Monatshefte für Chemie 120, 1175 – 1183 (1989)

Monatshefte für Chemie
Chemical Monthly

Observation of Slowed Rotation About the (η^6-Arene)-Chromium Bond in the Chromium Tricarbonyl Complex of the *syn-anti-syn* Trimer of Bicyclo[2.2.1]hept-2-yne**

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Summary. The crystal and molecular structures are reported for the chromium tricarbonyl complexes of the sterically-demanding and rigid *syn-anti-syn* and *all-syn* trimers of bicyclo[2.2.1]hept-2-yne, (**3-Cr**) and (**4-Cr**). At very low temperatures, a decoalescence phenomenon occurs in the 75.49 MHz ^{13}C-{^{1}H}-NMR spectrum of (**3-Cr**) and is unambiguously assigned to slowed rotation about the (η^6-arene)-chromium bond.

Keywords. Slowed rotation about an arene-chromium bond; Variable temperature ^{13}C-NMR; Crystal and molecular structure.

Die Beobachtung gehinderter Rotation um die (η^6-Arene)-Chrom-Bindung im Chromtricarbonyl-Komplex des *syn-anti-syn* Trimeren von Bicyclo[2.2.1]hept-2-in

Zusammenfassung. Die Kristallstrukturen der Chromtricarbonyl-Komplexe der sterisch anspruchsvollen und starren Trimeren des Bicyclo[2.2.1]hept-2-in[*syn-anti-syn* (**3-Cr**), *all-syn* (**4-Cr**)] wurden bestimmt. Bei sehr tiefen Temperaturen tritt im 75.49 MHz ^{13}C-{^{1}H}-NMR-Spektrum von (**3-Cr**) ein Dekoaleszenzphänomen auf, das eindeutig durch eine verlangsamte Rotation um die (η^6-Arene)-Chrom-Bindung hervorgerufen wird.

Introduction

The barrier to rotation about a (η^6-arene)-metal bond is normally too low for that process to be observed directly by NMR spectroscopy [1]. However, exceptional electronic or steric effects may sufficiently raise the barrier so that rotation can be slowed on the observational timescale at experimentally accessible temperatures.

Hoffmann has calculated that completely localising the arene π-system to one Kekulé resonance form (cyclohexatriene) raises the barrier from essentially zero to about 80 kJ mol^{-1} [1], and very recently Siegel has demonstrated experimentally

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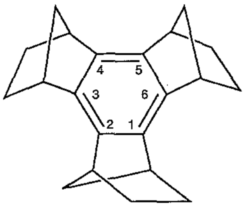
** Dedicated to Professor Dr. Karl Schlögl on the occasion of his 65th birthday the first example of restricted rotation in an arene-metal π-complex due to the localised π character of the bound arene *bent*-terphenylene [2]. As to steric effects, there are but few examples of complexes in which restricted arene-metal rotation has been unambiguously demonstrated [3]. Indeed, controversy still exists over the increase in barrier height caused by ethyl groups substituting the benzene ring. For example, in the crystal of dicarbonylthiocarbonyl(η^6-hexaethylbenzene)chromium(0), (**1**), the co-ordinated hexaethylbenzene adopts a conformation in which three ethyl groups are proximal to the chromium atom, and at low temperatures its ^{13}C-{^{1}H} NMR spectrum is consistent with C_s symmetry for the molecule [4]. McGlinchey et al. have thus strongly advocated that the heb conformation observed in the crystal is retained on dissolution, and that the C_s molecular symmetry results from slowed rotation about the (η^6-arene)-metal bond [4]; whereas one of us has adopted the more conservative position that the case for such slowed rotation remains not proven, as dissolution of **1** may lead to a facile change of heb conformation to one of C_s symmetry, and that what may have been monitored was ethyl group rotation [5]. By analogy with **1** it has been claimed that (η^6-arene)-metal rotation in tricarbonyl(η^6-hexaethylbenzene)chromium(0), (**2**), can also be slowed, although in the latter case the three-fold molecular symmetry prevents its direct observation by NMR spectroscopy [4].



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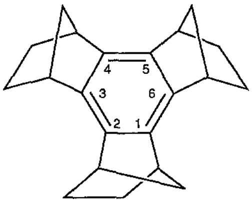

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To explore further the effect of steric hindrance on the (η^6-arene)-chromium rotational barrier and perhaps resolve the controversy concerning the hexaethylbenzene complexes, we have synthesized the chromium tricarbonyl complexes of the sterically-demanding and rigid *syn-anti-syn* and *all-syn* trimers of bicyclo[2.2.1]hept-2-yne, (**3-Cr**) and (**4-Cr**), and observed their crystal and molecular structures and 75.49 MHz ^{13}C-{^{1}H} NMR spectra.

