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A unusual bridging mode of vinylidene ligands in nonacarbonyl(vinylidene)dichromium complexes

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Dedicated to Professor Warren R. Roper on the occasion of his 65th birthday

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Abstract

Thermolysis of the pentacarbonyl(vinylidene)chromium complexes [(CO)$_5$Cr=C=C(R^1)R^2] (**1a**–**d**) (C(R^1)R^2 = CMe$_2$ (**a**), C(CH$_2$)$_5$ (**b**), C(Et)Me (**c**), C(^{t}Bu)Me (**d**)), affords binuclear, vinylidene-bridged nonacarbonyldichromium complexes, [(CO)$_5$Cr(μ-η^1,η^2-C=C(R^1)R^2)Cr(CO)$_4$] (**2a**–**d**). The solid-state structures of **2a** and **2d** have been established by X-ray structural analyses. The structural data prove the μ-η^1,η^2-C=C(R^1)R^2 bonding mode. To account for the NMR spectroscopic features a dynamic process is proposed involving rapid coordination site exchange of the C=C bond between Cr(1) and Cr(2) (windshield wiper mechanism) and of one CO ligand.

Keywords: Vinylidene complexes; Binuclear complexes; Thermolysis; Chromium

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1. Introduction

Transition-metal coordinated vinylidenes have been proposed as key intermediates in several catalytic processes such as alkyne dimerization, alkyne polymerization and various C–O and C–C bond forming reactions. In addition, vinylidene complexes are building blocks in the synthesis of organometallic and organic compounds as well as of clusters [1]. Routes for the synthesis of vinylidene complexes of various transition metals have been developed.

Pentacarbonyl(vinylidene)chromium complexes are usually thermally unstable due to the poor π-basicity of the pentacarbonylchromium fragment. At room temperature these complexes quickly decompose. Therefore, until now only few pentacarbonyl(vinylidene)chromium complexes have been isolated in a pure form, among them two complexes carrying π-acceptor substituents at the vinylidene C$_\beta$ atom [2,3]. Although labile, alkyl- and aryl-substituted vinylidene complexes could be generated at low temperature and used as starting material for a series of transformations of the vinylidene ligand. For instance the reactions with ynamines and alkoxyacetylene afforded 3-amino- and 3-alkoxy-substituted cyclobutenylidene complexes, respectively [4–6], those with alkynyl complexes gave bi-, tri- and tetra-nuclear complexes with bridging cyclobutenylidene ligands [7,8]. Monosubstituted pentacarbonyl(vinylidene)chromium complexes, [(CO)$_5$Cr=C=C(R)H], were also proposed as intermediates in the synthesis of 2-azetidin-1-ylidene complexes by reactions of imines and carbodiimides with pentacarbonyl[hydroxy-(methyl)carbene]chromium (R = H) [9], tetramethylammonium acetyl(pentacarbonyl)chromate toluene-4-sulfonyl chloride [10,11] and alkyne(pentacarbonyl)chromium complexes [12,13], respectively. In contrast, disubstituted vinylidene complexes add imines to the α-carbon atom of the vinylidene ligand to form zwitterionic adducts [14].

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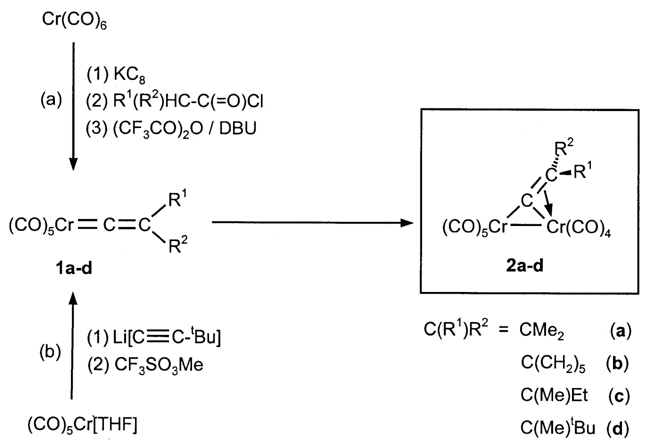
We now report on the thermolysis of some disubstituted pentacarbonyl(vinylidene)chromium complexes in the absence of unsaturated substrates and on the unusual bonding mode of the bridging vinylidene ligand in the resulting binuclear complexes.

