

Reactivity of a two heteroatom stabilized anionic chromium (0) carbene complex towards a mono- and a disubstituted alkyne: new synthesis of γ -aminobutenolides and formation of a novel oligomer chromium (0) complex

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Abstract

The reaction of the chromium anionic carbene complex **1** towards diphenylacetylene and phenylacetylene is reported. In the former case the synthesis of γ -functionalized butenolides results after demetallation of the chromium complex **2** and the latter leads to the formation of a novel oligomer chromium complex **5**. These complexes were characterized by mass spectrometry, IR and ¹H and ¹³C NMR spectroscopies and their structures were confirmed by single-crystal X-ray analysis. © 1997 Elsevier Science S.A.

Keywords: Chromium; Anionic carbene; Alkynes; γ -Aminobutenolides

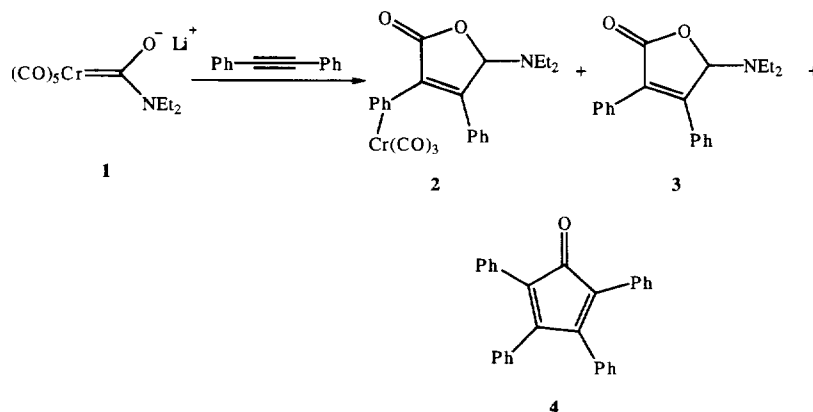
1. Introduction

Considerable effort has been devoted to understanding the reactivity of Fischer-type carbene complexes over the last years. These neutral compounds are known to be valuable reagents for stereoselective carbon–carbon bond formation which may occur either at the low-valent metal template or within the carbene ligand [1,2]. Along this line, one of the most useful and interesting reactions of Fischer neutral carbenes is the insertion of CO and alkyne molecules to form vinylketene intermediates, which may then lead to the corresponding organometallic or organic derivatives [3]. A logical extension concerning the reactivity of transition metal neutral carbenes bearing two heteroatoms has already been explored to some extent and this kind of

versatile reagent is becoming increasingly useful for the synthesis of novel compounds. For example, the preparation of new complexes has been performed by using two-heteroatom-substituted Fischer-type carbenes of iron, chromium and tungsten [4]; and the synthesis of either (E)- or (Z)-vinylsilanes with high stereoselectivities depending on the reaction conditions by addition of organometallic reagents to silyl substituted Fischer-type carbene complexes has been reported [5]. Carbenes substituted with two heteroatoms have also been used to prepare ketenes [6].

Anionic carbene complexes provide potentially valuable reagents or new results. In this context, an attractive approach was reported by Hoyer et al. [7] using the reaction of alkynes and one heteroatom stabilized (Fischer) anionic chromium carbenes for the synthesis of butenolides in good yields. These circumstances prompted us to investigate the reactions of two heteroatom stabilized anionic chromium (0) carbenes with a mono- and a disubstituted alkyne (i.e. phenyl- and

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Scheme 1.

diphenylacetylene) and here we present the main aspects of our work.

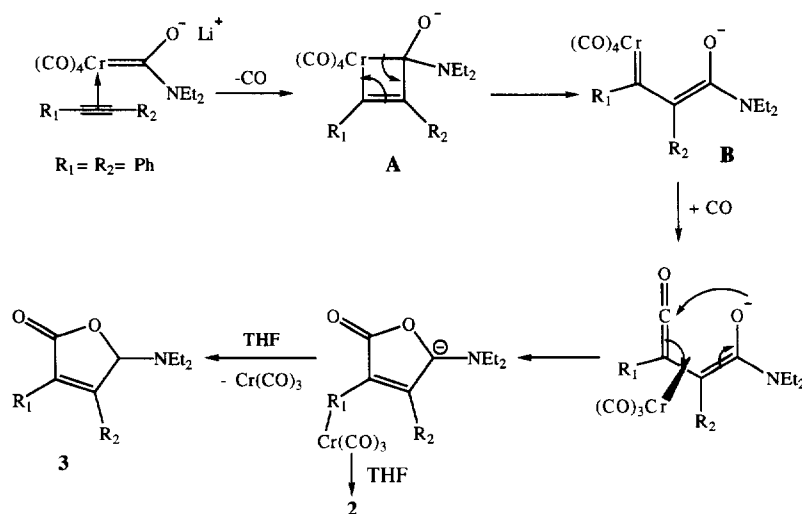
2. Results

2.1. Reactivity of lithium oxydiethylamino-pentacarbonylchromium carbene complex **1** towards diphenylacetylene

The starting carbene complex **1** was readily synthesized by reaction of chromium hexacarbonyl and lithium diethylamide prepared in situ. Upon reaction of diphenylacetylene with carbene complex **1** under reflux in anhydrous THF, after 24 h the formation of three products was observed, which were separated by silica-gel chromatography and their structures were established by spectroscopic methods.

The most abundant product, isolated as a red solid in 65% yield, was given structure **2**, i.e. 5-(N,N-diethylamino)-3-phenyltricarbonyl chromium-4-phenyl-3-butenolide complex, based partly on its spectroscopic features (Scheme 1).

Its IR spectrum exhibits $\nu_{\text{M-CO}}$ frequencies at 1968, 1894 and 1890 cm^{-1} and absorption at 1744 cm^{-1} for the α,β -unsaturated CO group. The highest ions of significant relative intensities in the mass spectrum for this compound correspond to the molecular ion with m/z 443 and to the fragments of successive loss of three CO groups. The ^1H NMR (200 MHz, CDCl_3) spectrum displays at δ 6 ppm a single signal for the methynic proton, at δ 2.8 ppm a multiple signal (4H) and a triplet centered at δ 1 ppm (6H) corresponding to ethyl groups attached to the N atom. Insertion of diphenylacetylene is inferred on the following grounds: a multiplet at δ 7.4 ppm appears owing to 5H for a free phenyl group, upfield shifts for 5H of a phenyl group coordinated to chromium shows signals at δ 5.8, 5.6, 5.4 and 5.1 ppm. The ^{13}C NMR spectrum displays a signal at δ 232 ppm ascribed to metallic CO groups, at δ 169 ppm a signal consistent with an α,β -unsaturated CO group, at δ 157 ppm a peak attributable to C_4 , at δ 131, 130.5, 129.9, 128.6 ppm the peaks owing to the free phenyl group and at δ 125.3 ppm a peak attributable to C_3 , and again upfield shifts for aromatic carbons attached to the chromium at δ 96.9, 96.4, 95.0,



Scheme 2.

