

The Structures of Dicarbonyl[1–4a(10a)- η -phenanthrene](triethylphosphine)chromium(0) and Dicarbonyl[1–4a(8a)- η -naphthalene](triphenyl phosphite)chromium(0)

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Abstract

[Cr(C₁₄H₁₀)₂(C₂H₅)₃P](CO)₂, C₂₂H₂₅CrO₂P (PCrP), is monoclinic, $a = 27.081$ (12), $b = 14.223$ (7), $c = 11.228$ (5) Å, $\beta = 111.45$ (4)°, space group $C2/c$, $Z = 8$, $D_x = 1.334$ Mg m⁻³. [Cr(C₁₀H₈)₂(C₆H₅O)₃P](CO)₂, C₃₀H₂₃CrO₅P (NCrP), is monoclinic, $a = 9.458$ (4), $b = 10.095$ (5), $c = 26.947$ (12) Å, $\beta = 99.63$ (4)°, space group $P2_1/c$, $Z = 4$, $D_x = 1.417$ Mg m⁻³. The structures were refined to $R = 0.052$ for 2462 reflections for PCrP and to $R = 0.060$ for 3290 reflections for NCrP. The octahedral arrangement around the Cr atom in PCrP is preserved and it is similar to that in the parent tricarbonyl(phenanthrene)chromium. There is geometrical evidence that the PEt₃ ligand does not introduce any distortion. The Cr–P distance is 2.323 (1) Å. Distances of Cr–C(phenanthrene) are different from those in the tricarbonyl complex. The bulky P(OPh)₃ ligand in NCrP gives rise to overcrowding and slightly distorts the octahedral arrangement of Cr. A very short Cr–P length of 2.217 (1) Å is observed. There are no significant changes in the bond distances Cr–C(naphthalene) compared with those in the tricarbonyl complex.

Introduction

The special catalytic activity of tricarbonyl–arene–chromium complexes in the hydrogenation of conjugated olefins has been studied and documented (Cais & Rejoan, 1970; Yagupsky & Cais, 1975; Cais, Fraenkel & Weidenbaum, 1975; Eden, Fraenkel, Cais & Halevi, 1977). Significant changes occur in the catalytic activity by the replacement of a CO group by other ligands which give complexes of the type Cr(arene)(CO)₂L (Dabard, Jaouen, Simonneaux, Cais, Kohn, Lapid & Tatarsky, 1980; Cais, Kaftory, Kohn & Tatarsky, 1980; Tatarsky, 1979).

The crystal structures of tricarbonylchromium complexes of phenanthrene and naphthalene have been studied (Muir, Ferguson & Sim, 1968; Guss & Mason, 1973; Kunz & Nowacki, 1967) and a possible

connection with their catalytic properties has been suggested (Cais, Fraenkel & Weidenbaum, 1975).

The replacement of a CO group by triethylphosphine (PCrP) and triphenyl phosphite (NCrP) lowered the catalytic properties.

It seemed desirable to determine the crystal and molecular structures of the title compounds and compare the geometrical features with those of the parent tricarbonyl complexes. The differences might lead to some conclusions as to the factors which govern the catalytic properties.

Experimental

Intensities from single crystals [red prisms of PCrP (0.2 × 0.2 × 0.3 mm) and red prismatic needles of NCrP (0.3 × 0.15 × 0.3 mm)] were collected on a PW 1100 Philips four-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Crystallographic data and details of intensity measurements are given in Table 1.

Table 1. Crystallographic data and experimental details

	PCrP	NCrP
Formula	C ₂₂ H ₂₅ CrO ₂ P	C ₃₀ H ₂₃ CrO ₅ P
a (Å)	27.081 (12)	9.458 (4)
b (Å)	14.223 (7)	10.095 (5)
c (Å)	11.228 (5)	26.947 (12)
β (°)	111.45 (4)	99.63 (4)
Z	8	4
Space group	$C2/c$	$P2_1/c$
D_x (Mg m ⁻³)	1.334	1.417
Scan mode	$\omega/2\theta$	ω
$\Delta\omega$ (°)	1.2	1.2
Scan time (s)	24	24
Background* (s)	24	20
θ_{\max} (°)	25	24
Number of reflections measured	3543	4242
Number of significant reflections ($F_o > 0.0$)	2462	3290
Weighting coefficients (k, g)†	0.4418, 0.0005	0.4411, 0.0006
R_w	0.048	0.053
R	0.052	0.060

* Total background counting time.

