexes **2** and with other reported α,β-unsaturated Fischer-type carbene complexes (see above).

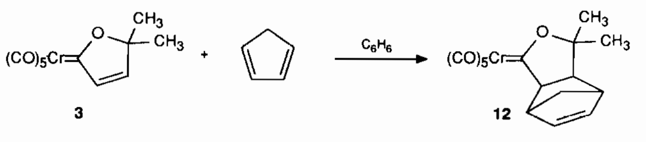
As far as the reaction with dienes are concerned, we tried 2,3-dimethyl-1,3-butadiene, *trans*-1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene (Danishefsky's diene) and cyclopentadiene. In the first two cases, no reaction was observed: the starting complex **3** was recovered in more than 90% yield after several days at reflux in 2,3-dimethyl-1,3-butadiene in the first case and after 8 h at reflux in benzene in the second case. However, complex **3** easily reacted with cyclopentadiene, and the corresponding Diels–Alder cycloadduct **12** was recovered as a mixture of the two *endo* and *exo* isomers (Scheme 5) after a few hours at room temperature, (see 'Experimental'). Although complex **3** only reacts with cyclopentadiene, this result indicates that there is an activation of the carbon–carbon double bond not only with respect to the double bond incorporated in a six-membered ring of complexes **2a–c**, but also with respect to terelactone **13**, the carbon analogue of complex **3** which does not react with cyclopentadiene even at 160 °C [24].

On the basis of the study on complexes **2a–c** and **3** reported here, we can draw the conclusion that there is a significant lowering in reactivity when the double bond in the α,β position with respect to a chromium pentacarbonyl group is part of a five- or six-membered ring, as compared with the reported reactivity of alkenyl carbene complexes [1]. However, this reduced reactivity does not seem to be related to a lack of conjugation between the carbon–carbon double bond and the $Cr(CO)_5$ group. Despite the fact that only the inductive effect of the $Cr(CO)_5$ moiety is operating, alkenyl carbene complexes are very reactive towards 1,3-dienes [1], as well as towards diazomethane and trimethylsylildiazomethane [3].

In the case of complexes **2a–c**, the ^{13}C NMR chemical shift values of the carbene carbon atoms, which are found in the range of 290–300 ppm, show that the carbene carbons are shielded. In principle, this could be related to a π interaction of the lone pair of the oxygen atom with the carbene carbon atom, leading to the organic ligand assuming a benzopyrilium-like structure (Fig. 3). Single crystals of compounds **2a** and **3**



Scheme 4.



Scheme 5.

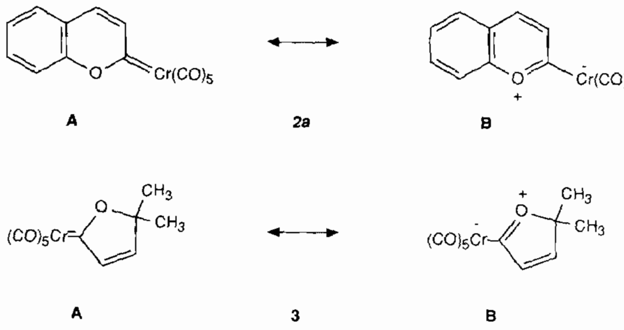


Fig. 3. Resonance formulas for complexes **2a** and **3**.

were submitted to X-ray analysis, and to resonance Raman spectroscopy studies in order to obtain further information concerning the molecular parameters and the electronic interactions between the $Cr(CO)_5$ unit and the organic ligand.