Table 1
Bond lengths (Å) and bond angles (°) for complex 2

O(1)–C(2)	1.348(7)	C(6)–C(11)	1.422(9)
O(1)–C(5)	1.486(8)	C(7)–C(8)	1.409(8)
O(2)–C(2)	1.196(8)	C(8)–C(9)	1.375(10)
C(2)–C(3)	1.493(9)	C(9)–C(10)	1.412(9)
C(3)–C(4)	1.332(6)	C(10)–C(11)	1.393(7)
C(3)–C(6)	1.486(7)	C(12)–C(13)	1.373(9)
C(4)–C(5)	1.533(8)	C(12)–C(17)	1.396(9)
C(4)–C(12)	1.469(7)	C(13)–C(14)	1.380(8)
C(5)–N(1)	1.401(7)	C(14)–C(15)	1.379(11)
Cr(1)–C(6)	2.219(4)	C(15)–C(16)	1.361(11)
Cr(1)–C(7)	2.203(7)	C(16)–C(17)	1.382(9)
Cr(1)–C(8)	2.213(7)	N(1)–C(18)	1.468(11)
Cr(1)–C(9)	2.204(7)	N(1)–C(20)	1.465(13)
Cr(1)–C(10)	2.193(6)	C(18)–C(19)	1.350(18)
Cr(1)–C(11)	2.190(4)	C(20)–C(21)	1.487(9)
Cr(1)–C(22)	1.837(7)	C(22)–O(22)	1.155(9)
Cr(1)–C(23)	1.822(8)	C(23)–O(23)	1.146(11)
Cr(1)–C(24)	1.836(7)	C(24)–O(24)	1.150(9)
C(6)–C(7)	1.400(8)		
C(2)–O(1)–C(5)	110.8(5)	C(8)–Cr(1)–C(24)	156.5(2)
O(1)–C(2)–O(2)	122.5(7)	C(9)–Cr(1)–C(24)	151.9(3)
O(1)–C(2)–C(3)	108.4(5)	C(10)–Cr(1)–C(24)	114.5(2)
O(2)–C(2)–C(3)	129.0(6)	C(11)–Cr(1)–C(24)	89.2(2)
C(2)–C(3)–C(4)	108.6(5)	C(22)–Cr(1)–C(24)	88.1(3)
C(2)–C(3)–C(6)	121.9(4)	C(23)–Cr(1)–C(24)	87.1(3)
C(4)–C(3)–C(6)	129.4(5)	C(3)–C(6)–Cr(1)	126.8(4)
C(3)–C(4)–C(5)	109.9(5)	C(3)–C(6)–C(7)	121.6(5)
C(3)–C(4)–C(12)	130.0(5)	Cr(1)–C(6)–C(7)	70.9(3)
C(5)–C(4)–C(12)	120.1(4)	C(3)–C(6)–C(11)	120.2(5)
O(1)–C(5)–C(4)	101.9(4)	Cr(1)–C(6)–C(11)	70.1(2)
O(1)–C(5)–N(1)	113.7(6)	C(7)–C(6)–C(11)	118.1(4)
C(4)–C(5)–N(1)	114.7(6)	Cr(1)–C(7)–C(6)	72.2(4)
C(6)–Cr(1)–C(7)	36.9(2)	Cr(1)–C(7)–C(8)	71.8(4)
C(6)–Cr(1)–C(8)	67.0(2)	C(6)–C(7)–C(8)	121.0(6)
C(7)–Cr(1)–C(8)	37.2(2)	Cr(1)–C(8)–C(7)	71.0(4)
C(6)–Cr(1)–C(9)	79.3(2)	Cr(1)–C(8)–C(9)	71.5(4)
C(7)–Cr(1)–C(9)	66.4(2)	C(7)–C(8)–C(9)	120.3(6)
C(8)–Cr(1)–C(9)	36.3(3)	Cr(1)–C(9)–C(8)	72.2(4)
C(6)–Cr(1)–C(10)	67.3(2)	Cr(1)–C(9)–C(10)	70.8(4)
C(7)–Cr(1)–C(10)	78.8(2)	C(8)–C(9)–C(10)	119.9(5)
C(8)–Cr(1)–C(10)	66.4(2)	Cr(1)–C(10)–C(9)	71.7(3)
C(9)–Cr(1)–C(10)	37.5(2)	Cr(1)–C(10)–C(11)	71.3(3)
C(6)–Cr(1)–C(11)	37.6(2)	C(9)–C(10)–C(11)	120.2(6)
C(7)–Cr(1)–C(11)	66.9(2)	Cr(1)–C(11)–C(6)	72.3(2)
C(8)–Cr(1)–C(11)	78.9(2)	Cr(1)–C(11)–C(10)	71.6(2)
C(9)–Cr(1)–C(11)	67.2(2)	C(6)–C(11)–C(10)	120.5(5)
C(10)–Cr(1)–C(11)	37.1(2)	C(4)–C(12)–C(13)	121.1(5)
C(6)–Cr(1)–C(22)	157.4(3)	C(4)–C(12)–C(17)	121.2(5)
C(7)–Cr(1)–C(22)	152.5(3)	C(13)–C(12)–C(17)	117.7(5)
C(8)–Cr(1)–C(22)	115.4(3)	C(12)–C(13)–C(14)	122.3(6)
C(9)–Cr(1)–C(22)	90.8(3)	C(13)–C(14)–C(15)	118.7(7)
C(10)–Cr(1)–C(22)	92.5(3)	C(14)–C(15)–C(16)	120.5(6)
C(11)–Cr(1)–C(22)	119.8(3)	C(15)–C(16)–C(17)	120.3(7)
C(6)–Cr(1)–C(23)	114.0(3)	C(12)–C(17)–C(16)	120.4(6)
C(7)–Cr(1)–C(23)	90.4(3)	C(5)–N(1)–C(18)	114.7(7)
C(8)–Cr(1)–C(23)	93.7(3)	C(5)–N(1)–C(20)	117.3(5)
C(9)–Cr(1)–C(23)	120.9(3)	C(18)–N(1)–C(20)	112.6(7)
C(10)–Cr(1)–C(23)	158.4(3)	N(1)–C(18)–C(19)	118.1(9)
C(11)–Cr(1)–C(23)	151.3(3)	N(1)–C(20)–C(21)	111.6(7)
C(22)–Cr(1)–C(23)	88.5(3)	Cr(1)–C(22)–O(22)	178.7(6)
C(6)–Cr(1)–C(24)	91.2(2)	Cr(1)–C(23)–O(23)	177.4(8)
C(7)–Cr(1)–C(24)	119.3(2)	Cr(1)–C(24)–O(24)	179.1(7)