2. Results and discussion

The vinylidene complexes **1a**–**d** were prepared by either pathways (a) or (b) as shown in Scheme 1. Sequential reaction of $[Cr(CO)_6]$ with KC_8, acid chlorides, $R^1(R^2)HC{-}C({=}O)Cl$, and trifluoroacetic anhydride/DBU afforded the complexes **1a**–**c** [5]. Reaction of $[(CO)_5Cr(THF)]$ with lithium *tert*-butylacetylide gave the alkynylchromate $Li[(CO)_5Cr{-}C{\equiv}C{-}{}^tBu]$, subsequently methylation with methyl triflate yielded complex **1d**.

In solution, the complexes **1a**–**d** are thermally unstable. When solutions of **1a**–**d**, obtained by dissolving the complexes at low temperature in dichloromethane or pentane–dichloromethane mixtures, were allowed to warm slowly to room temperature, the green solutions turned dark-violet to almost black. Purification by chromatography and recrystallization afforded the crystalline binuclear complexes **2a**–**d** in yields ranging from 18 to 92%. The new compounds were thermally more stable than their vinylidene precursors **1a**–**d**. In crystalline form they were stable at room temperature. However, they slowly decomposed in solution within about 24 h.

From the elemental analysis and the mass spectra (molecular peak and nine successive CO fragmentations) a binuclear $(CO)_9Cr_2$ complex containing one vinylidene ligand, $C{=}C(R^1)R^2$, could be deduced. Obviously, two molecules of **1a**–**d** dimerized with elimination of one CO and one vinylidene ligand. The fate of the second vinylidene group and the CO ligand is at present unknown.



Scheme 1.

The IR spectra of **2a**–**d** exhibit five to nine partly overlapping ν(CO) peaks the number of absorptions depending on the substitution pattern. It is not possible to separate these absorptions into those of a $(CO)_5Cr$ and a $(CO)_4Cr$ fragment. A CO absorption below 1800 cm^{-1} indicative for a bridging carbonyl group cannot be observed.

The ^{1}H-NMR spectra show one set of signals only. That is, in the case of **2a** only one singlet for the two Me substituents is observed in the temperature range from −80 °C to room temperature.

The solid-state structures of **2a** and **2d** were established by X-ray structural analyses (Tables 1 and 2, Figs. 1 and 2). In both complexes the vinylidene ligand unsymmetrically bridges a $(CO)_9Cr_2$ fragment. The Cr–Cr distance in both complexes [3.000(1) Å (**2a**) and 2.983(1) Å (**2d**)] is comparable to that in the homobinuclear complex $[ON(CO)_4Cr{-}Cr(CO)_4NO]$ (3.001(3) and 3.020(3) Å, two crystallographically independent molecules [15]) but it is significantly shorter than that in e.g. the neutral unbridged complexes $[Cp(CO)_3Cr{-}Cr(CO)_3Cp]$ (3.281(1) Å [16]) or $[Cp^*(CO)_3Cr{-}Cr(CO)_3Cp^*]$ (3.311(1) Å [17]) indicating a Cr–Cr single bond in **2a** and **2d**. The atoms Cr(1), Cr(2), C(10), and C(11) lie within or almost within a plane [torsion angle Cr(1)–Cr(2)–C(10)–C(11): −179.0(2)° (**2a**) and 174.5(4)° (**2d**)]. The molecular

Table 1
Crystallographic data for **2a** and **2d**

	2a	**2d**
Empirical formula	$C_{13}H_6Cr_2O_9$	$C_{16}H_{12}Cr_2O_9$
M_r (g mol^{-1})	410.18	452.26
Temperature (K)	228(2)	188(2)
Crystal size (mm^3)	0.3 × 0.3 × 0.3	0.5 × 0.3 × 0.2
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	12.249(2)	8.736(3)
b (Å)	9.2122(15)	26.187(9)
c (Å)	14.430(2)	9.243(3)
α (°)	90	90
β (°)	95.14(1)	116.58(2)
γ (°)	90	90
Cell volume ($Å^3$)	1621.7(5)	1891.1(10)
Z	4	4
D_{calc} (g cm^{-3})	1.680	1.588
μ (Mo–K_α) (mm^{-1})	1.383	1.194
$F(0\,0\,0)$ (e)	816	912
$\theta_{min}/\theta_{max}$	2.09/27.00	2.58/25.00
Reflections, collected	3695	4189
Reflections, unique	3542	3309
Min/max transmission	0.5532/0.5734	0.7139/0.8192
Parameters refined	217	244
R_1, all data	0.0589	0.0932
wR_2, all data	0.0944	0.1059
R_1 [$I > 2\sigma(I)$]	0.0381	0.0455
wR_2 [$I > 2\sigma(I)$]	0.0851	0.0894
Res. electron density (e $Å^{-3}$)	+0.361/−0.240	+0.438/−0.433