Description of the structures of 2a and 3

The crystal structures of **2a** and **3** consist of a packing of neutral discrete molecules with normal non-bonding interactions. Figures 4 and 5, show the ORTEP drawings of molecules **2a** and **3**, respectively, with a partial labelling scheme. Tables 8 and 9 give a list of the relevant bond distances and angles for the two complexes. In both complexes, the coordination around the Cr atom, defined by five CO ligands and the pertinent carbenic moiety, is octahedral with overall idealized C_{4v} symmetry. The carbenic moieties assume a staggered conformation with respect to the four *cis* carbonyl ligands, with a dihedral angle of 28.5(2)° between the Cr/C(1)/C(3)/C(6) and Cr/C(6)/C(7)/O(6) least-square planes in **2a** and 41.1(1)° between the C(2)/C(4)/C(5)/C(6) and C(6)/O(6)/C(8)/C(9) least-squares in **3**. The Cr, O(6), C(6) and C(7) (**2a**) and Cr, O(6), C(6) and C(9) (**3**) atoms are all coplanar within experimental error. The question of the relative contribution of resonance forms **A** and **B** (Fig. 3) to the stabilization of complexes **2a** and **3** can be discussed with the support of the structural parameters. The Cr–C(carbene) bond length for both compounds (**2a**: 2.037(6), **3**: 2.005(5) Å) falls in the lower part of the range displayed by Cr–C(carbene) interactions with a formal bond order of 2 (form **A** dominant) in related alkoxy carbene complexes (e.g. 2.051(4) in $(CO)_5Cr{=}C(OEt)C_6H_4{-}C_6H_4C(OEt){=}Cr(CO)_5$ [25], 2.010(4) in $(CO)_5Cr{=}C(OCH_3){-}C(CH_3){=}CHCH_3$ [26], 2.064(3) Å) in $(CO)_5Cr{=}C(OCH_3){-}C(OCH_3){=}CHOCH_3$ [27]), while the carbenes in which form **B** dominates have longer Cr–C(carbene) distances, as observed for example in $(CO)_5Cr{=}C(OSiCH_3)CH{=}P(CH_3)_3$ (2.137(7) Å) [28]