94.0, 92.9 ppm, at δ 90.1 ppm arises the peak for C₅ and finally at δ 42 and 13 ppm appear the signals for ethyl groups.

The second compound, colorless crystals in 21% yield, was assigned as 5-(N,N-diethylamino)-3,4-diphenyl-3-butenolide **3**, the organic framework of complex **2**, i.e. it is the same structure as complex **2** without the Cr(CO)₃ fragment. The IR spectrum reveals only the presence of an α,β -unsaturated CO group with absorption at 1737 cm⁻¹. The mass spectrum displays *m/z* 307, which matches the anticipated molecular weight for **3**. The ¹H NMR spectrum (200 MHz, CDCl₃) exhibits the following signals: at δ 7.4–7.2 ppm a multiplet (10H) for phenyl groups, at δ 6.2 ppm a singlet integrating for 1H assigned to the methynic proton and finally, at δ 2.9–2.7 ppm (4H) and δ 1.0 ppm

Table 2
Bond lengths (Å) and bond angles (°) for compound 4

O(1)–C(1)	1.211(4)	C(12)–C(17)	1.389(5)
C(1)–C(2)	1.500(6)	C(13)–C(14)	1.384(6)
C(1)–C(5)	1.504(4)	C(14)–C(15)	1.375(6)
C(2)–C(3)	1.350(4)	C(15)–C(16)	1.376(5)
C(2)–C(6)	1.476(4)	C(16)–C(17)	1.379(6)
C(3)–C(4)	1.521(5)	C(18)–C(19)	1.384(5)
C(3)–C(12)	1.480(5)	C(18)–C(23)	1.387(5)
C(4)–C(5)	1.349(5)	C(19)–C(20)	1.380(5)
C(4)–C(18)	1.484(3)	C(20)–C(21)	1.367(8)
C(5)–C(24)	1.476(6)	C(21)–C(22)	1.369(8)
C(6)–C(7)	1.390(6)	C(22)–C(23)	1.388(4)
C(6)–C(11)	1.400(5)	C(24)–C(25)	1.392(6)
C(7)–C(8)	1.379(5)	C(24)–C(29)	1.398(4)
C(8)–C(9)	1.367(6)	C(25)–C(26)	1.382(7)
C(9)–C(10)	1.371(8)	C(26)–C(27)	1.366(5)
C(10)–C(11)	1.383(5)	C(27)–C(28)	1.386(7)
C(12)–C(13)	1.394(4)	C(28)–C(29)	1.380(7)
O(1)–C(1)–C(2)	125.5(3)	C(3)–C(12)–C(17)	119.5(3)
O(1)–C(1)–C(5)	126.6(4)	C(13)–C(12)–C(17)	118.2(4)
C(2)–C(1)–C(5)	107.9(3)	C(12)–C(13)–C(14)	120.7(3)
C(1)–C(2)–C(3)	106.4(3)	C(13)–C(14)–C(15)	120.0(3)
C(1)–C(2)–C(6)	122.6(3)	C(14)–C(15)–C(16)	120.0(4)
C(3)–C(2)–C(6)	130.9(4)	C(15)–C(16)–C(17)	120.3(4)
C(2)–C(3)–C(4)	109.6(3)	C(12)–C(17)–C(16)	120.8(3)
C(2)–C(3)–C(12)	127.3(3)	C(4)–C(18)–C(19)	120.3(3)
C(4)–C(3)–C(12)	123.1(2)	C(4)–C(18)–C(23)	120.4(3)
C(3)–C(4)–C(5)	109.7(2)	C(19)–C(18)–C(23)	119.3(3)
C(3)–C(4)–C(18)	122.8(3)	C(18)–C(19)–C(20)	120.2(4)
C(5)–C(4)–C(18)	127.5(3)	C(19)–C(20)–C(21)	120.7(5)
C(1)–C(5)–C(4)	106.3(3)	C(20)–C(21)–C(22)	119.5(3)
C(1)–C(5)–C(24)	122.2(3)	C(21)–C(22)–C(23)	121.0(5)
C(4)–C(5)–C(24)	131.2(2)	C(18)–C(23)–C(22)	119.4(4)
C(2)–C(6)–C(7)	121.5(3)	C(5)–C(24)–C(25)	120.2(3)
C(2)–C(6)–C(11)	120.6(4)	C(5)–C(24)–C(29)	121.7(3)
C(7)–C(6)–C(11)	117.9(3)	C(25)–C(24)–C(29)	118.0(4)
C(6)–C(7)–C(8)	120.8(4)	C(24)–C(25)–C(26)	121.0(3)
C(7)–C(8)–C(9)	120.6(5)	C(25)–C(26)–C(27)	120.3(4)
C(8)–C(9)–C(10)	119.7(4)	C(26)–C(27)–C(28)	120.0(5)
C(9)–C(10)–C(11)	120.5(4)	C(27)–C(28)–C(29)	120.0(3)
C(6)–C(11)–C(10)	120.4(4)	C(24)–C(29)–C(28)	120.7(4)
C(3)–C(12)–C(13)	122.3(3)		