Table 2
Selected bond distances (Å) and angles (°) in **2a** and **2d**

	2a	**2d**
Bond lengths		
Cr(1)–Cr(2)	3.000(1)	2.983(1)
Cr(1)–C(1)	1.917(3)	1.918(5)
Cr(1)–C(2)	1.930(3)	1.949(5)
Cr(1)–C(3)	1.929(3)	1.959(5)
Cr(1)–C(4)	1.901(4)	1.933(5)
Cr(1)–C(5)	1.910(3)	1.940(5)
Cr(1)–C(10)	1.939(3)	1.943(4)
C(10)–C(11)	1.346(4)	1.369(6)
Cr(2)–C(10)	1.922(3)	1.999(4)
Cr(2)–C(11)	2.372(3)	2.508(4)
Cr(2)–C(6)	1.903(3)	1.890(5)
Cr(2)–C(7)	1.904(3)	1.938(5)
Cr(2)–C(8)	1.833(3)	1.853(5)
Cr(2)–C(9)	1.921(3)	1.919(5)
Bond angles		
C(1)–Cr(1)–C(2)	89.6(1)	90.1(2)
C(2)–Cr(1)–C(5)	85.7(1)	82.4(2)
C(3)–Cr(1)–C(4)	92.0(2)	90.7(2)
C(4)–Cr(1)–C(10)	82.1(1)	86.0(2)
Cr(1)–C(10)–C(11)	166.6(2)	166.1(3)
Cr(1)–C(2)–O(2)	165.8(3)	162.0(4)
C(6)–Cr(2)–C(7)	86.2(1)	82.9(2)
C(6)–Cr(2)–C(8)	98.0(1)	93.2(2)
C(6)–Cr(2)–C(9)	86.6(1)	84.1(2)
C(7)–Cr(2)–C(11)	94.3(1)	100.9(2)
C(8)–Cr(2)–C(11)	80.0(1)	83.1(2)
C(9)–Cr(2)–C(11)	92.6(1)	91.9(2)
C(10)–Cr(1)–Cr(2)	38.8(1)	41.6(1)
C(10)–Cr(2)–Cr(1)	39.2(1)	40.1(1)
C(10)–Cr(2)–C(11)	34.6(1)	33.0(2)
C(10)–C(11)–Cr(2)	54.1(2)	52.6(2)
C(12)–C(11)–C(13)	114.2(3)	114.7(4)
Cr(1)–C(10)–Cr(2)	102.0(1)	98.3(2)
Cr(2)–C(10)–C(11)	91.4(2)	94.4(3)

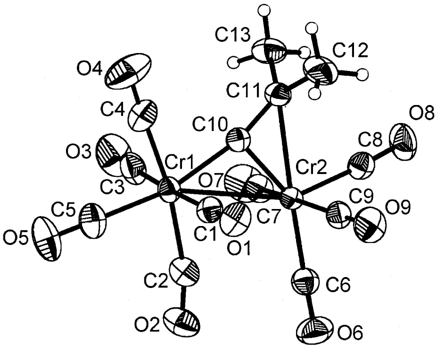


Fig. 1. Structure of complex **2a**.