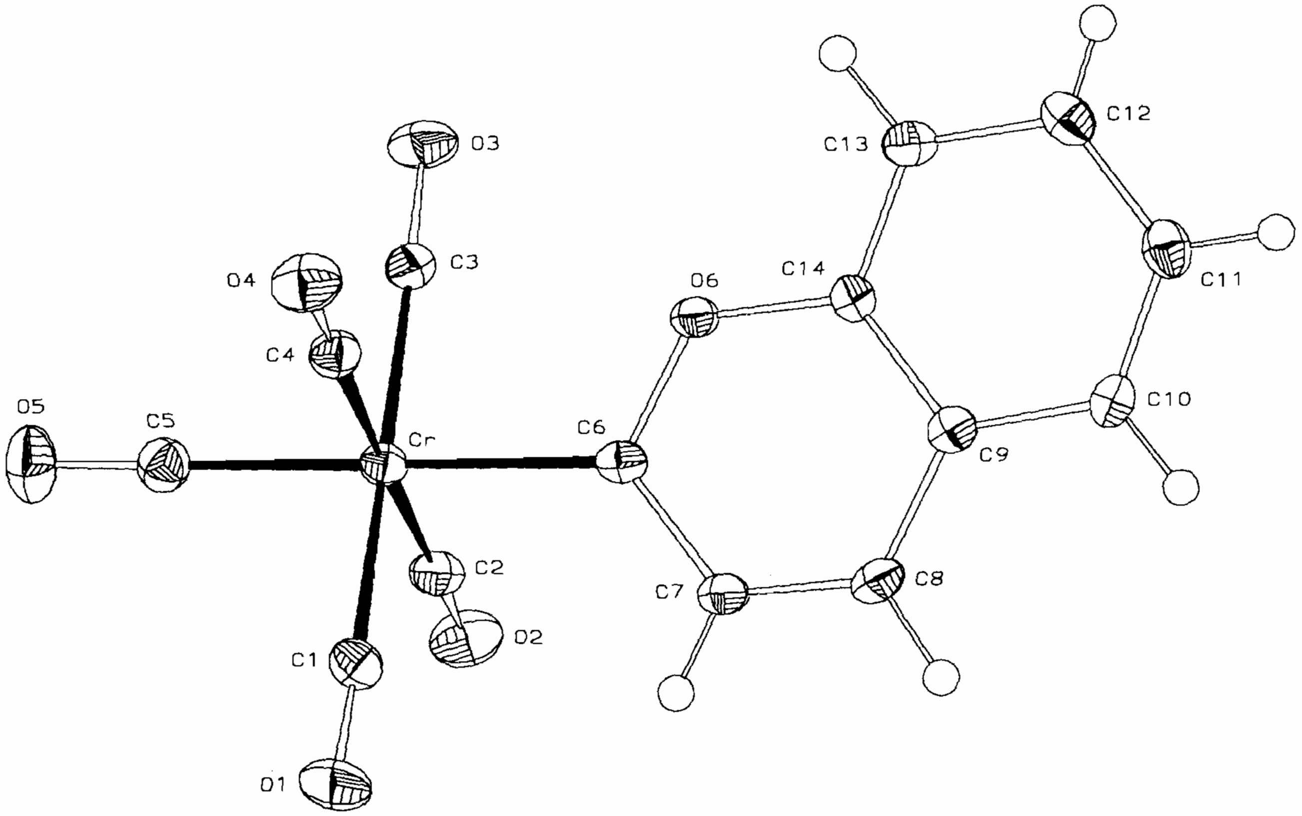


Fig. 4. ORTEP drawing of compound **2a**. Hydrogen atoms were given arbitrary radii. Thermal ellipsoids are drawn at the 30% probability level.

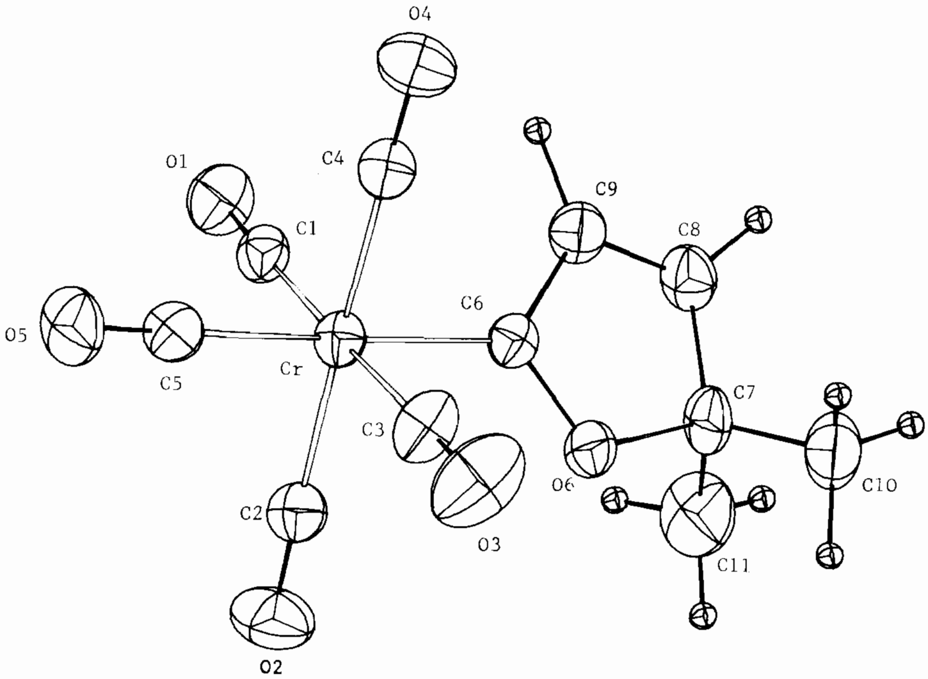


Fig. 5. ORTEP drawing of compound **3**. Hydrogen atoms were given arbitrary radii. Thermal ellipsoids are drawn at the 30% probability level.

TABLE 8. Selected bond distances (Å) and angles (°) for **2a** with e.s.d.s on the least significant digit in parentheses

Cr–C(1)	1.914(7)	C(7)–C(8)	1.352(8)
Cr–C(2)	1.904(7)	C(8)–C(9)	1.416(8)
Cr–C(3)	1.899(6)	C(9)–C(10)	1.419(8)
Cr–C(4)	1.892(8)	C(9)–C(14)	1.388(7)
Cr–C(5)	1.888(7)	C(10)–C(11)	1.363(9)
Cr–C(6)	2.037(6)	C(11)–C(12)	1.386(9)
O(6)–C(6)	1.370(7)	C(12)–C(13)	1.376(8)
O(6)–C(14)	1.376(6)	C(13)–C(14)	1.387(8)
C(6)–C(7)	1.424(8)		
Cr–C(6)–O(6)	118.0(4)	C(6)–O(6)–C(14)	123.8(4)
Cr–C(6)–C(7)	127.6(4)	C(9)–C(10)–C(11)	118.6(6)
O(6)–C(6)–C(7)	114.3(5)	C(10)–C(11)–C(12)	122.9(6)
C(6)–C(7)–C(8)	123.4(5)	C(11)–C(12)–C(13)	119.1(6)
C(7)–C(8)–C(9)	120.7(5)	C(12)–C(13)–C(14)	119.1(6)
C(8)–C(9)–C(10)	125.3(5)	C(9)–C(14)–O(6)	121.3(5)
C(8)–C(9)–C(14)	116.5(5)	C(9)–C(14)–C(13)	122.1(5)
C(10)–C(9)–C(14)	118.2(5)	C(13)–C(14)–O(6)	116.6(5)