Table 3
Bond lengths (Å) and bond angles (°) for complex 5

Cr–C(1)	2.242(9)	C(6)–C(61)	1.488(12)
Cr–C(2)	2.157(11)	C(6)–C(7)	1.333(14)
Cr–C(3)	2.150(10)	C(61)–C(62)	1.377(13)
Cr–C(4)	2.250(9)	C(61)–C(66)	1.397(11)
Cr–C(5)	2.247(8)	C(62)–C(63)	1.396(14)
Cr–C(9)	2.188(8)	C(63)–C(64)	1.348(14)
Cr–C(10)	2.206(9)	C(64)–C(65)	1.380(16)
Cr–C(111)	2.064(10)	C(65)–C(66)	1.364(15)
Cr–C(112)	1.887(10)	C(7)–C(8)	1.518(13)
Cr–C(113)	1.868(9)	C(8)–C(81)	1.528(13)
C(1)–C(11)	1.477(13)	C(8)–C(9)	1.520(13)
C(1)–C(2)	1.394(13)	C(81)–C(82)	1.398(13)
C(1)–C(5)	1.451(12)	C(81)–C(86)	1.382(15)
C(11)–C(12)	1.378(12)	C(82)–C(83)	1.364(15)
C(11)–C(16)	1.396(12)	C(83)–C(84)	1.350(17)
C(12)–C(13)	1.385(14)	C(84)–C(85)	1.345(20)
C(13)–C(14)	1.369(14)	C(85)–C(86)	1.390(16)
C(14)–C(15)	1.369(17)	C(9)–C(10)	1.394(12)
C(15)–C(16)	1.391(15)	C(10)–C(101)	1.494(13)
C(2)–C(3)	1.416(14)	C(10)–C(111)	1.451(13)
C(3)–C(4)	1.428(12)	C(101)–C(102)	1.392(13)
C(4)–C(41)	1.476(13)	C(101)–C(106)	1.367(12)
C(4)–C(5)	1.412(12)	C(102)–C(103)	1.369(16)
C(41)–C(42)	1.392(14)	C(103)–C(104)	1.353(16)
C(41)–C(46)	1.387(13)	C(104)–C(105)	1.383(16)
C(42)–C(43)	1.382(18)	C(105)–C(106)	1.373(16)
C(43)–C(44)	1.385(19)	C(111)–O(111)	1.183(12)
C(44)–C(45)	1.362(20)	C(112)–O(112)	1.129(13)
C(45)–C(46)	1.379(15)	C(113)–O(113)	1.129(11)
C(5)–C(6)	1.481(11)		
C(1)–Cr–C(2)	36.9(3)	Cr–C(4)–C(3)	67.3(5)
C(1)–Cr–C(3)	62.9(4)	Cr–C(4)–C(41)	126.2(6)
C(2)–Cr–C(3)	38.4(4)	C(3)–C(4)–C(41)	125.5(8)
C(1)–Cr–C(4)	62.5(3)	Cr–C(4)–C(5)	71.6(5)
C(2)–Cr–C(4)	63.0(3)	C(3)–C(4)–C(5)	106.7(8)
C(3)–Cr–C(4)	37.8(3)	C(41)–C(4)–C(5)	127.8(7)
C(1)–Cr–C(5)	37.7(3)	C(4)–C(41)–C(42)	119.9(8)
C(2)–Cr–C(5)	62.3(3)	C(4)–C(41)–C(46)	122.7(9)
C(3)–Cr–C(5)	62.4(3)	C(42)–C(41)–C(46)	117.4(9)
C(4)–Cr–C(5)	36.6(3)	C(41)–C(42)–C(43)	120.4(10)
C(1)–Cr–C(9)	98.3(3)	C(42)–C(43)–C(44)	120.6(12)
C(2)–Cr–C(9)	135.2(4)	C(43)–C(44)–C(45)	119.7(12)
C(3)–Cr–C(9)	138.6(3)	C(44)–C(45)–C(46)	119.6(11)
C(4)–Cr–C(9)	101.1(3)	C(41)–C(46)–C(45)	122.2(11)
C(5)–Cr–C(9)	80.2(3)	Cr–C(5)–C(1)	70.9(5)
C(1)–Cr–C(10)	115.2(3)	Cr–C(5)–C(4)	71.8(5)
C(2)–Cr–C(10)	142.4(4)	C(1)–C(5)–C(4)	108.9(7)
C(3)–Cr–C(10)	175.6(3)	Cr–C(5)–C(6)	132.0(6)
C(4)–Cr–C(10)	137.9(3)	C(1)–C(5)–C(6)	124.2(8)
C(5)–Cr–C(10)	113.6(3)	C(4)–C(5)–C(6)	125.9(7)
C(9)–Cr–C(10)	37.0(3)	C(5)–C(6)–C(61)	116.7(7)
C(1)–Cr–C(111)	90.8(4)	C(5)–C(6)–C(7)	119.6(8)
C(2)–Cr–C(111)	104.8(4)	C(61)–C(6)–C(7)	123.7(8)
C(3)–Cr–C(111)	142.5(4)	C(6)–C(61)–C(62)	120.5(7)
C(4)–Cr–C(111)	149.6(4)	C(6)–C(61)–C(66)	122.6(8)
C(5)–Cr–C(111)	113.2(3)	C(62)–C(61)–C(66)	116.8(8)
C(9)–Cr–C(111)	67.0(3)	C(61)–C(62)–C(63)	121.4(8)
C(10)–Cr–C(111)	39.6(3)	C(62)–C(63)–C(64)	119.8(9)
C(1)–Cr–C(112)	148.4(4)	C(63)–C(64)–C(65)	120.7(10)
C(2)–Cr–C(112)	131.4(4)	C(64)–C(65)–C(66)	119.2(9)
C(3)–Cr–C(112)	94.4(4)	C(61)–C(66)–C(65)	122.2(10)
C(4)–Cr–C(112)	86.0(4)	C(6)–C(7)–C(8)	124.3(8)
C(5)–Cr–C(112)	113.4(4)	C(7)–C(8)–C(81)	112.8(7)

Table 3 (continued)