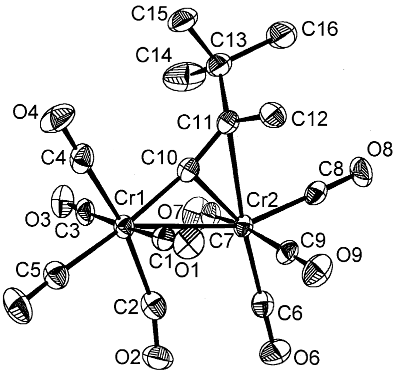
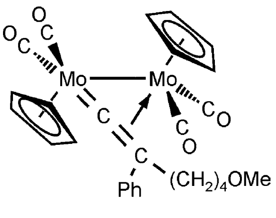


Fig. 2. Structure of complex **2d** (hydrogen atoms omitted for clarity).

plane (Cr(1)/Cr(2)/C(10)) bisects the C(12)–C(11)–C(13) angle [C(10)–C(11)–C(12) 121.7(3)° {118.7(4)°} and C(10)–C(11)–C(13) 121.3(3)° {123.6(4)°} in **2a** {**2d**}]. The slight deviation from coplanarity of the planes formed by the atoms Cr(1)/Cr(2)/C(10) and Cr(2)/C(10)/C(11) in **2d** and the small difference in the angles C(10)–C(11)–C(12) and C(10)–C(11)–C(13) are very likely due to the different steric requirements of the substituents at C_β in **2d** (^{t}Bu versus Me).

Both chromium atoms are hepta-coordinated. Hepta-coordination in organometallic molybdenum and tungsten complexes is quite common. However, it is rather rare with mono- or bi-nuclear chromium complexes apart from complexes with sterically unassuming ligands such as hydride complexes. To meet the electronic requirements of both chromium atoms the vinylidene ligand has to adopt an unusual μ-η^1,η^2-coordination mode acting obviously as a 1e-donor towards Cr(1) and as 3e-donor towards Cr(2). Thus C(10) coordinates to Cr(2) as bridging carbon and additionally as part of an olefin [C(10)=C(11)].

Several homobinuclear complexes of molybdenum and tungsten with μ-η^1,η^2-bridging vinylidene ligands have previously been reported: [Cp*(CO)$_2$Mo(μ-η^1,η^2-C=CH$_2$)Mo(CO)$_2$Cp*] [18], [Cp(CO)$_2$M(μ-η^1,η^2-C=C(R^1)R^2)M(CO)$_2$Cp] (M = Mo; W) [19,20], and [CpMo(μ-SMe)$_3$(μ-η^1,η^2-C=C(R)H)MoCp]BF$_4$ [21]. They were obtained by alkylation or protonation of the corresponding alkynyl-bridged binuclear complexes. In contrast to **2a–d**, in these molybdenum and tungsten complexes the C_α atom is linked to one of the metal atoms by a double bond similar to the M=C_α bond in mononuclear vinylidene complexes such as **1a–d**. The bonding of the vinylidene ligand to the second metal is of an olefinic type formed through interaction of the C_α=C_β bond with d orbitals of the metal. The structures of **3** and of the triply SMe-bridged complex [CpMo(μ-SMe)$_3$(μ-η^1,η^2-C=C(Ph)H)MoCp]BF$_4$ (**4**) have been determined by X-ray analyses [19,21].



(**3**)

The Cr(1)–C(10) distance in **2a** and **2d** is within error limits identical, however, is significantly longer than the corresponding distance in **3** (1.909(5) Å) and **4** (1.893(6) Å). The Cr(2)–C(11) is longer than the Cr(2)–C(10) bond by more than 20% indicating a significantly weaker interaction of Cr(2) with C(11) than with C(10). In **3** and **4** the difference in bond length is less pronounced (12 and 15%). The $C(R^1)R^2$ fragment is in both complexes bent away from $Cr(CO)_4$ [Cr(1)–C(10)–C(11) 166.4(2)° (**2a**), 166.1(3)° (**2d**)]. The elongation of the Cr(2)–C(10) and Cr(2)–C(11) bond in **2d** with respect to **2a** is presumably due to steric interaction of the bulky *tert*-butyl substituent with the CO ligands of the $(CO)_4Cr$ fragment.

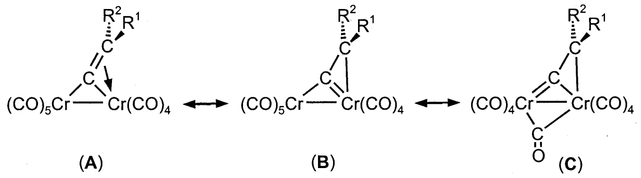
The C(2)–O(2) ligand is bent towards Cr(2) [Cr(2)–Cr(1)–C(2): 69.0(1)° in **2a**, 64.1(1)° in **2d**] and bent at C(2) [Cr(1)–C(2)–O(2): 165.8(3)° in **2a**, 162.0(4)° in **2d**]. Thus, it adopts a hemibridging position [Cr(2)–C(2): 2.931 Å in **2a** and 2.760 Å in **2d**]. Conversely, C(6)–O(6) is bent away from Cr(1) towards a position *trans* to C(10) [Cr(1)–Cr(2)–C(6): 108.3(1)° in **2a**, 110.7(1)° in **2d**].