TABLE 9. Selected bond distances (Å) and angles (°) for **3** with e.s.d.s. on the least significant digit in parentheses

Cr–C(1)	1.900(5)	O(6)–C(7)	1.488(6)
Cr–C(2)	1.899(5)	C(6)–C(9)	1.452(7)
Cr–C(3)	1.905(5)	C(7)–C(8)	1.459(7)
Cr–C(4)	1.876(5)	C(7)–C(10)	1.526(8)
Cr–C(5)	1.891(5)	C(7)–C(11)	1.500(8)
Cr–C(6)	2.005(5)	C(8)–C(9)	1.318(7)
O(6)–C(6)	1.324(5)		
C(6)–O(6)–C(7)	111.3(3)	O(6)–C(7)–C(8)	101.5(4)
Cr–C(6)–O(6)	123.9(3)	C(10)–C(7)–C(11)	111.3(5)
O(6)–C(6)–C(9)	106.8(4)	C(8)–C(7)–C(11)	115.3(5)
Cr–C(6)–C(9)	129.3(3)	C(8)–C(7)–C(10)	114.5(5)
O(6)–C(7)–C(11)	106.5(4)	C(7)–C(8)–C(9)	110.5(4)
O(6)–C(7)–C(10)	106.5(4)	C(6)–C(9)–C(8)	109.9(4)

and $(CO)_5Cr{=}C(OCH_3)CH{=}CHN(CH_3)_2$ (2.130(5) Å) [29]. In the present case, the apparently low contribution of the pyrilium form **B** to the stabilization of complex **2a** is in line with the observed pattern of intra-ring bond distances, which closely resembles that of the coumarin molecule [30]. The C(6)–O(6) and C(14)–O(6) bond lengths (1.370(7) and 1.376(6) Å, respectively) are similar to their coumarin counterparts (1.367(4) and 1.378(4) Å respectively), and the C–C double bond appears to be mainly localized between the C(7) and C(8) atoms (1.352(8), as compared with 1.344(5) Å in coumarin). For **3**, the C(8)–C(9) double bond character is in agreement with the bond distance value (1.318(7) Å), while the C(6)–O(6) interaction is shorter than that observed in **2a** and in close agreement with the typical value of about 1.33 Å reported for alkoxy carbene complexes [31]. Taking into account the average value of 1.36 Å found in molecules akin to **3** in which the $Cr(CO)_5$ moiety is replaced by a C=O function (e.g. refs. 32 and 33), it seems that O(6) exhibits a higher p overlap with the Cr atom in the carbene derivative **3** than in compound **2a**. The Cr–C(carbonyl) and C–O(carbonyl) bond distances are normal for both compounds, with values comparable to those of related systems [34].

Spectroscopic results

According to X-ray diffraction data, the chromium atoms of compounds **2a** and **3** (as well as that of compound **2d**), occupy sites of C_1 symmetry, while the idealized symmetry of the $Cr(CO)_5$ moiety is C_{4v}. For such a locally symmetrical moiety, three IR active ($2A_1 + E$) and four Raman active ($2A_1 + B_1 + E$) ν(CO) stretching vibrations are expected. Among these vibrations, the one indicated as A_1^1 [35–38] is due to the group which is *trans* to the ligand, while the A_1^2, B_2 and E vibrations must be assigned to the equatorial CO groups.

The FT-IR spectra recorded on solutions of the three compounds show a medium-intense (A_1), a weak (A_1) and a strong band (E), as might be expected on the basis of the C_{4v} local symmetry. The frequencies of the IR active ν(CO) stretching vibrations obtained from the solution spectra are reported in Table 10. The highest frequency value could be assigned to what will hereafter be described as the A_1^2 vibration, taking into account the resonance Raman spectra. It must be pointed out that the same assignment has been proposed for some similar compounds [38], although for other molecules of the same class, the highest frequency band has been attributed to the A_1^1 vibration [37].