Results and Discussion

The molecular structures of (**3-Cr**) and (**4-Cr**) are shown in Fig. 1 and selected bond lengths reported in Table 1. As predicted from MMP2 Force Field calculations for the uncomplexed trimers [7], in neither complex is there any detectable alternation in the carbon-carbon bond lengths of the unsaturated rings, all of which fall within the range expected for a purely aromatic system. Although the individual bond lengths differ somewhat from each other, they do not alternate regularly as expected for a cyclohexatriene system. If, however, chemically equivalent bond lengths are averaged (**4-Cr**: 1–2, 3–4, 5–6 and 2–3, 4–5, 6–1), the differences become less than 0.01 Å (**4-Cr**: 0.007 Å). There is thus no evidence for localisation of the

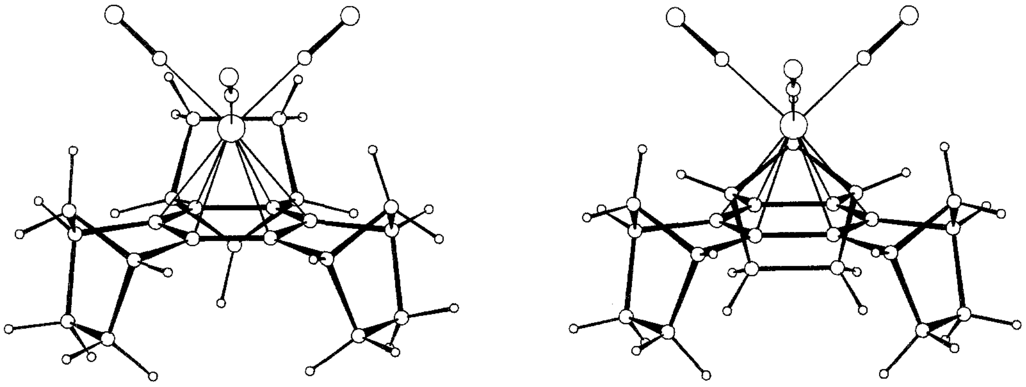

Fig. 1. Molecular structures of (**3-Cr**) (left) and (**4-Cr**) (right)

arene π-system and therefore no exceptional electronic factor which could cause a significant barrier to rotation about the (η^6-arene)-chromium bond.

Complex **4-Cr** is of C_{3v} molecular symmetry which prevents direct observation by NMR spectroscopy of slowed tripodal rotation and unsurprisingly its ^{13}C-{^{1}H} NMR spectrum in $CDFCl_2$ solution was unchanged down to 142 K. In contrast, for complex **3-Cr** of C_s symmetry the ^{13}C-{^{1}H} NMR spectrum in $CDFCl_2$ solution (δ, 238.11 (CO); 122.97, 112.36, 110.25 (C_{ar}); 54.50, 47.31 (CH_2); 41.16, 39.76 (CH); 31.14, 27.14, 26.95 (CH_2) ppm) exhibited a decoalescence phenomenon involving only the carbonyl resonance: at 150 K this resonance was broadened compared to the other resonances in the spectrum; at 145 K it has become asymmetric; at 142 K a definite shoulder had appeared on the resonance (Fig. 2). A fully-decoalesced spectrum could not be observed as below the last temperature the solution froze. Nevertheless, this temperature-dependent decoalescence phenomenon can be unambiguously assigned to slowed rotation of the chromium tricarbonyl tripod in **3-Cr**. This complex is the first reported for which such rotation of an unsubstituted metal-tripod can be slowed by purely steric interactions. From line shape fitting [8] we estimate the rate of tripodal rotation at 142 K to be about $250\,s^{-1}$, giving a barrier with $\Delta G^{\ddagger}_{142} \simeq 27\,kJ\,mol^{-1}$, almost at the very lowest experimental limit for processes directly observable by variable-temperature NMR spectroscopy.

