

O2—C1	1.226 (3)	C8—O3	1.220 (3)
N1—C7	1.346 (3)	C8—N2	1.324 (3)
N1—C3	1.348 (3)	C6—C7	1.373 (4)
N1—C2	1.477 (3)	C6—C5	1.390 (3)
C1—C2	1.526 (3)		
O1—Zn—O1 ⁱ	109.24 (9)	N1—C2—C1	114.4 (2)
O1—Zn—I	111.68 (5)	N1—C3—C4	121.0 (2)
O1—Zn—I ⁱ	109.94 (5)	C3—C4—C5	118.7 (2)
I—Zn—I ⁱ	104.29 (2)	C3—C4—C8	115.7 (2)
C1—O1—Zn	110.52 (14)	C5—C4—C8	125.5 (2)
C7—N1—C3	120.7 (2)	O3—C8—N2	123.7 (2)
C7—N1—C2	120.2 (2)	O3—C8—C4	118.9 (2)
C3—N1—C2	119.0 (2)	N2—C8—C4	117.4 (2)
O2—C1—O1	125.9 (2)	C7—C6—C5	119.3 (2)
O2—C1—C2	115.9 (2)	C4—C5—C6	119.5 (2)
O1—C1—C2	118.1 (2)	N1—C7—C6	120.7 (2)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Table 3. *Hydrogen-bonding geometry* ($\text{\AA}, ^\circ$)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H8...O2 ⁱ	0.76 (4)	2.22 (4)	2.965 (3)	167 (4)
N2—H7...O1 ⁱⁱ	0.83 (3)	2.32 (4)	3.133 (3)	166 (3)

Symmetry codes: (i) $x, 1 - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

The Zn and I atoms were located from Patterson synthesis and the remaining non-H atoms were located from weighted Fourier syntheses. Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were located from difference syntheses and allowed to refine freely with individual isotropic displacement parameters.

Data collection: *CAD-4-PC* (Enraf-Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *CADRED* in *CAD-4-PC*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: JZ1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 1919–1921

trans-2,2,4,4-Tetrafluoro-1,3-diphenyl-1,3-diphosphetanediy-1,3-bis[pentacarbonyl-chromium(0)]

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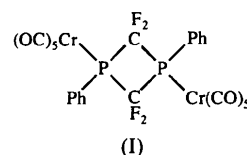
(Received 25 March 1996; accepted 11 April 1996)

Abstract

The title compound, $[\text{Cr}_2(\text{CO})_{10}(\text{C}_{14}\text{H}_{10}\text{F}_4\text{P}_2)]$, displays inversion symmetry. The P—CF₂ bond is somewhat lengthened on complexation and the phenyl–diphosphetane interplanar angle reduced from 89.15 (6)° in the free ligand to 61.4 (1)° in the complex. The P—Cr bond is short [2.3149 (6) Å].

Comment

We recently reported the preparation and structure of *trans*-2,2,4,4-tetrafluoro-1,3-diphenyl-1,3-diphosphetane (Fild, Jones, Ruhnau & Thöne, 1994). Here we extend our studies to the structure of its 1,3-bis[pentacarbonyl-chromium(0)] complex, (I).



The title complex crystallizes with inversion symmetry (as does the free ligand) and the central four-membered diphosphetane ring is thus exactly planar (Fig. 1). The P—CF₂ bond is significantly lengthened on complexation, with values of 1.9089 (14) and 1.9065 (13) Å [1.8932 and 1.8886 (14) Å for the free ligand, hereafter in square brackets]. In previous papers, we suggested that P—C_{halide} bonds are systematically lengthened with respect to non-halogenated systems (Jones & Bembek, 1996, and references therein), but here the long bonds may at least in part be attributed to the diphosphetane ring system, for which a search of the Cambridge Structural Database (Allen & Kennard, 1993) gave a mean P—C bond length of 1.881 Å (sample e.s.d. 0.017 Å for 29 values).

Other bond lengths and angles in the diphosphetane ring are scarcely altered on complexation; P—C_{Ph} 1.8146 (14) Å [1.8161 (14) Å], P—CF₂—P 97.43 (6)° [98.20 (6)°] and CF₂—P—CF₂ 82.57 (6)° [81.80 (6)°]. The conformation, however, shows a major difference,

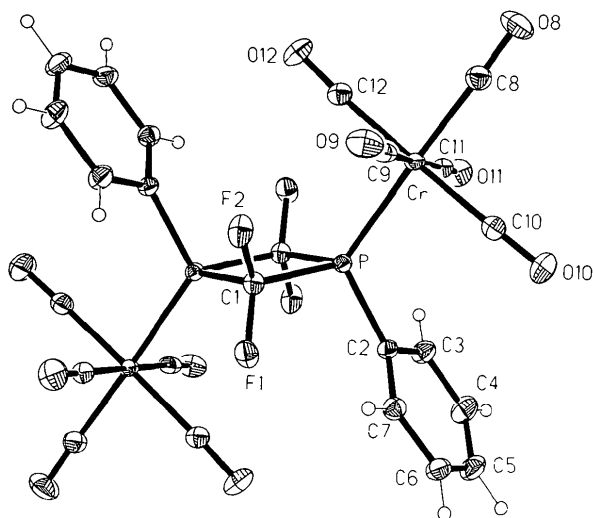


Fig. 1. A view of the molecule of the title compound in the crystal. Ellipsoids correspond to 50% probability levels and H-atom radii are arbitrary. Only the asymmetric unit is numbered.

in that the phenyl–diphosphetane interplanar angle is reduced from 89.15 (6)° in the free ligand to 61.4 (1)° in the complex, presumably because of the steric demands of the metal fragment.