C(9)–Cr–C(112)	84.3(4)	C(7)–C(8)–C(9)	113.1(8)
C(10)–Cr–C(112)	85.7(4)	C(81)–C(8)–C(9)	105.7(7)
C(111)–Cr–C(112)	118.7(4)	C(8)–C(81)–C(82)	120.8(8)
C(1)–Cr–C(113)	116.6(4)	C(8)–C(81)–C(86)	121.6(8)
C(2)–Cr–C(113)	86.5(4)	C(82)–C(81)–C(86)	117.2(9)
C(3)–Cr–C(113)	91.4(4)	C(81)–C(82)–C(83)	121.4(9)
C(4)–Cr–C(113)	126.9(4)	C(82)–C(83)–C(84)	120.2(11)
C(5)–Cr–C(113)	148.6(4)	C(83)–C(84)–C(85)	120.3(11)
C(9)–Cr–C(113)	129.3(4)	C(84)–C(85)–C(86)	121.0(11)
C(10)–Cr–C(113)	93.0(4)	C(81)–C(86)–C(85)	120.0(10)
C(111)–Cr–C(113)	76.4(4)	Cr–C(9)–C(8)	117.8(6)
C(112)–Cr–C(113)	83.7(4)	Cr–C(9)–C(10)	72.2(5)
Cr–C(1)–C(11)	129.4(6)	C(8)–C(9)–C(10)	118.8(8)
Cr–C(1)–C(2)	68.3(6)	Cr–C(10)–C(9)	70.8(5)
C(11)–C(1)–C(2)	124.2(8)	Cr–C(10)–C(101)	127.7(6)
Cr–C(1)–C(5)	71.3(5)	C(9)–C(10)–C(101)	127.3(8)
C(11)–C(1)–C(5)	129.1(7)	Cr–C(10)–C(111)	64.9(5)
C(2)–C(1)–C(5)	106.5(8)	C(9)–C(10)–C(111)	111.2(8)
C(1)–C(11)–C(12)	123.5(7)	C(101)–C(10)–C(111)	121.3(7)
C(1)–C(11)–C(16)	118.9(8)	C(10)–C(101)–C(102)	117.5(8)
C(12)–C(11)–C(16)	117.5(9)	C(10)–C(101)–C(106)	124.0(8)
C(11)–C(12)–C(13)	121.3(8)	C(102)–C(101)–C(106)	118.4(9)
C(12)–C(13)–C(14)	120.0(10)	C(101)–C(102)–C(103)	120.6(9)
C(13)–C(14)–C(15)	120.7(10)	C(102)–C(103)–C(104)	120.3(10)
C(14)–C(15)–C(16)	119.0(9)	C(103)–C(104)–C(105)	120.0(11)
C(11)–C(16)–C(15)	121.6(9)	C(104)–C(105)–C(106)	119.7(9)
Cr–C(2)–C(1)	74.9(6)	C(101)–C(106)–C(105)	120.9(9)
Cr–C(2)–C(3)	70.6(6)	Cr–C(111)–C(10)	75.5(5)
C(1)–C(2)–C(3)	109.5(8)	Cr–C(111)–O(111)	142.8(8)
Cr–C(3)–C(2)	71.1(6)	C(10)–C(111)–O(111)	140.9(10)
Cr–C(3)–C(4)	74.9(5)	Cr–C(112)–O(112)	178.8(9)
C(2)–C(3)–C(4)	108.3(8)	Cr–C(113)–O(113)	178.0(9)

(6H), the signals of ethyl groups connected to the N atom. The ^{13}C NMR spectrum exhibits a peak at δ 171.9 ppm for the CO belonging to the lactam function, at δ 154.4 ppm the signal for the C_4 , at δ 131.3–128.4 ppm the peaks fitting for phenyl groups and C_3 , the signal for C_5 appears at δ 96.9 ppm and at δ 43 and 13 ppm the signals for carbons of ethyl groups.

The least abundant product, isolated as a red solid (10% yield), was given structure 4, i.e. 2,3,4,5-tetra-phenyl-2,4-cyclopentadienone based on spectroscopic analysis. The IR spectrum shows absorption at 1712 cm^{-1} for a CO ketonic group. The mass spectrum displays the molecular ion m/z 384 which holds for the expected molecular weight. In the ^1H NMR spectrum (200 MHz, CDCl_3) there appears only two multiplets at δ 7.4–6.8 ppm for phenyl groups and in the ^{13}C NMR spectrum there are nothing more than the peak for the CO group at δ 154 ppm and signals at δ 133–125 ppm for the conjugated system.

2.2. Reactivity of lithium oxydiethylamino-penta-carbonyl chromium carbene complex 1 towards phenylacetylene

Refluxing of a solution of complex 1 and phenylacetylene in anhydrous THF for 24 h gave a reaction

mixture that, after silica-gel chromatography separation, gave as the only stable compound a red solid (30% yield) which was partly characterized by spectroscopic methods as a chromium dicarbonyl complex **5** (Scheme 3), with five units of phenylacetylene and a conjugated ketone function attached to the metal atom on the basis of the following observations. Its IR spectrum exhibits two strong absorptions for $\nu_{\text{M-CO}}$ at 1993 and 1942 cm^{-1} , besides a frequency at 1744 cm^{-1} corresponding to a conjugated CO group linked to the metallic center. The mass spectrum displays a molecular ion with m/z 646 and two successive CO units lost, which imply a dicarbonyl chromium complex accounting for $\text{C}_{43}\text{H}_{30}\text{O}_3\text{Cr}$ species. The ^1H NMR spectrum (200 MHz, CDCl_3) shows a multiplet at δ 7.7–7.0 ppm for protons of the aromatic rings, two doublets (2H) at δ 5.1 and 5.4 ppm, a doublet (1H) at δ 6.9 ppm with $J = 1.8$ Hz for a vinylic proton, a doublet (1H) at δ 5.6 ppm for another vinylic proton ($J = 6.7$ Hz) and a doublet of doublets (1H) at δ 2.4 ppm ($J_1 = 1.8$, $J_2 = 6.7$) assigned to an allylic proton.

Taken together, the simplicity of the NMR and MS data suggested a chromium complex resulting from oligomerisation of five phenylacetylene molecules with CO insertion. In order to establish firmly the structure of compounds **2**, **4** and **5**, a single-crystal X-ray diffraction study was carried out. The results are summarized in Tables 1–4 and molecular structures are illustrated in Figs. 1–3, which also show the atomic numbering scheme.

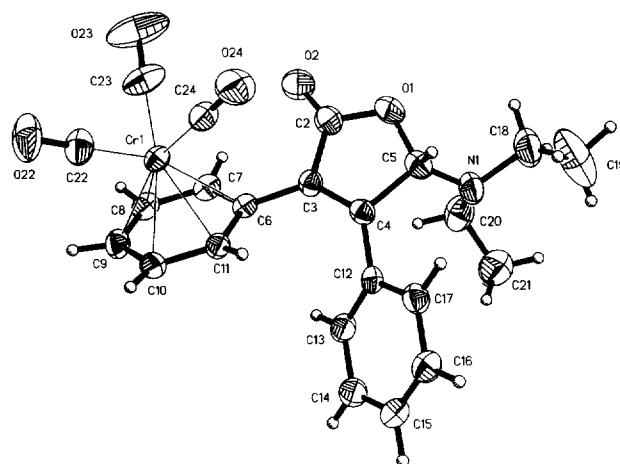


Fig. 1. The molecular structure and atom-numbering scheme for **2**. Thermal ellipsoids at 30% probability level.