Therefore, the complexes **2a**–**d** are best represented by the resonance forms **A**–**C** depicted in Scheme 2.

The significantly shorter average Cr–CO distances in the $Cr(CO)_4$ fragment compared to those in the $Cr(CO)_5$ indicate that $Cr(CO)_4$ is more electron-rich.

In accord with these solid-state structures, only one resonance for the two Me substituents in the vinylidene ligand of **2a** and only three peaks for the five CH_2 groups in **2b** are found. The resonance of the bridging C_α atom in **2a**–**d** is at very low field (δ between 379.1 and 419.3 ppm), that of C_β is at high field (δ between 110.3 and 133.8 ppm) in a range usually observed with mononuclear vinylidene complexes. For the nine CO ligands at least 7 ^{13}C-NMR resonances are to be expected. However, in contrast to expectations only three CO peaks are observed in solution. Obviously, **2a**–**d** show a dynamic behavior in solution.

To account for the results of variable temperature ^{1}H-NMR measurements on the dimethyl analogue of **3**, $[Cp(CO)_2Mo(\mu\text{-}\eta^1,\eta^2\text{-}C{=}CMe_2)Mo(CO)_2Cp]$ (**5**), a facile σ,η^2(4e) to σ,σ(2e) to σ,η^2(4e) switch was proposed (Scheme 3) [20]. At 213 K, complex **5** exhibited two Me and two Cp signals which coalesced reversibly on warming. At room temperature, only one Me and one Cp peak was observed.



Scheme 2.

The observation of only three CO resonances in **2a**–**d** can likewise be explained by a site exchange process (Scheme 4).

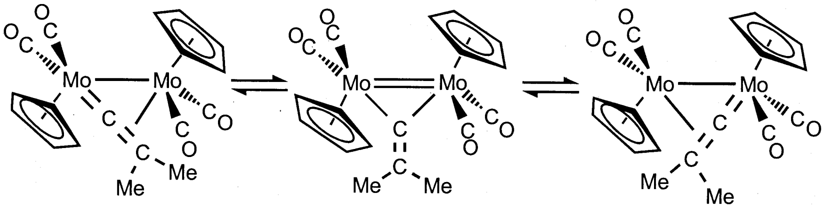
The C=C bond of the vinylidene ligand and one '*cis*'-CO group mutually exchange the coordinating metal presumably through a symmetrical high energy (μ-σ,σ-vinylidene)(μ-CO) complex. The solid structures of **2a** and **2d** already give some hints on both transformations (switch of C=C coordination from Cr(2) to Cr(1) and migration of CO from Cr(1) to Cr(2)). One *cis*-CO ligand of the $(CO)_5Cr$ fragment is already bent towards $Cr(CO)_4$, $C(11)R_2$ is bent away from Cr(2), and C(6)–O(6) of Cr(2) is 'on the move' towards a position *trans* to C(10).

The two processes shown in Schemes 3 and 4 differ in several aspects:

a) In **5** only the C=C bond changes the coordinating metal whereas in **2a**–**d** the C=C bond *and* one CO ligand are involved in the change of the coordination site.
b) In addition to the change in the coordination site of C(10)=C(11) and C(2)O(2), the dynamic process also involves substantial movement of those CO ligands [C(4)O(4), C(5)O(5), C(6)O(6), and C(8)O(8)] that are located in the molecular plane. These ligands alternate between *cis* and *trans* positions with respect to the Cr(1)–Cr(2) bond. In contrast, the exchange process in **5** was proposed to proceed without substantial movement of the carbonyl and cyclopentadienyl ligands.

In addition to these structural features, the compounds **2a**–**d** exhibit a unusually strong negative solvatochromic effect. The UV–vis absorption at lowest energy shifts toward shorter wavelength when nonpolar pentane is replaced by polar dimethyl formamide. In pentane λ_{max} is at 574–578 nm, in dimethyl formamide at 434 nm ($\Delta\nu = 5680$–5740 cm^{-1}). From these data it follows that excitation from the ground to the first excited state induces a pronounced change in the dipole moment of the complex. The good solubility of **2a**–**d** in unpolar pentane indicates that the excited state is the more polar one.