† $W = k/[\sigma^2(F_o) + g(F_o)^2]$.

Table 2. PCrP: coordinates for non-hydrogen atoms ($\times 10^4$) and for H atoms ($\times 10^3$) Table 3. NCrP: coordinates for non-hydrogen atoms ($\times 10^4$) and for H atoms ($\times 10^3$)

E.s.d.'s are in parentheses.

	x	y	z		x	y	z
Cr	9273 (0)	1951 (0)	4916 (0)	Cr	2114 (1)	3722 (1)	3145 (0)
P	8411 (0)	1538 (1)	3644 (1)	P	2749 (1)	3681 (1)	3975 (0)
O(1)	9312 (1)	301 (2)	6580 (2)	O(1)	1077 (3)	1008 (3)	3325 (1)
O(2)	8846 (1)	3028 (2)	6606 (2)	O(2)	-755 (3)	4834 (3)	3248 (1)
C(1)	9962 (1)	2862 (3)	5558 (3)	O(3)	3654 (2)	4808 (2)	4326 (1)
C(2)	10136 (1)	1943 (3)	5662 (3)	O(4)	3734 (2)	2457 (2)	4224 (1)
C(3)	9962 (1)	1363 (2)	4581 (4)	O(5)	1394 (2)	3443 (2)	4259 (1)
C(4)	9606 (1)	1690 (2)	3407 (3)	C(1)	4675 (4)	6190 (5)	3248 (1)
C(5)	8966 (1)	2542 (2)	888 (3)	C(2)	4204 (6)	7447 (5)	3215 (2)
C(6)	8666 (2)	2960 (3)	-260 (3)	C(3)	2893 (6)	7786 (4)	2916 (2)
C(7)	8539 (2)	3898 (3)	-308 (4)	C(4)	2068 (5)	6853 (4)	2647 (1)
C(8)	8710 (1)	4430 (3)	770 (4)	C(5)	2553 (4)	5510 (4)	2658 (1)
C(9)	9188 (1)	4589 (2)	3099 (4)	C(6)	1721 (4)	4487 (4)	2377 (1)
C(10)	9473 (1)	4216 (2)	4226 (3)	C(7)	2259 (5)	3219 (4)	2366 (1)
C(11)	9639 (1)	3248 (2)	4353 (3)	C(8)	3582 (4)	2885 (4)	2664 (1)
C(12)	9455 (1)	2658 (2)	3257 (3)	C(9)	4331 (4)	3823 (4)	2973 (1)
C(13)	9136 (1)	3070 (2)	2019 (3)	C(10)	3874 (4)	5168 (4)	2960 (1)
C(14)	9011 (1)	4035 (2)	1961 (3)	C(11)	1459 (3)	2082 (4)	3247 (1)
C(15)	9288 (1)	942 (2)	5915 (3)	C(12)	366 (4)	4403 (4)	3221 (1)
C(16)	9003 (1)	2619 (2)	5920 (3)	C(13)	3414 (3)	6175 (3)	4323 (1)
C(17)	7989 (1)	2389 (2)	2489 (3)	C(14)	2105 (3)	6738 (3)	4148 (1)
C(18)	7929 (2)	3321 (3)	3073 (4)	C(15)	1993 (4)	8107 (4)	4161 (2)
C(19)	8317 (1)	505 (2)	2600 (3)	C(16)	3157 (5)	8865 (4)	4365 (2)
C(20)	8539 (2)	-400 (2)	3301 (4)	C(17)	4434 (4)	8272 (4)	4552 (1)
C(21)	8009 (1)	1239 (2)	4601 (3)	C(18)	4574 (3)	6926 (3)	4528 (1)
C(22)	7442 (1)	931 (3)	3906 (4)	C(19)	5036 (3)	2162 (3)	4065 (1)
H(1)	1010 (2)	326 (3)	628 (4)	C(20)	5072 (4)	1118 (3)	3734 (1)
H(2)	1038 (2)	170 (3)	645 (4)	C(21)	6346 (4)	812 (4)	3579 (1)