These results clearly confirm the presence of a staggered chromium tricarbonyl moiety π -bonded to one of the phenyl rings of the γ -butenolide in compound **2** (Fig. 1 and Tables 1–4). The Cr–C(phenyl) bond lengths (average 2.204(10) Å) as well as the Cr–C(O) (average 1.832(7) Å) and the distance of the Cr atom to the centroid of the phenyl ring, 1.705 Å, compare well with the values found for the benzene chromium tricarbonyl complex [8].

The 1993 version of the NIST Crystal Data [9] for a previous structure determination of compound **4** (Fig. 2 and Tables 2–4) reveals that this was already done [10]

Table 4
Crystal data and refinement details for compounds **2**, **4** and **5**

	2	4	5
Formula	$\text{C}_{23}\text{H}_{21}\text{CrNO}_5$	$\text{C}_{29}\text{H}_{20}\text{O}$	$\text{C}_{43}\text{H}_{30}\text{CrO}_3$
M_w	443	384	646
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$
a (Å)	8.722(3)	26.213(3)	9.839(2)
b (Å)	12.283(5)	8.409(10)	16.170(2)
c (Å)	12.486(3)	21.591(2)	20.463(3)
α (deg)	115.37(2)		
β (deg)	96.00(2)	119.47(0)	97.26(0)
γ (deg)	109.58(2)		
V (Å ³)	1089.3(8)	4143.1(10)	3229.4(9)
Z	2	8	4
D_c (Mg m^{-3})	1.352	1.233	1.330
$F(000)$	460	1616	1344
Diffractionmeter	Siemens P4/PC	Siemens P4/PC	Siemens R3m/V
Radiation	Mo K α	Mo K α	Mo K α
Scan type	ω	ω	ω
Scan range (deg)	$3 < 2\theta < 50$	$3 < 2\theta < 50$	$3 < 2\theta < 50$
Data collected	3842	7430	6070
Data used (criterion)	2395 ($F > 4.0\sigma(F)$)	2048 ($F > 4.0\sigma(F)$)	2399 ($F > 4.0\sigma(F)$)
R (R_w) (%)	5.67 (6.50)	5.14 (5.99)	6.72 (7.33)
l.s. parameters	271	272	439
G.O.F.	1.25	1.18	1.15

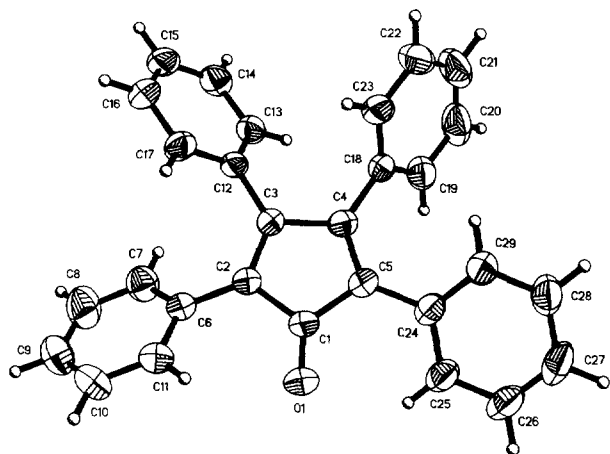


Fig. 2. The molecular structure and atom-numbering scheme for **4**. Thermal ellipsoids at 50% probability level.

although a different synthetic approach was used on that work and only slightly better refinement results were reached by us.

Compound **5**, 1-(η^5 -2,5-diphenylcyclopenta-2,4-dien-1-yl)-4,5,6- η^3 -(1,3,5-triphenyl-6-oxo-hexa-1,4-dienyl) chromium dicarbonyl complex (Fig. 3 and Tables 3 and 4) is unique in several ways. It not only represents the first report for the addition of five units of alkyne (sequential linking of up to four alkyne molecules has been reported in Ref. [11]), but also the occurrence of both linear- and cycloaddition processes in the same product. (Transition-metal mediated linear polymerization and arene formation by cycloaddition of alkynes are well-known processes; for reviews see Refs. [2,12].)

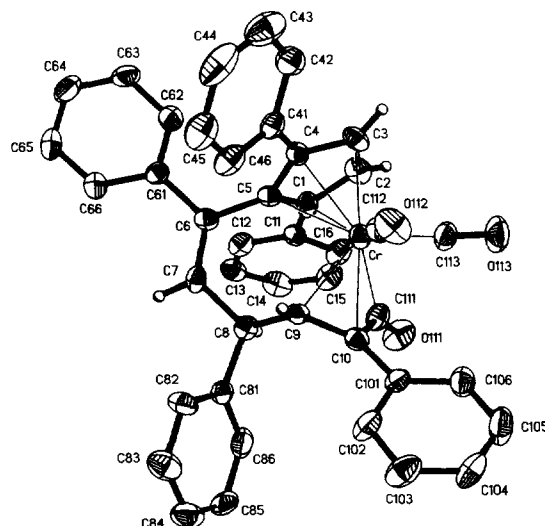
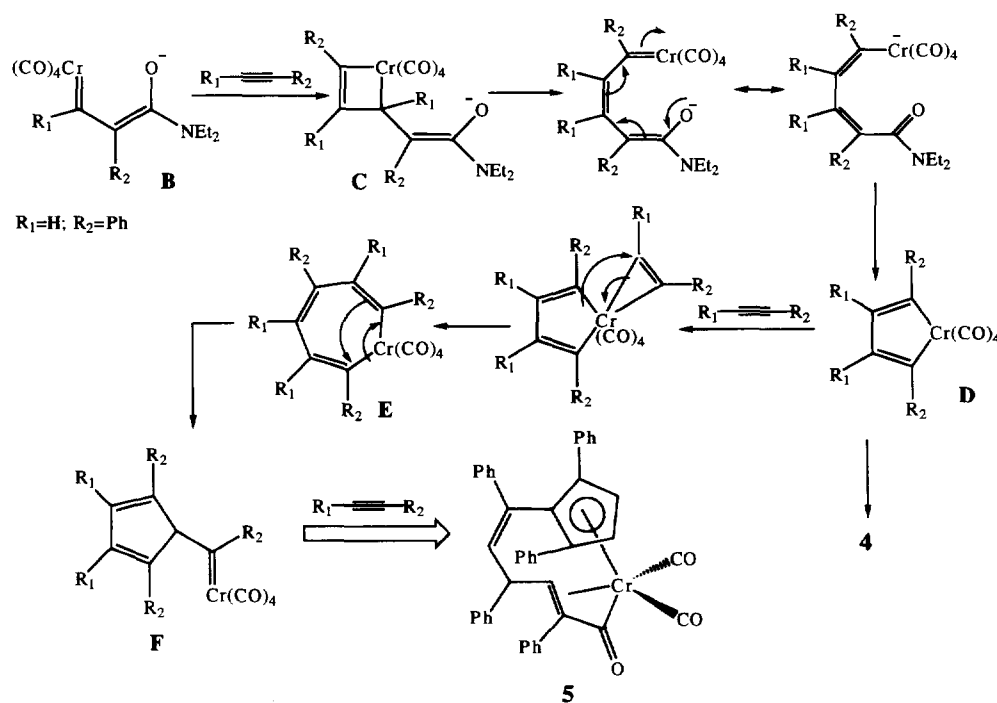