Table 1. Calculated bond lengths (Å) for **3**, **4** (MMP2), and for **3-Cr** and **4-Cr** (crystal structures)

	3	**4**	**3-Cr**[a,b]		**4-Cr**[b]
C1–C2	1.395	1.395	1.412 (12)	1.419 (12)	1.426 (6)
C2–C3	1.391	1.391	1.410 (11)	1.417 (11)	1.403 (4)
C3–C4	1.395	1.395	1.416 (11)	1.414 (13)	1.411 (4)
C4–C5	1.391	1.391	1.416 (12)	1.409 (12)	1.420 (6)
C5–C6	1.395	1.395	1.408 (12)	1.423 (11)	1.411 (4)
C6–C1	1.391	1.391	1.407 (12)	1.416 (13)	1.403 (4)

[a] Two molecules in the asymmetric unit

[b] Standard deviations in parentheses

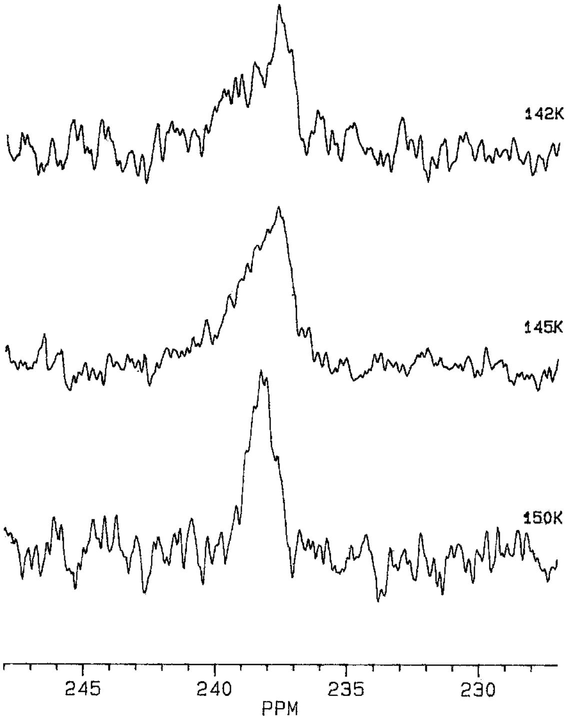

Fig. 2. Variable temperature 75.49 MHz ^{13}C-$\{^1H\}$-NMR spectrum of the carbonyl region of (**3-Cr**) dissolved in $CDFCl_2$

The slowed tripodal rotation in **3-Cr** undoubtedly arises from substantial steric interactions between the carbonyl groups and the rigidly fixed alkyl substituents on the benzene ring proximal to the chromium atom. As the proximal C_2H_4 bridge is likely to provide an obstacle at least as high, and certainly wider, than a proximal ethyl group, we therefore consider that the corresponding barriers in **1** and **2** are probably even lower than that found for **3-Cr**, and thus slowed tripodal rotation remains as yet unobserved for the hexaethylbenzene complexes.

Acknowledgements

We thank the Royal Society and the Österreichische Akademie der Wissenschaften for financial support.

Experimental

Crystal Data for **3-Cr**

$C_{24}H_{24}CrO_3$, yellow crystals (from hexane/CH_2Cl_2), m. p. 211°C (dec.), monoclinic, space group An (9), a = 15.559(15), b = 31.210(8), c = 8.180(3) Å, β = 104.85(4), V = 3 840(1) Å^3, Z = 8, 4 012 independent reflections were measured at 100(3) K on a modified STOE diffractometer, equipped with a NONIUS low temperature unit (Mo-K_α radiation, λ = 0.71069 Å), of which 3 313 were considered observed $[|F_0| \geqslant 4.0 * \sigma(F_0)]$. Short term temperature deviations of 10 K occurred due to malfunctioning of the temperature control unit. No absorption or extinction corrections were applied to the measured intensities. The structure was solved by direct methods and refined by least squares techniques. The positions of all hydrogen atoms were calculated based on stereochemical plausibility. In the final refinement, ansiotropic thermal parameters were used for the chromium atoms, isotropic thermal parameters for carbon, oxygen and hydrogen atoms (428 parameters, 3 358 observations).