H(3)	1008 (2)	73 (3)	462 (4)	C(22)	7558 (4)	1515 (4)	3746 (2)
H(4)	947 (2)	128 (3)	271 (4)	C(23)	7522 (4)	2540 (4)	4085 (1)
H(5)	907 (2)	188 (3)	95 (4)	C(24)	6257 (3)	2873 (3)	4248 (1)
H(6)	855 (2)	258 (3)	-100 (4)	C(25)	1505 (3)	3110 (3)	4772 (1)
H(7)	832 (2)	413 (3)	-115 (4)	C(26)	1454 (4)	1802 (4)	4901 (1)
H(8)	863 (2)	511 (3)	79 (4)	C(27)	1545 (5)	1478 (5)	5404 (2)
H(9)	908 (2)	524 (3)	299 (4)	C(28)	1676 (4)	2458 (6)	5769 (2)
H(10)	959 (2)	457 (3)	499 (4)	C(29)	1679 (4)	3747 (5)	5628 (1)
H(171)	762 (2)	208 (3)	201 (4)	C(30)	1605 (3)	4100 (4)	5127 (1)
H(172)	813 (2)	247 (3)	183 (4)	H(1)	558 (5)	590 (4)	345 (2)
H(181)	828 (2)	359 (3)	349 (4)	H(2)	472 (5)	814 (5)	341 (2)
H(182)	775 (2)	326 (4)	367 (5)	H(3)	255 (4)	872 (3)	294 (1)
H(183)	767 (2)	369 (4)	243 (5)	H(4)	102 (5)	704 (4)	242 (2)
H(191)	851 (1)	65 (3)	198 (3)	H(6)	84 (5)	470 (4)	221 (2)
H(192)	792 (1)	43 (2)	209 (3)	H(7)	169 (4)	261 (4)	219 (2)
H(201)	845 (2)	-90 (3)	275 (4)	H(8)	387 (4)	197 (3)	267 (1)
H(202)	836 (2)	-60 (3)	388 (4)	H(9)	522 (3)	357 (3)	317 (1)
H(203)	891 (2)	-35 (3)	383 (4)	H(14)	131 (4)	625 (3)	402 (1)
H(211)	801 (2)	178 (3)	511 (4)	H(15)	114 (4)	851 (4)	399 (2)
H(212)	818 (2)	73 (3)	518 (4)	H(16)	306 (4)	979 (4)	438 (1)
H(221)	727 (2)	76 (4)	441 (5)	H(17)	530 (4)	880 (3)	468 (1)
H(222)	721 (2)	144 (4)	349 (5)	H(18)	540 (4)	652 (3)	462 (1)
H(223)	740 (2)	37 (4)	339 (5)	H(20)	418 (3)	62 (3)	363 (1)
				H(21)	633 (4)	15 (3)	330 (1)
				H(22)	845 (4)	133 (3)	364 (1)
				H(23)	828 (4)	301 (4)	419 (2)
				H(24)	620 (3)	358 (3)	449 (1)
				H(26)	124 (4)	118 (3)	462 (1)
				H(27)	154 (4)	60 (4)	549 (1)
				H(28)	166 (4)	219 (4)	609 (2)
				H(29)	174 (4)	449 (4)	588 (2)
				H(30)	165 (4)	499 (3)	502 (1)

The crystal structures were solved with *MULTAN* 77 (Main, Woolfson, Lessinger, Germain & Declercq, 1977).

The refinement was carried out by least squares with *SHELX* (Sheldrick, 1976) using three separate blocks: anisotropic for the arene and dicarbonylchromium phosphorylated ligands, isotropic for H atoms.