The formation of binuclear vinylidene complexes by thermolysis of the corresponding mononuclear complexes has been observed before. These reactions sometimes proceed spontaneously. The synthesis of heterodinuclear vinylidene complexes through metallation of the M=C=C system with L_nM fragments has also been reported [1]. However in contrast to **2**, in all of the resulting binuclear complexes the vinylidene ligand bridges the two metals either in a σ,σ or a σ,π fashion like that in **3**–**5**.



$\mathbf{5}(\sigma,\eta^2)$ $\mathbf{5}(\sigma,\sigma)$ $\mathbf{5}(\eta^2,\sigma)$

Scheme 3.

3. Experimental

3.1. General

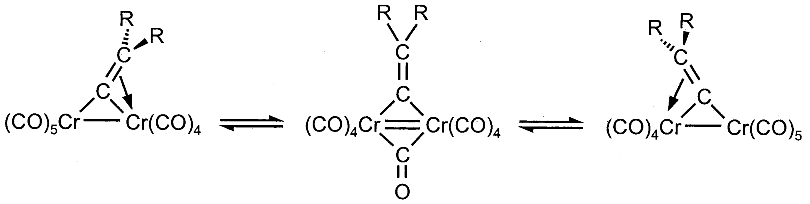
All operations were carried out under nitrogen by using conventional Schlenk techniques. Solvents were dried by refluxing over sodium-benzophenone ketyl (THF) or CaH_2 (pentane, dichloromethane) and were freshly distilled prior to use. The silica gel used for chromatography (J.T. Baker, silica gel for flash chromatography) was nitrogen saturated. The yields refer to analytically pure compounds and were not optimized. The complexes **1a** and **1b** were prepared as previously reported [5]. Complex **1c** [IR (pentane, cm^{-1}): ν(CO) 2083 m, 1987 s, 1978 s] was synthesized analogously. $[Cr(CO)_6]$ and 3,3-dimethylbut-1-yne were commercial products (Aldrich) and were used without further purification. IR: FT-IR spectrophotometer (FTS70), Bio-Rad. All IR measurements were carried out at 298 K. ^{1}H-NMR, ^{13}C-NMR: Bruker AC 250, Bruker DRX 600. Unless specifically mentioned, NMR spectra were recorded at room temperature (r.t.). ^{13}C-NMR spectra are ^{1}H decoupled. Chemical shifts are reported in ppm relative to internal TMS. MS: Finnigan MAT 312 (EI). UV–vis: Hewlett-Packard diode array spectrophotometers 8452A and 8453. Elemental analysis: CHN-Analyser (CHN-O-RAPID) Heraeus. Photolysis reactions were carried out in a duran glass apparatus using a mercury high pressure lamp (TQ 150, Fa. Heraeus).

3.2. Pentacarbonyl[tert-butyl(methyl)vinylidene]chromium (1d)

$[(CO)_5Cr(THF)]$ was generated by irradiation of 4.4 g (20 mmol) of $[Cr(CO)_6]$ in 300 ml of THF at −30 °C for 100 min. A solution of 24 mmol of $Li[C\equiv C-{}^tBu]$ in 30 ml of tetrahydrofuran was added. The solution was stirred and allowed to warm to r.t. The solvent was removed in vacuo. The residue was dissolved at −80 °C in 30 ml of CH_2Cl_2 and 1.9 ml (24 mmol) of CF_3SO_3Me was added. The solution was slowly (within ca. 4–5 h) warmed to r.t. The solvent was removed in vacuo. Fifty milliliter of pentane was added and the solution was chromatographed at −30 °C on silica with pentane. A green band was eluted. Removal of the solvent gave a dark green oil. Yield: 3.7 g (13 mmol, 65% relative to $[Cr(CO)_6]$). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2082 m, 1994 s, 1976 s, 1955 s, ν(C=C) 1672 w. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 1.12 (s, 9H, $C(CH_3)_3$), 1.63 (s, 3H, $=CCH_3$). ^{13}C-NMR ($CDCl_3$, 62.5 MHz): δ 402.6 (C_α), 225.3 (*trans*-CO), 213.6 (*cis*-CO), 130.5 (C_β), 34.0 (CH_3), 29.5 ($C(CH_3)_3$), 6.6 ($C(CH_3)_3$).