Table 2. Atomic coordinates and equivalent isotropic temperature factors ($*10^4$, U-values in $Å^2$) for the Cr atoms in the crystal structure of **3-Cr**. For all other atoms isotropic temperature factors are given. Standard deviations are listed in parentheses. The equivalent isotropic temperature factors were obtained as one third of the trace of the orthogonalized U_{ij} tensor, and it corresponds to an isotropic temperature factor of the form $T = \exp(-8\pi^{2*} u^* \sin^2 \delta/\lambda^2)$

	Molecule 1			
	x/a	y/b	z/c	U_{eq}
CR 1	5 219 (0)	−7 565 (0)	−1 954 (0)	108 (6)
C 1	4 752 (6)	−7 798 (3)	318 (12)	125 (17)
C 2	4 547 (5)	−7 363 (2)	32 (11)	100 (16)
C 3	4 026 (5)	−7 220 (3)	−1 556 (12)	125 (17)
C 4	3 740 (6)	−7 520 (3)	−2 883 (13)	175 (19)
C 5	3 981 (6)	−7 954 (3)	−2 601 (12)	182 (19)
C 6	4 463 (5)	−8 099 (3)	−1 000 (11)	131 (17)
C 7	5 179 (6)	−8 052 (3)	1 903 (12)	161 (18)
H	5 306 (58)	−7 862 (24)	3 044 (59)	187 (229)
C 8	4 547 (6)	−8 443 (3)	1 571 (13)	201 (20)
H	3 916 (35)	−8 338 (29)	1 755 (131)	249 (281)
H	4 720 (48)	−8 694 (17)	2 509 (69)	39 (192)
C 9	4 708 (6)	−8 530 (3)	−203 (13)	185 (19)
H	4 394 (56)	−8 817 (18)	−824 (109)	184 (289)
C 10	6 054 (6)	−8 258 (3)	1 706 (12)	184 (19)
H	6 505 (39)	−8 021 (17)	1 437 (97)	1 (192)
H	6 356 (50)	−8 422 (24)	2 875 (57)	114 (233)
C 11	5 733 (6)	−8 593 (3)	273 (12)	159 (18)
H	5 997 (47)	−8 491 (24)	−763 (65)	36 (188)
H	5 840 (60)	−8 920 (12)	706 (118)	142 (263)
C 12	4 658 (6)	−6 979 (3)	1 173 (13)	161 (18)
H	5 243 (29)	−6 995 (23)	2 223 (65)	1 (190)
C 13	4 689 (6)	−6 610 (3)	−62 (12)	162 (18)
H	4 553 (48)	−6 308 (12)	471 (92)	1 (190)
H	5 305 (35)	−6 611 (29)	−439 (121)	248 (266)
C 14	3 839 (6)	−6 752 (3)	−1 357 (12)	159 (18)
H	3 432 (43)	−6 674 (24)	−2 602 (41)	123 (206)
C 15	3 715 (6)	−6 905 (3)	1 477 (12)	156 (18)
H	3 362 (55)	−7 178 (18)	1 799 (127)	197 (278)
H	3 828 (59)	−6 652 (19)	2 407 (84)	272 (249)
C 16	3 152 (5)	−6 744 (3)	−272 (12)	126 (17)
H	2 615 (32)	−6 964 (18)	−788 (91)	1 (193)
H	2 957 (59)	−6 416 (10)	−140 (127)	259 (267)
C 17	3 135 (6)	−7 484 (3)	−4 658 (13)	192 (19)
H	3 012 (48)	−7 177 (12)	−5 286 (86)	1 (192)
C 18	3 521 (6)	−7 832 (3)	−5 590 (12)	157 (18)
H	4 170 (27)	−7 713 (28)	−5 621 (124)	247 (255)
H	2 962 (30)	−7 944 (23)	−6 572 (70)	60 (190)
C 19	3 521 (6)	−8 187 (3)	−4 242 (13)	237 (21)
H	3 735 (63)	−8 513 (11)	−4 342 (132)	305 (285)
C 20	2 262 (7)	−7 700 (3)	−4 563 (14)	246 (21)

Table 2 (continued)

	Molecule 1			
	x/a	y/b	z/c	U_{eq}
H	2047 (94)	−7500 (40)	−3654 (127)	907 (501)
H	1826 (60)	−7622 (36)	−5781 (64)	506 (341)
C21	2512 (6)	−8172 (3)	−4248 (14)	224 (20)
H	2304 (126)	−8296 (60)	−5533 (68)	1519 (756)
H	2394 (58)	−8325 (25)	−3140 (63)	128 (234)
C22	5290 (6)	−7158 (3)	−3503 (13)	189 (20)
C23	6303 (5)	−7372 (3)	−677 (11)	129 (17)
C24	5779 (5)	−7953 (3)	−3037 (12)	132 (17)
O25	5314 (4)	−6886 (2)	−4471 (9)	253 (15)
O26	6969 (5)	−7244 (2)	95 (9)	284 (16)
O27	6111 (4)	−8194 (2)	−3738 (9)	231 (15)