Scattering factors for Cr were taken from *International Tables for X-ray Crystallography* (1974), for other heavy atoms from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). The final agreement factors and type of weighting scheme are given in Table 1. Final positional parameters are listed in Tables 2 and 3.*

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35530 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Comparison of bond lengths (Å) in Cr(CO)₂PEt₃(phen)(PCrP) and Cr(CO)₃(phen)(PCrC) (monoclinic form)

The e.s.d.'s for bond lengths in Cr(CO)₂PEt₃(phen) are: Cr—C 0.003; Cr—P 0.001; P—C 0.003; C—C, C—O 0.003–0.004 Å.

	PCrP	PCrC		PCrP	PCrC
Cr—C(1)	2.166	2.208	C(1)—C(2)	1.380	1.365
Cr—C(2)	2.175	2.207	C(1)—C(11)	1.424	1.435
Cr—C(3)	2.199	2.214	C(2)—C(3)	1.400	1.422
Cr—C(4)	2.222	2.213	C(3)—C(4)	1.397	1.379
Cr—C(12)	2.322	2.278	C(4)—C(12)	1.428	1.441
Cr—C(11)	2.288	2.289	C(11)—C(12)	1.421	1.399
Cr—C(15)	1.813	1.832	C(12)—C(13)	1.464	1.455
Cr—C(16)	1.820	1.845	C(13)—C(5)	1.400	1.401
Cr—P	2.323	1.826*	C(13)—C(14)	1.410	1.415
P—C(17)	1.836	—	C(5)—C(6)	1.381	1.370
P—C(19)	1.838	—	C(6)—C(7)	1.375	1.382
P—C(21)	1.839	—	C(7)—C(8)	1.357	1.367
C(15)—O(1)	1.166	1.140	C(8)—C(14)	1.403	1.414
C(16)—O(2)	1.163	1.146†	C(9)—C(14)	1.427	1.423
C(17)—C(18)	1.512	—	C(9)—C(10)	1.329	1.349
C(19)—C(20)	1.514	—	C(10)—C(11)	1.439	1.444
C(21)—C(22)	1.511	—			

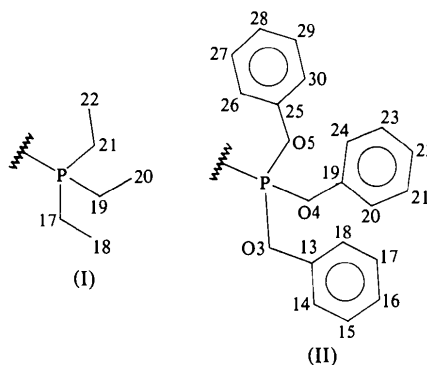
* P should be replaced by C for PCrC.

† The third C=O length is 1.157 Å.

Bond lengths and angles are given in Tables 4 and 5 (PCrP), 6 and 7 (NCrP).

Description of the structures

Schematic drawings and numbering of atoms are given in Figs. 1 (PCrP) and 2 (NCrP). For comparison, positions (17) and (3) in Fig. 1 represent the PEt₃ group (I) while positions (13) and (3) in Fig. 2 represent the P(OPh)₃ group (II).



Stereoviews of the complexes are shown in Figs. 3 (PCrP) and 4 (NCrP). In both structures the Cr atom is lying above one of the rings but shifted from the centre towards the atoms opposite to the projected Cr—P bond on that ring.

The orientation of the phenanthrene or naphthalene ligand and the substituted Cr(CO)₃ fragment is

Table 5. Comparison of bond angles in Cr(CO)₂PEt₃(phen) (PCrP) and in Cr(CO)₃(phen) (PCrC) (monoclinic)

The e.s.d.'s of bond angles are: P—Cr—C, C—Cr—C, Cr—P—C 0.1; P—C—C, C—O—C, C—C—C 0.2–0.3°.