Fig. 3. The molecular structure and atom-numbering scheme for **5**. Thermal ellipsoids at 30% probability level.

As a result the unprecedented formation of a cyclopentadienyl moiety by alkyne insertion solely was observed. The regiochemistry on the formation of the five-membered ring seems to involve the initial linkage of two units of phenyl acetylene in a head-to-head arrangement, followed by a dual head-to-tail linkage of a third alkyne molecule to produce the ring closure. The remaining carbon chain is formed by sequential head-to-tail linear addition of the last two molecules of alkyne. At this stage, the oligomerization process is stopped by insertion of a CO group to produce the also unusual vinylformyl entity.



Scheme 3.

The observed chromium coordination sphere may be regarded as octahedral if the vinylformyl–Cr interaction is considered as a single coordination site and represented by the C(9)–C(10)–C(11) centroid vector. This group functions as a π -allyl ligand so that the complex closely resembles the structure of $\text{Cp}(\eta^3\text{-C}_5\text{H}_7)\text{Cr}(\text{CO})_2$ [13]. An unsymmetrical coordination of the chromium atom towards the five-membered ring can be inferred from the splitting of the Cr–C distances into two groups, being shorter for the unsubstituted C(2) and C(3) (average 2.153(4) Å) and larger for the rest of the ring forming C-atoms (average 2.246(3) Å), possibly as a result of steric hindrance of substituents or by the strain introduced to form the metallacycle Cr–C(5)–C(6)–C(7)–C(8)–C(9).

3. Discussion

In the reaction of complex **1** with diphenylacetylene the formation of two types of product is observed:

complex **2** and compound **3** whose formation is quite similar, the former remaining coordinated to the metallic center by means of an aromatic system and the latter losing the metallic fragment;
compound **4** whose formation follows another pathway.

On the other hand, reaction of phenylacetylene with carbene complex **1** gave only one stable compound, the oligomer chromium complex **5**, which arises from insertion of five unsaturated molecules and a CO unit.

3.1. Insertion reaction of alkynes with the two heteroatom-stabilized Fischer anionic carbene **1**

3.1.1. Formation of **2** and **3**

Tricarbonyl arene chromium complexes easily undergo insertion of alkynes in a well-documented process [11]. However, in our case, the anionic Fischer carbene complex **1** goes through coordination of a diphenylacetylene molecule to give a metallocyclobutene intermediate **A**, which first generates a new carbene **B**, and then a vinylketene is formed by CO insertion. The synthesis of the corresponding lactone is observed later via a nucleophilic attack to the vinylketene intermediate without migration of any alkyl group or proton, as in the case of neutral chromium aminocarbene complexes in the formation of lactams (Scheme 2).

3.1.2. Formation of **4** and **5**.

On the basis of the mechanism postulated for **2** and **3** (vide supra), another metallocyclobutene **C** arising from a phenylacetylene insertion in the key chromium carbene intermediate **B** is proposed to be implicated, which in its turn originates a metallocyclopentadiene **D** promoting insertion of a CO molecule in order to give **4**.

After that, in a phenylacetylene insertion a metallocycloheptatriene **E** is supposed to be formed which rearranges to the pentadiene-derivative chromium complex **F**, and the subsequent insertion of another two phenylacetylene molecule results in the formation of **5** (Scheme 3).

It is worthy of comment that metallocycloheptatriene **E** has been found to be involved in the formation of aromatic rings in other carbene–alkyne cyclization reactions [11].

4. Conclusion

In summary our work describes the synthesis of two novel chromium (0) complexes **2** and **5**, whose pathways of formation are tentatively proposed and structures partly assessed by spectroscopic methods and unequivocally established by X-ray diffraction studies.

For the reaction with a disubstituted alkyne, i.e. diphenylacetylene, the products were, in principle, those expected for this type of reaction: formation of butenolides, but actually this constitutes a new method for the synthesis of γ -aminobutenolides according to our approach by using a two heteroatom-stabilized anionic carbene complex.

On the other hand, the reaction with the mono-substituted alkyne, i.e. phenylacetylene, leads to the formation of an oligomer chromium complex of dual nature (cyclic–linear), which displays a cyclopentadienyl unit instead of a cyclopentenone or aromatic rings as is usually found in cycloaddition reactions of alkynes and anionic carbene complexes. Work is in progress to increase our understanding and attempts to broaden the applications are also underway.

5. Experimental section

5.1. General methods

^1H NMR and ^{13}C NMR spectra were recorded on a Varian 300S spectrometer, using CDCl_3 as solvent and TMS as internal reference. IR spectra were recorded on a Perkin–Elmer 283 B or 1420 spectrometer. The electron impact (EI) ionization mass spectra were acquired on a JEOL JMS-AX505 HA mass spectrometer operated in the positive ion mode. The acquisition conditions were ion source temperature 230 °C, ionization energy 70 eV, emission current 0.14 μA and ionization current 100 μA . Melting points were measured using a Mel-Temp II apparatus and are uncorrected. Column chromatography was performed with Merck silica-gel (70–230 mesh) using methylene chloride/hexane in different ratios as eluent. All reagents were obtained from commercial suppliers and used as received. Reac-

tions were performed under nitrogen atmosphere in carefully dried glassware. Diethyl ether and benzene were distilled from sodium–benzophenone ketyl under argon and/or nitrogen atmosphere.