3.3. Nonacarbonyl[μ_2-η^1,η^2-dimethylvinylidene]dichromium (2a)

At −78 °C 0.50 g (2.0 mmol) of **1a** was dissolved in 20 ml of CH_2Cl_2. The solution was gradually warmed to r.t. within 3 h. The color of the solution changed from green to dark-violet. The solution was stirred for another 30 min at r.t. The solvent was removed in vacuo. The residue was dissolved in 50 ml of pentane and chromatographed at −40 °C on silica with pentane/CH_2Cl_2 (9:1). The black–violet band was collected. Removal of the solvent in vacuo and recrystallization from 15 ml of pentane afforded **2a** as black–violet prisms. Yield: 0.26 g (0.63 mmol, 63%). M.p.: 69 °C (dec.). IR (pentane, cm^{-1}): ν(CO) 2086 w, 2026 s, 1996 vs, 1958 w, 1928 m. ^{1}H-NMR (CD_2Cl_2, 250 MHz): δ 2.21 (s, 6H, CH_3). ^{13}C-NMR (CD_2Cl_2, 150.92 MHz): δ 27.2 (CH_3), 110.3 (C_β),



Scheme 4.

212.1, 219.8, 228.8 (CO), 379.1 (C_α). UV–vis: λ_{max} (log ε) [solvent]: 578 nm (3.462) [pentane], 434 nm (3.081) [DMF]. MS (EI, 70 eV): *m/z* (%) = 410 (11) [M^+], 382 (4), 354 (2), 326 (6), 298 (7), 270 (31), 242 (31), 214 (24), 186 (29), 158 (35) [$M^+ - n$CO, $n = 1$–9], 80 (28) [$Cr(CO)^+$], 52 (100) [Cr^+]. Anal. Found: C, 37.68; H, 1.48. Calc. for $C_{13}H_6Cr_2O_9$ (410.18): C, 38.07; H, 1.47%.

*3.4. Nonacarbonyl[μ_2-η^1,η^2-cyclohexylvinylidene]dichromium (**2b**)*

A dark-green solution obtained by dissolving 3.3 g (11.8 mmol) of **1b** in ca. 50 ml of pentane/CH_2Cl_2 (7:1) at −78 °C was allowed to slowly warm to r.t. and was then stirred for 2 h at ambient temp. The solution turned dark-brown. The solvent was removed in vacuo and the residue was chromatographed at −40 °C on silica. With pentane/CH_2Cl_2 (7:1) a violet band was eluted. Removal of the solvent and recrystallization from pentane/CH_2Cl_2 gave black-violet crystals. Yield: 0.47 g (1.06 mmol, 18%). M.p.: 81 °C. IR (pentane, cm^{-1}): ν(CO) 2085 w, 2060 vw, 2024 vs, 2011 w, 1996 vs, 1987 vs, 1956 m, 1943 w, 1927 s. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.88 (m, 1H), 1.25 (m, 1H), 1.55 (m, 2H), 1.79–1.93 (m, 4H), 2.38 (m, 2H). ^{13}C-NMR ($CDCl_3$, 62.5 MHz): δ 25.5, 29.5, 38.9 (CH_2), 115.6 (C_β), 211.5, 219.0, 228.1 (CO), 374.8 (C_α). UV–vis: λ_{max} (log ε) [solvent]: 574 (3.433) [pentane], 434 (3.399) [DMF]. MS (EI, 70 eV): *m/z* (%) = 450 (6) [M^+], 422 (3), 394 (1), 366 (5), 338 (10), 310 (35), 282 (8), 254 (25), 226, 198 (35) [$M^+ - n$CO, $n = 1$–9]. Anal. Found: C, 42.31; H, 2.13. Calc. for $C_{16}H_{10}Cr_2O_9$ (450.24): C, 42.68; H, 2.24%.