	PCrP	PCrC		PCrP	PCrC
P—Cr—C(15)	88.3	88.6*	C(6)—C(5)—C(13)	120.1	120.3
P—Cr—C(16)	88.4	89.1*	C(5)—C(6)—C(7)	120.5	121.6
C(15)—Cr—C(16)	87.3	87.3	C(6)—C(7)—C(8)	120.4	119.6
Cr—P—C(17)	119.6	—	C(7)—C(8)—C(14)	121.1	120.7
Cr—P—C(19)	118.0	—	C(10)—C(9)—C(14)	121.4	121.3
Cr—P—C(21)	112.1	—	C(9)—C(10)—C(11)	121.9	119.9
C(17)—P—C(19)	99.9	—	C(1)—C(11)—C(10)	121.5	119.7
C(17)—P—C(21)	102.4	—	C(1)—C(11)—C(12)	119.6	119.7
C(19)—P—C(21)	102.4	—	C(10)—C(11)—C(12)	118.8	120.6
Cr—C(15)—O(1)	178.1	179.2	C(4)—C(12)—C(11)	118.2	118.3
Cr—C(16)—O(1)	177.2	179.2†	C(4)—C(12)—C(13)	122.8	122.5
P—C(17)—C(18)	114.2	—	C(11)—C(12)—C(13)	118.9	119.3
P—C(19)—C(20)	114.3	—	C(5)—C(13)—C(12)	122.0	123.0
P—C(21)—C(22)	118.2	—	C(5)—C(13)—C(14)	119.1	118.7
C(2)—C(1)—C(11)	121.2	121.2	C(12)—C(13)—C(14)	118.8	118.3
C(1)—C(2)—C(3)	119.2	119.5	C(8)—C(14)—C(9)	121.4	120.3
C(2)—C(3)—C(4)	121.3	120.4	C(8)—C(14)—C(13)	118.7	119.1
C(3)—C(4)—C(12)	120.1	120.8	C(9)—C(14)—C(13)	120.0	120.6

* P should be replaced by C for PCrC.

† The third Cr—C=O angle in PCrC is 179.0°

Table 6. Comparison of bond lengths (Å) in Cr(CO)₂-P(OPh)₃(naph) (NCrP) and Cr(CO)₃(naph) (NCrC)

The e.s.d.'s for bond lengths (NCrP) are: Cr-P 0.001; Cr-C 0.004; P-O 0.002; C-O, C-C 0.004-0.007 Å.

	NCrP	NCrC		NCrP
Cr-C(5)	2.310	2.306	P-O(3)	1.629
Cr-C(6)	2.182	2.186	P-O(4)	1.624
Cr-C(7)	2.185	2.191	P-O(5)	1.617
Cr-C(8)	2.218	2.213	C(13)-O(3)	1.399
Cr-C(9)	2.224	2.214	C(19)-O(4)	1.402
Cr-C(10)	2.329	2.337	C(25)-O(5)	1.409
Cr-P	2.217	1.818*	C(13)-C(14)	1.373
Cr-C(11)	1.805	1.815	C(13)-C(18)	1.370
Cr-C(12)	1.833	1.830	C(14)-C(15)	1.387
C(1)-C(2)	1.343	1.375	C(15)-C(16)	1.378
C(1)-C(10)	1.430	1.438	C(16)-C(17)	1.367
C(2)-C(3)	1.403	1.392	C(17)-C(18)	1.368
C(3)-C(4)	1.354	1.415	C(19)-C(20)	1.385
C(4)-C(5)	1.430	1.406	C(19)-C(24)	1.380
C(5)-C(6)	1.435	1.404	C(20)-C(21)	1.375
C(5)-C(10)	1.415	1.439	C(21)-C(22)	1.359
C(6)-C(7)	1.380	1.389	C(22)-C(23)	1.384
C(7)-C(8)	1.410	1.375	C(23)-C(24)	1.383
C(8)-C(9)	1.375	1.383	C(25)-C(26)	1.368
C(9)-C(10)	1.424	1.447	C(25)-C(30)	1.376
C(11)-O(1)	1.173	1.147	C(26)-C(27)	1.383
C(12)-O(2)	1.160	1.137†	C(27)-C(28)	1.385
			C(28)-C(29)	1.356
			C(29)-C(30)	1.386

* P should be replaced by C for NCrC.

† The third C=O distance in NCrC is 1.167 Å.

Table 7. Comparison of bond angles (°) in Cr(CO)₂-P(OPh)₃(naph) (NCrP) and in Cr(CO)₃(naph) (NCrC)

The e.s.d.'s of bond angles (NCrP) are: P-Cr-C 0.1; C-Cr-C, Cr-P-O, P-O-C 0.2; Cr-C-O 0.3; C-C-O, C-C-C 0.3-0.4°.