The FT-IR and Raman spectra (see Fig. 6 for example) recorded on the solid samples show four or five bands in the region of ν(CO) stretching vibrations. In interpreting these spectra it must be remembered that, as indicated by the structural data, the symmetry of the $Cr(CO)_5$ moiety is lower than C_{4v} in the solid state; in order to interpret the experimental data, it is sufficient to hypothesize a C_{2v} symmetry without invoking the lower C_1 symmetry. In a C_{2v} symmetry, the number of expected ν(CO) stretching vibrations agrees with that of the experimental bands:

ν(CO), C_{4v}		ν(CO), C_{2v}
A_1^2 (IR, R)	$\longrightarrow$	A_1 (IR, R)
A_1^1 (IR, R)	$\longrightarrow$	A_1 (IR, R)
B_1 (R)	$\longrightarrow$	A_1 (IR, R)
E (IR, R)	$\longrightarrow$	B_1 (IR, R), B_2 (IR, R)

The assignment of the IR and Raman ν(CO) stretching frequencies of the solid samples reported in Table 10 has been obtained by attributing the most intense Raman bands to the A_1 modes and the most intense IR bands to those vibrations of the C_{2v} group originating from the splitting of the E vibration of the C_{4v} group. Table 10 also lists the frequencies of the ν(Cr–CO) vibrations.

The vibrational spectra from 1700 to 1000 cm^{-1} are particularly interesting (see Fig. 6 for example), especially with regard to the interpretation of the RR spectra. On the basis of published data, it was possible to single out the stretching vibrations of the ethereal function (two bands at about 1240 and 1110 cm^{-1}, respectively) [39] and the C=C and C–C conjugated bonds (two bands at about 1600 and 1170 cm^{-1}, respectively) [40], the δ(CH) vibrations of the *o*-disubstituted aromatic ring [39] and of the CH=CH group (two bands at about 1260 and 1060 cm^{-1}). The assignment of these vibrational modes allowed us to hypothesize that the distribution of π bonds in the molecules of the examined compounds should be as shown in structures **2a**, **2d** and **3**. This hypothesis is in agreement with XRD results and has been confirmed by RR spectra (see below).

The electronic spectra of the three compounds in n-hexane solutions are shown in Fig. 7. These spectra made it possible to identify the suitable frequencies for obtaining the resonance Raman spectra. The assignment of the electronic transitions (Table 11) is in

TABLE 10. C–O and Cr–C stretching frequencies (cm^{-1}) of the $Cr(CO)_5$ moiety for compounds **2a**, **2d** and **3**

Compound		ν(C–O)					ν(Cr–C)				
	C_{4v}	A_1^2	A_1^1	E		B_1	B_1	E		A_1^1	A_1^2
	C_{2v}	A_1	A_1	B_1	B_2	A_1	A_1	B_1	B_2	A_1	A_1
2a	IR[a]	2067m	1988w	1958s							
	IR[b]	2063m	1979sh	1966m	1931s			460wm	453wm		
	R[c]	2055s	1967m		1939w	1922m	520vw			456w	394m
2d	IR[a]	2066m	1986w	1955s							
	IR[b]	2064m	1976m	1950sh	1929s	1916s		467sh	452m		
	R[c]	2058s	1972m	1955w	1935w	1918w	520vw			450w	394m
3	IR[a]	2062m	1987w	1951s							
	IR[b]	2062m	1988m	1949s	1920s			464w			
	R[c]	2060s	1980s		1924m	1911m	536w			451w	395s

[a] N-heptane solution (Cr–C stretching bands not easily distinguishable). [b] KBr pellet. [c] Powdered sample. w = weak, wm = weak medium, sh = shoulder, m = medium, s = strong, vw = very weak.