	Molecule 2			
	x/a	y/b	z/c	U_{eq}
CR2	3128 (1)	−4959 (0)	−3019 (2)	71 (6)
C101	2765 (5)	−5178 (2)	−5761 (11)	96 (16)
C102	2467 (5)	−4753 (2)	−5637 (11)	109 (17)
C103	1881 (5)	−4657 (2)	−4621 (11)	77 (16)
C104	1650 (5)	−4981 (3)	−3613 (11)	132 (17)
C105	1965 (5)	−5408 (2)	−3671 (11)	95 (16)
C106	2514 (5)	−5503 (2)	−4762 (11)	72 (15)
C107	3245 (5)	−5400 (3)	−6931 (12)	135 (18)
H	3055 (92)	−5254 (38)	−8170 (71)	1003 (470)
C108	2683 (5)	−5813 (3)	−7253 (11)	128 (17)
H	2896 (46)	−6054 (17)	−8010 (81)	1 (191)
H	1984 (13)	−5786 (23)	−7880 (88)	1 (188)
C109	2830 (5)	−5928 (3)	−5360 (12)	128 (17)
H	2495 (55)	−6201 (18)	−4993 (120)	290 (273)
C110	4147 (5)	−5584 (3)	−5889 (12)	125 (17)
H	4434 (45)	−5724 (21)	−6834 (68)	8 (190)
H	4521 (41)	−5348 (17)	−5027 (76)	1 (191)
C111	3858 (6)	−5935 (3)	−4801 (13)	170 (19)
H	4079 (46)	−5881 (22)	−3454 (20)	1 (192)
H	4198 (61)	−6236 (17)	−4818 (137)	358 (262)
C112	2541 (6)	−4354 (3)	−6637 (12)	163 (19)
H	3131 (53)	−4363 (42)	−7099 (166)	841 (463)
C113	2437 (6)	−4006 (3)	−5370 (13)	183 (19)
H	3000 (39)	−4018 (29)	−4278 (71)	224 (262)
H	2402 (49)	−3683 (9)	−5865 (90)	1 (184)
C114	1590 (6)	−4203 (3)	−5009 (12)	158 (18)
H	1469 (59)	−4051 (27)	−3903 (70)	238 (256)
C115	1617 (6)	−4321 (3)	−7945 (12)	148 (18)
H	1346 (49)	−4612 (15)	−8595 (96)	104 (223)

Table 2 (continued)

Molecule 2

	x/a	y/b	z/c	U_{eq}
H	1 519 (52)	-4 062 (17)	-8 846 (79)	112 (214)
C116	967 (6)	-4 217 (3)	-6 801 (13)	205 (20)
H	632 (59)	-3 912 (15)	-7 037 (134)	406 (301)
H	486 (35)	-4 474 (16)	-7 000 (98)	1 (191)
C117	1 003 (5)	-4 998 (3)	-2 502 (11)	127 (17)
H	942 (53)	-4 682 (11)	-2 010 (100)	85 (217)
C118	1 430 (6)	-5 345 (3)	-1 224 (12)	130 (17)
H	1 005 (41)	-5 464 (23)	-467 (82)	72 (199)
H	2 072 (26)	-5 295 (26)	-353 (83)	184 (236)
C119	1 533 (5)	-5 675 (3)	-2 587 (12)	145 (18)
H	1 857 (66)	-5 974 (18)	-2 120 (141)	536 (340)
C120	182 (5)	-5 255 (3)	-3 563 (12)	134 (18)
H	6 (53)	-5 079 (23)	-4 740 (53)	176 (231)
H	-322 (39)	-5 224 (24)	-2 875 (89)	86 (211)
C121	540 (6)	-5 720 (3)	-3 631 (13)	166 (18)
H	482 (75)	-5 861 (33)	-4 860 (62)	538 (361)
H	54 (36)	-5 913 (19)	-3 235 (94)	1 (189)
C122	3 150 (5)	-4 554 (3)	-1 393 (12)	143 (18)
C123	4 218 (5)	-4 751 (2)	-3 179 (12)	123 (17)
C124	3 652 (5)	-5 343 (2)	-1 386 (11)	90 (16)
O125	3 165 (4)	-4 295 (2)	-390 (8)	215 (15)
O126	4 896 (4)	-4 617 (2)	-3 267 (9)	235 (15)
O127	3 946 (4)	-5 593 (2)	-357 (8)	162 (13)

The C – H distances were restrained to 1.08 Å. Final residual $R = 0.067$, $R_w = 0.063$ (weighting system $w = a/\sigma^2(F) + b^*(F^2)$; $a = 1.48$, $b = 0.00056$). Largest peak in the final difference Fourier map 0.95 eÅ^{-3}. Fractional atomic coordinates and isotropic or equivalent isotropic temperature coefficients are listed in Table 2.