	NCrP	NCrC		NCrP
P-Cr-C(11)	82.6	90.7*	Cr-C(11)-O(1)	177.7
P-Cr-C(12)	89.5	87.0*	Cr-C(12)-O(2)	177.3
C(11)-Cr-C(12)	89.3	90.1	O(3)-C(13)-C(14)	123.1
C(2)-C(1)-C(10)	120.4	118.5	O(3)-C(13)-C(18)	115.2
C(1)-C(2)-C(3)	121.3	119.6	C(14)-C(13)-C(18)	121.7
C(2)-C(3)-C(4)	120.9	124.9	C(13)-C(14)-C(15)	118.2
C(3)-C(4)-C(5)	119.6	116.0	C(14)-C(15)-C(16)	120.3
C(4)-C(5)-C(6)	121.7	121.8	C(15)-C(16)-C(17)	120.1
C(4)-C(5)-C(10)	119.5	120.0	C(16)-C(17)-C(18)	120.3
C(6)-C(5)-C(10)	118.8	118.2	C(17)-C(18)-C(13)	119.4
C(5)-C(6)-C(7)	120.4	120.8	O(4)-C(19)-C(20)	118.5
C(6)-C(7)-C(8)	120.4	122.5	O(4)-C(19)-C(24)	120.4
C(7)-C(8)-C(9)	119.9	118.5	C(20)-C(19)-C(24)	121.1
C(8)-C(9)-C(10)	121.2	121.6	C(19)-C(20)-C(21)	119.0
C(1)-C(10)-C(9)	122.9	121.4	C(20)-C(21)-C(22)	121.0
C(1)-C(10)-C(5)	118.3	120.6	C(21)-C(22)-C(23)	119.8
C(5)-C(10)-C(9)	118.8	118.0	C(22)-C(23)-C(24)	120.6
Cr-P-O(3)	126.9		C(23)-C(24)-C(19)	118.5
Cr-P-O(4)	118.1		O(5)-C(25)-C(26)	118.6
Cr-P-O(5)	112.2		O(5)-C(25)-C(30)	119.6
O(3)-P-O(4)	94.7		C(26)-C(25)-C(30)	121.7
O(3)-P-O(5)	102.1		C(25)-C(26)-C(27)	118.6
O(4)-P-O(5)	97.8		C(26)-C(27)-C(28)	120.6
P-O(3)-C(13)	128.1		C(27)-C(28)-C(29)	119.5
P-O(4)-C(19)	120.5		C(28)-C(29)-C(30)	121.0
P-O(5)-C(25)	124.4		C(29)-C(30)-C(25)	118.5

* P should be replaced by C(13) for NCrC.

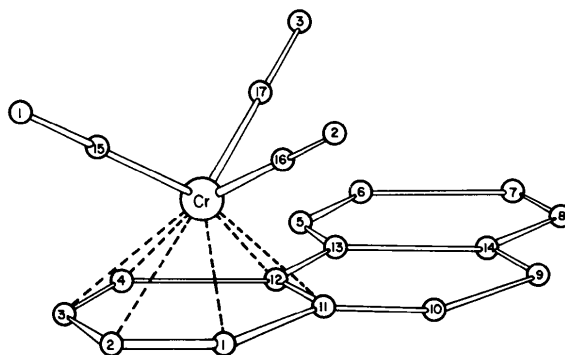
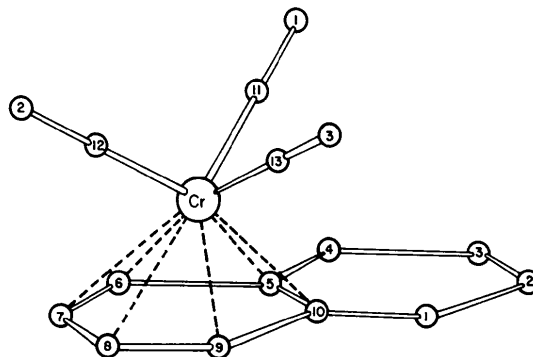
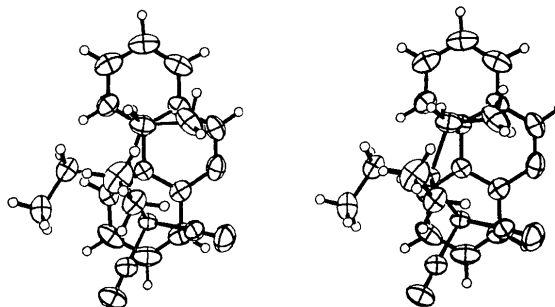
Fig. 1. Schematic drawing and numbering of atoms in PCrC and PCrP. [(17) and (3) represent PEt₃ in PCrP.]Fig. 2. Schematic drawing and numbering of atoms in NCrP and NCrC. [(13) and (3) represent P(OPh)₃ in NCrP.]