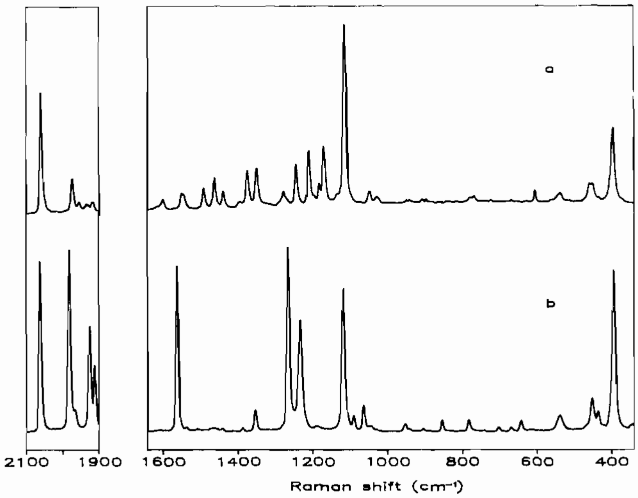


Fig. 6. FT-Raman spectra (λ_{exc} = 1064 nm) obtained on powdered samples of (a) compound **2d** and (b) compound **3**.

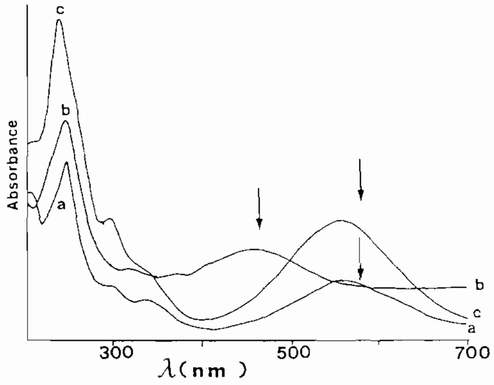


Fig. 7. Electronic spectra of compounds (a) **2d**, (b) **3** and (c) **2a** (n-hexane solution). Arrows indicate the wavelengths chosen for the excitation of RR spectra.

TABLE 11. Electronic transitions (assignment and wavelength in nm) observed for compounds **2a**, **2d** and **3** in n-hexane solution

Compound	d→π*(CO)	d→π*(CO)	d→d	d→π*(L)
2a	235	298	340	548
2d	243	287	333	554
3	239	310	358	452

accordance with previously published reports [35, 41–43] and, once again, was confirmed by the RR spectra (Fig. 8).

The RR spectra of compounds **2a** and **2d**, substantially identical to each other, show an enhancement of the bands due to the δ(CH) vibrations of the aromatic ring and the ν(C=C) vibrations in comparison with the vibrations of the ethereal group. At the same time, in the spectrum of compound **3**, the bands assigned to the vibrations of the CH=CH group are enhanced.

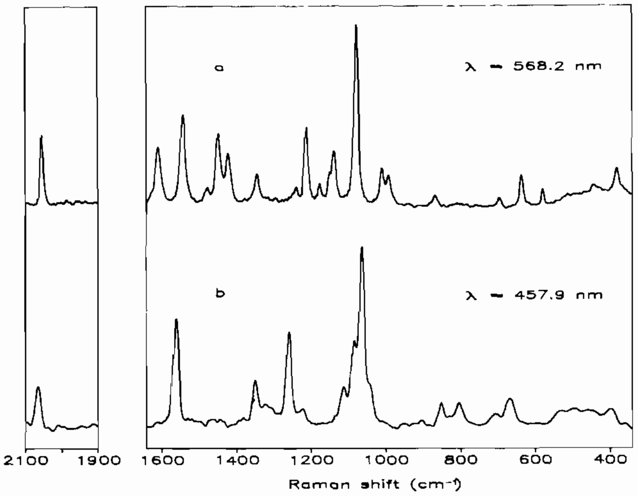


Fig. 8. Resonance Raman spectra obtained on n-hexane solutions of (a) compound **2d** (λ_{exc} = 568.2 nm) and (b) compound **3** (λ_{exc} = 457.9 nm).

Consequently, the use of RR spectra made it possible to assign the bands at 548, 554 and 452 nm in the electronic spectra of our compounds to d→π*(L) transitions. The distributions of the π bonds illustrated above for compounds **2a**, **2d** and **3** is confirmed by the fact that, when the RR spectra of the samples were excited by radiation at a wavelength near to the maximum of the d→π* transition, the stretching vibrations of the ethereal group were not enhanced.

Also of interest is the fact that, when a comparison of the different RR enhancements of the three compounds was made, the most intense enhancement was observed for compound **3**.

Since π delocalization increases with the increase in the wavelength of the d→π*(L) transition [43], we can conclude that compounds **2a**, **2d** and **3** have better delocalization than $Cr(CO)_5$(pyridine) and $Cr(CO)_5$(pyrazine) [35]. Moreover, it can be pointed out that the increases in π delocalization follow the order **3** < **2a** < **2d**.