Crystal Data for **4-Cr**

$C_{24}H_{24}CrO_3$, yellow crystals (from hexane/CH_2Cl_2), m.p. 240°C (dec.), orthorhombic, space group Pnma, $a = 12.843(3)$, $b = 15.140(4)$, $c = 10.173(2)$ Å, $V = 1\,978.2(0.5)$ Å^3, $Z = 4$, 1 813 independent reflections were measured at room temperature of which 1 332 were considered observed [$|F_0| \geqslant 4.0 * \sigma(F_0)$]. Extinction corrections but no absorption corrections were applied to the measured intensities ($F^* = F(1 - 0.001 * x^* F^2/\sin\Phi$, $x = 0.00446$). The structure was solved by the heavy atom method and refined by least squares techniques. In the final refinement, anisotropic thermal parameters were used for all nonhydrogen atoms, hydrogen atoms were included at observed positions and refined with isotropic temperature factors (184 parameters, 1 373 observations). Final residual $R = 0.046$, $R_w = 0.046$ (weighting system $w = a/\sigma^2(F) + b^*(F^2)$; $a = 1.75$, $b = 0.00032$). Largest peak in the final difference Fourier map 0.68 eÅ^{-3}. The used computer programs are listed in Ref. [10]. Fractional atomic coordinates and isotropic or equivalent istropic temperature coefficients are listed in Table 3.

Table 3. Atomic coordinates and equivalent isotropic temperature factors ($*10^4$, U-values in Å^2) for all non-hydrogen atoms in the crystal structure of **4-Cr**. Isotropic temperature factors are given for all hydrogens. Standard deviations are listed in parentheses

	x/a	y/b	z/c	U_{eq}
CR 1	966 (1)	2 500	419 (1)	306 (4)
C 1	1 677 (2)	2 971 (2)	−1 447 (3)	296 (17)
C 2	2 137 (2)	3 429 (2)	−398 (3)	287 (15)
C 3	2 603 (2)	2 969 (2)	655 (3)	307 (16)
C 7	1 218 (3)	3 244 (2)	−2 744 (3)	433 (21)
H	938 (25)	3 848 (22)	−2 719 (32)	391 (91)
C 8	443 (5)	2 500	−2 993 (7)	486 (35)
H	172 (36)	2 500	−3 849 (48)	326 (129)
H	−84 (38)	2 500	−2 468 (49)	300 (142)
C 10	2 071 (4)	3 013 (3)	−3 761 (4)	547 (26)
H	1 924 (35)	3 246 (30)	−4 643 (50)	841 (149
H	2 732 (33)	3 314 (28)	−3 515 (41)	614 (129)
C 12	2 337 (3)	4 404 (2)	−149 (4)	403 (20)
H	1 925 (25)	4 807 (24)	−574 (33)	426 (100)
C 13	2 299 (3)	4 420 (3)	1 360 (4)	478 (22)
H	1 580 (27)	4 309 (24)	1 681 (32)	477 (106)
H	2 573 (25)	4 983 (25)	1 757 (32)	425 (95)
C 14	3 067 (3)	3 655 (3)	1 538 (4)	448 (22)
H	3 238 (25)	3 476 (21)	2 310 (36)	340 (98)
C 15	3 519 (3)	4 523 (3)	−372 (5)	509 (24)
H	3 693 (29)	5 156 (27)	−333 (34)	522 (105)
H	3 704 (27)	4 300 (24)	−1 176 (34)	407 (101)
C 16	4 010 (3)	4 027 (3)	781 (5)	536 (24)
H	4 397 (29)	4 406 (27)	1 322 (40)	643 (126)
H	4 575 (30)	3 564 (27)	543 (37)	572 (116)
C 22	844 (4)	2 500	2 204 (6)	491 (33)
C 23	−34 (3)	3 350 (3)	313 (4)	502 (22)
O 25	814 (4)	2 500	3 340 (4)	860 (37)
O 26	−649 (2)	3 898 (2)	234 (4)	909 (26)

Supplementary Material Available

Anisotropic temperature coefficients for the anisotropically refined atoms for the crystal structures of **3-Cr** and **4-Cr** are available on request from the authors. Ordering information is given on any masthead page.

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Received September 4, 1989. Accepted September 28, 1989