Fig. 3. Stereoview of PCrP (Johnson, 1965).

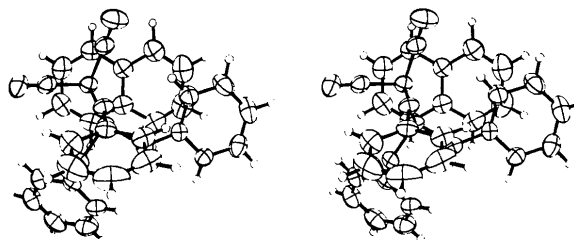


Fig. 4. Stereoview of NCrP (Johnson, 1965).

staggered. The same conformation was observed in the unsubstituted complexes.

Discussion

Comparison of bond distances and angles in tricarbonyl(phenanthrene)chromium (PCrC) and PCrP are given in Tables 4 and 5, for tricarbonyl(naphthalene)chromium (NCrC) and NCrP in Tables 6 and 7. The data used for the comparison of PCrC were taken from the monoclinic form [Guss & Mason, 1973; (GM)], for NCrC from Kunz & Nowacki (1967) (KN).

The coordination of Cr is octahedral in both structures. The angles P–Cr–CO and OC–Cr–CO in PCrP are close to those of the tricarbonyl compound and to the ideal value of 90°. Thus the substitution of a CO group by PEt_3 does not cause any appreciable distortion of the coordination polyhedron, *i.e.* does not give rise to considerable overcrowding. In contrast to PCrP, there are significant distortions from an ideal octahedron in NCrP. The P–Cr–CO angles tend to be smaller [82.6 (1)–89.5 (1)°]; these deformations are likely to arise from steric interactions between the phosphite moiety and the overlapped ring of the naphthalene molecule. No evidence for such steric interactions was found in dicarbonyl[η -(methyl benzoate)](triphenylphosphine)chromium (Andrianov, Struchkov, Baranetskaya, Setkina & Kursanov, 1975) as no overlapping groups to the phosphorylated ligand are present.

The most interesting aspects of the comparison between the title compounds and their parent tricarbonyl complexes are the Cr–P and Cr–C(arene) lengths. The Cr–P length in the phosphite complex NCrP is 2.217 (1) Å, significantly shorter than in the phosphine complex PCrP [2.323 (1) Å]; furthermore it is the shortest Cr–P length ever observed. The shortening of Cr–P in NCrP may be explained according to Preston, Stewart, Plastas & Grim (1972), Plastas, Stewart & Grim (1973) and Caldwell, Manojlović-Muir & Muir (1977) (CMM). Triethylphosphine is more basic than triphenyl phosphite but the latter is expected to be a better π -acceptor than triethylphosphine because of the electronegative O atoms attached to P. Hence the P atom in triphenyl phosphite will tend to have a greater interaction with the metal atom. These differences in behaviour are well observed in the structures of pentacarbonyl(triphenylphosphine)chromium and the triphenyl phosphite compound (Plastas, Stewart & Grim, 1973); Cr–P distances are 2.422 and 2.309 Å respectively. The further shortening of Cr–P distances in the title compound (NCrP) might be explained by the weaker competitive ligand (naphthalene) compared with carbonyl (Plastas, Stewart & Grim, 1973).