Finally, it is interesting to note that the ν(Cr–CO) vibrations are not enhanced in the RR spectra, and that, in accordance with the literature [44], only the A_1^2 vibration among the ν(CO) stretching modes gives rise to a band that is strong enough to be easily identified.

Conclusions

X-ray analysis of a single crystal and RR studies show that the metal–carbene carbon bond of complexes **2** and **3** has a high double bond character. Only in the case of **3** does the C_{carb}–O bond length reflect the presence of π donation from the oxygen to the carbene carbon atom. In addition, the relevant stability and the

^{13}C NMR chemical shifts of the carbene carbon atom of complexes **2** indicate that at least one of the three substituents at the carbene carbon atom must act as a good π donor. Bond lengths, in particular that of the C_{carb}–O bond which is longer than expected for alkoxy alkyl carbene complexes, clearly show that in complexes **2** the $Cr(CO)_5$ group is a much better π donor than the other two substituents at the carbene carbon atom. Complexes **2** therefore can be considered as carbene complexes with a pure metal–carbon double bond [45], and the structure that best describes them is the resonance form **A** (Fig. 3). The above considerations are confirmed by the RR spectroscopy studies and are also in agreement with the unexpected low reactivity of the carbon–carbon double bond which only reacted with diazomethane.

Supplementary material

Tables S1–S4, giving hydrogen atoms coordinates, and anisotropic thermal parameters for **2a** and **3** (3 pages) are available from the authors on request.

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References

1 (a) C.P. Casey and W.R. Brunsvold, *Inorg. Chem., 16* (1977) 391; (b) *J. Organomet. Chem., 77* (1974) 345; (c) W.D. Wulff, W.E. Bauta, R.W. Kaesler, P.J. Lankford, R.A. Miller, C.K, Murray and D.C. Yang, *J. Am. Chem. Soc., 112* (1990) 3642, and refs. therein; (d) K.H. Dötz, R. Noack and K. Harms, *Tetrahedron, 46* (1990) 1235; (e) W.D. Wulff and T.S. Powers, *J. Org. Chem., 58* (1983) 2381.

2 (a) R. Hoffmann, *Angew. Chem., Int. Ed. Engl., 21* (1982) 711; (b) F.G.A. Stone, *Angew. Chem., Int. Ed. Engl., 23* (1984) 89.

3 C. Baldoli, P. Del Buttero, E. Licandro, S. Maiorana, A. Papagni and A. Zanotti Gerosa, *J. Organomet. Chem.,* (1994) in press.

4 C. Baldoli, P. Del Buttero, S. Maiorana, G. Zecchi and M. Moret, *Tetrahedron Lett., 34* (1993) 2529.

5 (a) F. Camps, J.M. Moretò, S. Ricart, J.M. Vinas, E. Molinas and C. Miravitless, *J. Chem. Soc., Chem. Commun.,* (1989) 1560; (b) K.N. Juneau, L.S. Hegedus and F.W. Roepke, *J. Am. Chem. Soc., 111* (1989) 4762; (c) K.L. Faran and W.D. Wulff, *J. Am. Chem. Soc., 112* (1990) 6419; (d) S.L.B. Wang and W.D. Wulff, *J. Am. Chem. Soc., 112* (1990) 4550.

6 L. Lattuada, E. Licandro, S. Maiorana, H. Molinari and A. Papagni, *Organometallics, 10* (1991) 807.

7 M. Darbarwar and V. Sundaramurthy, *Synthesis,* (1982) 337.

8 R. Grigg and D. Vipond, *Tetrahedron, 45* (1989) 7587.

9 R. Adams, W.D. McPhee, R.B. Carlin and Z.W. Wicks, *J. Am. Chem. Soc., 65* (1943) 356.

10 C. Baldoli, F. Gioffreda and G. Zecchi, *J. Heterocycl. Chem.,* (1994) in press.

11 F.M. Dean and B.K. Park, *J. Chem. Soc., Perkin Trans. I,* (1980) 2937.

12 R. Aumann and E.O. Fischer, *Angew. Chem., Int. Ed. Engl., 6* (1967) 879.

13 R. Aumann and H. Heinen, *Chem. Ber., 120* (1987) 537.

14 (a) *Dictionary of Organic Compounds,* Vol. 4, Chapman and Hall, London, 1982, p. 3692; (b) Vol. 1, p. 573.