*3.5. Nonacarbonyl[μ_2-η^1,η^2-ethyl(methyl)vinylidene]dichromium (**2c**)*

The synthesis of **2c** from 2.5 g (9.6 mmol) of **1c** was carried out analogously to that of **2b**. Black-violet crystals. Yield: 0.42 g (0.98 mmol, 20%). M.p.: 99 °C. IR (pentane, cm^{-1}): ν(CO) 2084 m, 2024 s, 2012 vw, 1995 vs, 1988 s, 1983 m, sh, 1956 vw, 1936 w, sh, 1928 m. ^{1}H-NMR (CD_2Cl_2, 250 MHz): δ 1.37 (t, $J = 7.4$ Hz, 3H, CH_2CH_3), 2.23 (s, 3H, CH_3), 2.38 (q, $J = 7.4$ Hz, 2H, CH_2CH_3). ^{13}C-NMR (CD_2Cl_2, 203 K, 62.5 MHz): δ 13.6 (CH_2CH_3), 23.2 (CH_3), 34.5 (CH_2CH_3), 114.4 (C_β), 214.4, 219.0, 236.6 (CO), 402.9 (C_α). UV–vis: λ_{max} (log ε) [solvent]: 578 (3.356) [pentane], 434 (3.316) [DMF]. MS (EI, 70 eV): *m/z* (%) = 424 (30) [M^+], 396 (11), 368 (5), 340 (20), 312 (22), 284 (20), 256 (6), 228 (25), 200 (18), 172 (27) [$M^+ - n$CO, $n = 1$–9], 52 (100) [Cr^+]. Anal. Found: C, 39.38; H, 2.51. Calc. for $C_{14}H_8Cr_2O_9$ (424.20): C, 39.64; H, 1.90%.

*3.6. Nonacarbonyl[μ_2-η^1,η^2-tert-butyl(methyl)vinylidene]dichromium (**2d**)*

At −30 °C, 1.96 g of **1d** (6.8 mmol) was dissolved in 50 ml of pentane/CH_2Cl_2 (1:1). The solution was stirred and allowed to gradually warm to r.t. The color of the solution changed from green to gray. After 6 h, the volume of the solution was reduced in vacuo to about 5 ml and chromatographed at −30 °C on silica. With pentane a gray band was eluted. Removal of the solvent in vacuo and crystallization from pentane afforded 1.12 g (73%) of **2d**. Gray crystals. M.p.: 82 °C. IR (pentane, cm^{-1}): ν(CO) 2083 m, 2057 m, 2020 s, 1992 s, 1987 vs, 1953 m, 1924 m. ^{1}H-NMR ($CDCl_3$, 243 K): δ 1.32 (s, 9H, $C(CH_3)_3$), 2.33 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$, 243 K): δ 25.2 (CH_3), 29.9 ($C(CH_3)_3$), 41.1 ($C(CH_3)_3$), 133.8 ($=C(^t\mathrm{Bu})$Me), 219.5, 223.1, 228.6 (CO), 419.3 ($C=$CMe). UV–vis: λ_{max} (log ε, solvent]: 599 nm (3.455) [CH_2Cl_2]. MS (*m/z*, %): 452 (22), 424 (7), 396 (2), 368 (12) [$M^+ - n$CO] ($n = 1$–3), 356 (13) [$M^+ - C{=}C(^t\mathrm{Bu})$Me], 340 (20), 312 (89), 284 (16), 256 (78), 228 (58), 200 (97) [$M^+ - n$CO] ($n = 4$–9). Anal. Found: C, 42.57; H, 2.89. Calc. for $C_{16}H_{12}Cr_2O_9$ (452.26): C, 42.49; H, 2.67%.

*3.7. X-ray structural analyses of **2a** and **2d***

Single crystals of **2a** and **2d** suitable for an X-ray structural analyses were obtained from pentane at −30 °C. The measurements were performed with a crystal mounted in a glass capillary on a Siemens P4 diffractometer (graphite monochromator, Mo–K_α radiation, $\lambda = 0.71073$ Å). For the data collection the Wykoff technique was used. Semiempirical absorption correction (ψ scan with 10 reflections) was performed. The structures were solved by direct methods using the SHELXTL-97 program package [22]. The positions of the hydrogen atoms were calculated by assuming ideal geometry, and their coordinates were refined together with those of the attached carbon atoms as ‘riding model’. All other atoms were refined anisotropically.

4. Supplementary material

Crystallographic data for the structural analyses of complexes **2a** and **2d** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 201352 (**2a**) and CCDC 201353 (**2d**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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