The replacement of a carbonyl group by triethylphosphine (PCrP) decreases the bond distances of

Cr–C(phenanthrene) *trans* to that ligand. Cr–C(1), Cr–C(2) in PCrP [2.166 (3), 2.175 (3) Å] are shorter by 0.041 Å (averaged) than those distances in the unsubstituted tricarbonyl complex; this difference is >13 e.s.d.'s and therefore significant. Similar differences, to a lesser extent, have been observed in dicarbonyl[η -(methyl benzoate)](triphenylphosphine)chromium (Andrianov *et al.*, 1975) compared with its parent tricarbonyl complex (Carter, McPhail & Sim, 1967). On the other hand, such differences were not observed in dicarbonyl(naphthalene)(triphenyl phosphite)chromium (NCrP) compared with its parent compound.

According to the trend of increasing interaction with Cr [CO > P(OPh)₃ ≫ PEt_3], Cr, bonded to PEt_3 , will have higher electron density which will be partially distributed to the remaining carbonyl groups by back donation from $d\pi$ metal orbitals to the empty π^* orbitals of CO and will shorten the Cr–CO bond. The Cr–CO length in chromium hexacarbonyl is 1.909 Å (Whitaker & Jeffery, 1967); the bond is shorter in tricarbonyl(phenanthrene)chromium (1.834 Å) and even shorter when a carbonyl group is replaced by the more basic ligand PEt_3 (1.816 Å in PCrP). The replacement by P(OPh)₃ does not show the same effect; the bond length is 1.819 Å in NCrP compared with 1.821 Å in the parent tricarbonyl complex. Since in both title compounds Cr–CO lengths are practically the same one cannot rule out the possibility that the more negative Cr bonded to the triethylphosphine ligand will interact strongly by back donation to the phenanthrene C(1), C(2) atoms causing the shortening of those bonds. In order to prove this possibility it seems necessary to compare those bond distances in compounds composed of the same arene moiety and different substituted ligands.

Phosphine and phosphite ligands

Bond lengths and angles in the PEt_3 ligand are in good agreement with corresponding values in, for example, *cis*-dichloro(triethylphosphine)(triphenyl phosphite)platinum(II) (CMM). The mean P–C and C–C distances, 1.838 and 1.512 Å respectively, agree well with 1.828 and 1.511 Å in the latter.

The P atom is tetrahedrally bonded; C–P–C angles are somewhat smaller than ideal tetrahedral angles within the ethyl moieties (mean value 101.6°) compared with 104.5° (CMM).

Bond lengths and angles within the triphenyl phosphite ligand are close to values observed by CMM. The mean O–C distance is 1.403 compared with 1.406 Å in CMM. The P–O bond is slightly longer (1.623 Å) than the 1.586 Å found by CMM and the 1.598 Å found by Plastas, Stewart & Grim (1973). This lengthening is likely to be affected by the rather short Cr–P distance found in the same manner as the

lengthening of C—O bonds of the carbonyls. P—O—C angles of 120.5–128.1° are similar to 122.8–128.90° given by CMM.

Arenes

Bond lengths and angles in the phenanthrene molecule (PCrP) are in good agreement with those found in the tricarbonyl complex. All geometrical values are within the 3 e.s.d.'s test. However, a mean plane through the central ring shows that the external rings are bowed away from the Cr atom. C(1), C(2) and C(3) are displaced by 0.055, 0.154, 0.131 Å respectively from the best plane, away from the Cr atom; this distortion is different from that found in crystalline phenanthrene, where the external rings are twisted in opposite directions (Kay, Okaya & Cox, 1971), or in tricarbonyl(phenanthrene)chromium (GM).

Bond lengths and angles in the naphthalene molecule need no comments. A mean plane through the rings shows that the molecule is significantly non-planar. The ring involved with the Cr atom has the same bow shape as that in the parent tricarbonyl complex (Kunz & Nowacki, 1967); C(6), C(9) (0.047, 0.045 Å) are displaced towards C(7), C(8) (−0.040, −0.052 Å) away from the Cr atom. The other ring has a somewhat different shape compared with the parent complex due to the more bulky triphenyl phosphite ligand which overlaps this ring.

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