5.2. Reaction of **1** with diphenylacetylene: formation of **2**, **3**, and **4**

A solution of diethylamine (1.6 g, 22.7 mmol) in anhydrous ethyl ether was allowed to react with butyllithium (14.2 ml, 22.7 mmol) in N_2 atmosphere at -78°C for 20 min, and then warmed to room temperature. This mixture was then added through a cannula to a solution of hexacarbonylchromium (5 g, 22.7 mmol) in anhydrous ethyl ether in order to form **1**. After 1 h evaporation of the solvent and addition of anhydrous THF along with diphenylacetylene (4 g, 22.7 mmol) took place, followed by refluxing for 24 h.

The reaction mixture was evaporated under vacuum and the residue chromatographed on silica-gel. Elution with methylene chloride gave first complex **2** (65% yield), as a red solid, m.p. 118°C , then butenolide **3** (21%) as colorless crystals, m.p. 118 – 119°C and, finally, the cyclopentadienone **4** (10%) as a red solid, m.p. 210°C .

5.2.1. Complex **2**

IR (KBr): 1968, 1894 and 1890 cm^{-1} ($\nu_{\text{M-CO}}$). ^1H NMR (200 MHz, CDCl_3): δ 7.4 ppm (m, 5H, Ph); δ 6 ppm (s, 1H, CH); δ 5.8 ppm (d, 1H, H_6); δ 5.6 ppm (d, 1H, H_{10}); δ 5.4 ppm (t, 1H, H_8); δ 5.1 ppm (m, 2H, H_7 and H_9); δ 2.8 ppm (m, 4H, NCH_2CH_3); δ 1.0 ppm (t, 6H, NCH_2CH_3). ^{13}C NMR (50 MHz, CDCl_3): δ 232 ppm (M–CO); δ 169 ppm (α,β -unsaturated CO); δ 157 ppm ($\text{C}=\text{C}-\text{C}=\text{O}$); δ 131, 130.5, 129.9, 128.6 ppm (free Ph); δ 125.3 ppm (C_3); δ 96.9, 96.4, 95.0, 94.0, 92.9 ppm (aromatic Cs); δ 90.1 ppm (C_5); δ 42 ppm (NCH_2CH_3); δ 13 ppm (NCH_2CH_3). EI-MS: m/z 443 (M^+), 415 ($\text{M}^+ - \text{CO}$), 387 ($\text{M}^+ - 2\text{CO}$), 359 ($\text{M}^+ - 3\text{CO}$), 307 ($\text{M}^+ - \text{CrCO}_3$).

5.2.2. Butenolide **3**

IR (KBr): 1737 cm^{-1} (α,β -unsaturated CO). ^1H NMR (200 MHz, CDCl_3): δ 7.4–7.2 ppm (m, 10H, phenyl groups); δ 6.2 ppm (s, 1H, CHON); δ 2.9–2.7 ppm (m, 4H, NCH_2CH_3); δ 1.0 ppm (t, 6H, NCH_2CH_3). ^{13}C NMR (50 MHz, CDCl_3): δ 171.9 ppm (CO); δ 154.4 ppm (C_4); δ 131.3–128.4 ppm (C-aromatic + C_3); δ 96.9 ppm (C_5); δ 43 and 13 ppm (CH_2CH_3). EI-MS: m/z 307 (M^+).

5.2.3. Cyclopentadienone **4**

IR (KBr): 1712 cm^{-1} (CO ketonic). ^1H NMR (200 MHz, CDCl_3): δ 7.4–6.8 ppm (m, 20H, phenyl groups). ^{13}C NMR (50 MHz, CDCl_3): δ 154 ppm (CO); δ 133–125 ppm (C-aromatic). EI-MS: m/z 384 (M^+).

5.3. Reaction of **1** with phenylacetylene: formation of **5**

Treatment as above upon the same quantities of reagents gave, by using silica-gel chromatography with hexane/methylene chloride in different ratios as eluent, **5** (30% yield) as the only stable product, isolated as dark red solid (m.p. 188°C).

5.3.1. Complex **5**

IR (KBr): 1993 and 1942 cm^{-1} ($\nu_{\text{M-CO}}$); 1744 cm^{-1} (conjugated M–CO). ^1H NMR (200 MHz, CDCl_3): δ 7.7–7.0 ppm (m, 25H, Ph); δ 6.9 ppm (d, 1H, $J = 1.8\text{ Hz}$, H_7); δ 5.4 ppm (d, 1H, $J = 2\text{ Hz}$, H_2); δ 5.1 ppm (d, 1H, $J = 2\text{ Hz}$, H_3); δ 5.6 ppm (d, 1H, $J = 6.7\text{ Hz}$, H_9); δ 2.4 ppm (d, d, 1H, $J_1 = 1.8$, $J_2 = 6.7$, H_8). EI-MS: m/z 646 (M^+).

5.4. X-ray data collection, structure solution and refinement

Suitable crystals of complexes **2**, **4** and **5** were grown by slowly cooling to 0°C hexane/dichloromethane solutions. A crystal summary is given in Table 4. As a general procedure, for each compound the accurate cell dimension and orientation matrix were obtained from least-squares refinement of the setting angles of 25 centered reflections. Diffraction intensities were collected at room temperature and all data were corrected for usual Lorentz and polarization effects and placed on an approximately absolute scale. An empirical absorption correction face-indexed was applied for compounds **2** and **4** (correction factors in the range 0.785–0.843 and 0.920–0.969 respectively). The space groups for **4** and **5** were determined from systematic absences. The structures were solved by direct methods and refined by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included as idealized isotropic contributions (riding model) except for those of the cyclopentadienyl and hexadienyl moieties on compound **5** which were located on a difference Fourier map and their positional parameters refined. All computations were performed using the SHELXTL PC program package [14].

6. Supplementary material available

Tables giving fractional coordinates (Tables S5, S8, S11), anisotropic thermal parameters (Tables S6, S9, S12), hydrogen atom parameters (Tables S7, S10, S13) and structure factors.

Acknowledgements

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