15 F. Richter (ed.), *Beilstein Handbuch der Organischen Chemie,* Vol. 17, Verlag von Julius Springer, Berlin, 1934, p. 171.

16 S.L. Lawton and R.A. Jacobson, *TRACER,* a cell reduction program, Ames Laboratory, Iowa State University of Science and Technology, 1965.

17 A.C.T. North, D.C. Phillips and F.S. Mathews, *Acta Crystallogr., Sect. A, 24* (1968) 351.

18 (a) D.T. Cromer and J.T. Waber, *International Tables for X-Ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974, Table 2.2.B; (b) R.F. Stewart, E.R. Davidson and W.T. Simpson, *J. Chem. Phys., 42* (1965) 3175; (c) D.T. Cromer, *International Tables for X-Ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974, Table 2.3.1.

19 G.M. Sheldrick, *SHELX-76,* system of crystallographic computer programs, University of Cambridge, UK, 1976.

20 M.J. O'Connor and B.O. West, *Aust. J. Chem., 21* (1968) 369.

21 G. Canalini, I. Degani, R. Fochi and G. Spunta, *Ann. Chim. (Rome), 57* (1967) 1045.

22 B.A. Anderson, W.D. Wulff and A. Rahm, *J. Am. Chem. Soc., 115* (1993) 4602.

23 K. Shing Chan and W.D. Wulff, *J. Am. Chem. Soc., 108* (1986) 5229.

24 T.R. Kelly and R.W. McNutt, *Tetrahedron Lett.,* (1975) 285.

25 N. Hoa Tran Huy, P. Lefloch, F. Robert and Y. Jeannin, *J. Organomet. Chem., 327* (1987) 211.

26 U. Schubert and K.H. Dötz, *Z. Naturforsch., Teil B, 39* (1984) 1624.

27 K.H. Dötz, W. Kuhn and U. Thewalt, *Chem. Ber., 118* (1985) 1126.

28 S. Voran, H. Blau, W. Malisch and U. Schubert, *J. Organomet. Chem., 232* (1982) C33.

29 L. Lattuada, E. Licandro, A. Papagni, S. Maiorana, A. Chiesi Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.,* (1988) 1092.

30 E. Gavuzzo, F. Mazza and E. Giglio, *Acta Crystallogr., Sect. B, 301* (1974) 1351.

31 K.H. Dötz, H. Fischer, P. Hofmann, F. Kreissl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes,* Verlag Chemie, Weinheim, 1983, pp. 73–149.

32 A. Mondon, B. Epe and H. Callsen, *Liebigs Ann. Chem.,* (1983) 1760.

33 J. Bigorra, J. Font, R.M. Ortuno, F. Sanchez-Ferrando, F. Florencio, S. Martinez-Carrera and S. Garcia-Blanco, *Tetrahedron, 41* (1985) 5589.

34 A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.,* (1989) S1.

35 G. Boxhorn, D.J. Stufkens and A. Oskam, *Inorg. Chim. Acta, 33* (1979) 215.

36 D.M. Adams, *Metal-ligand and Related Vibrations,* E. Arnold, London, 1967.

37 F.A. Cotton and C.S. Kraihanzel, *J. Am. Chem. Soc., 84* (1962) 4432.

38 C.S. Kraihanzel and F.A. Cotton, *Inorg. Chem., 2* (1963) 533.

39 N.B. Colthup, L.H. Daly and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy,* Academic Press, New York, 1964.

40 G.A. Sultanov and M.M. Musaev, *Izv. Akad. Nauk. Az. SSR, N1* (1957) 31.

41 M. Brigodiot and J.M. Lebas, *J. Mol. Struct., 32* (1976) 297.

42 H. Daamen and A. Oskam, *Inorg. Chim. Acta, 26* (1978) 81.

43 E.O. Fischer, C.G. Kreiter, H.J. Kollmeier, J. Müller and R.D. Fischer, *J. Organomet. Chem., 28* (1971) 237.

44 R.W. Balk, G. Boxhoorn, T.L. Snoeck, G.C. Schoemaker and D.J. Stufkens, *J. Chem. Soc. Dalton Trans.,* (1981) 1524.

45 U. Schubert, *Coord. Chem. Rev., 55* (1984) 261.