The P–Cr bond of 2.3149 (6) Å is much shorter than that in Ph₃PCr(CO)₅ [2.422 (1) Å; Plastas, Stewart & Grimm, 1973] and the *trans*-Cr–C bond is correspondingly longer [1.8794 (15) *cf.* 1.845 (4) Å]. We and others have already noted the tendency of phosphines bearing electronegative substituents to form short metal–phosphorus bonds (Heuer, Bode, Jones & Schmutzler, 1989, and references therein).

Experimental

The title compound was obtained from pre-irradiated Cr(CO)₆ and the diphosphetane ligand in tetrahydrofuran. It was purified chromatographically and recrystallized from petroleum ether (Ruhnau, 1992).

Crystal data

[Cr ₂ (CO) ₁₀ (C ₁₄ H ₁₀ F ₄ P ₂)]	Mo Kα radiation
<i>M_r</i> = 700.26	λ = 0.71073 Å
Triclinic	Cell parameters from 70 reflections
<i>P</i> $\bar{1}$	θ = 10–11.5°
<i>a</i> = 8.427 (2) Å	μ = 0.998 mm ⁻¹
<i>b</i> = 9.043 (2) Å	<i>T</i> = 123 (2) K
<i>c</i> = 10.195 (2) Å	Prism
α = 115.61 (2)°	0.50 × 0.40 × 0.30 mm
β = 102.39 (2)°	Pale yellow
γ = 90.07 (2)°	
<i>V</i> = 680.4 (3) Å ³	
<i>Z</i> = 1	
<i>D_x</i> = 1.709 Mg m ⁻³	
<i>D_m</i> not measured	

Data collection

Stoe Stadi-4 diffractometer *R*_{int} = 0.0105

ω/θ-scans *θ*_{max} = 27.52°
 Absorption correction: *h* = -10 → 10
 none *k* = -11 → 11
 5285 measured reflections *l* = -13 → 13
 3106 independent reflections 3 standard reflections
 2972 observed reflections frequency: 100 min
 [*I* > 2σ(*I*)] intensity decay: none

Refinement

Refinement on *F*² (Δ/σ)_{max} = -0.001
R(*F*) = 0.0219 Δρ_{max} = 0.463 e Å⁻³
wR(*F*²) = 0.0632 Δρ_{min} = -0.418 e Å⁻³
S = 1.080 Extinction correction: none
 3101 reflections Atomic scattering factors
 190 parameters from *International Tables*
 H atoms refined as riding for *Crystallography* (1992,
w = 1/[σ²(*F*_o²) + (0.0289*P*)² + 0.3557*P*] Vol. C, Tables 4.2.6.8 and
 where *P* = (*F*_o² + 2*F*_c²)/3 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cr	0.30097 (2)	0.31958 (2)	0.64309 (2)	0.01346 (7)
P	0.13640 (4)	0.51516 (4)	0.61822 (3)	0.01253 (8)
C1	0.0945 (2)	0.5421 (2)	0.43888 (14)	0.0154 (2)
C2	0.1661 (2)	0.71795 (15)	0.77623 (14)	0.0156 (2)
C3	0.1138 (2)	0.7310 (2)	0.90176 (15)	0.0213 (3)
C4	0.1520 (2)	0.8768 (2)	1.0329 (2)	0.0269 (3)
C5	0.2432 (2)	1.0093 (2)	1.0405 (2)	0.0258 (3)
C6	0.2958 (2)	0.9964 (2)	0.9170 (2)	0.0223 (3)
C7	0.2580 (2)	0.8514 (2)	0.78448 (15)	0.0182 (2)
C8	0.4358 (2)	0.1653 (2)	0.6714 (2)	0.0217 (3)
C9	0.4185 (2)	0.3209 (2)	0.5039 (2)	0.0188 (3)
C10	0.4531 (2)	0.4933 (2)	0.8010 (2)	0.0223 (3)
C11	0.1830 (2)	0.3149 (2)	0.78214 (15)	0.0192 (3)
C12	0.1563 (2)	0.1404 (2)	0.48246 (15)	0.0186 (3)
F1	0.13473 (10)	0.69503 (10)	0.45406 (9)	0.0217 (2)
F2	0.17691 (10)	0.43889 (11)	0.34076 (9)	0.0231 (2)
O8	0.5185 (2)	0.07063 (14)	0.68539 (14)	0.0341 (3)
O9	0.49202 (13)	0.31668 (13)	0.42078 (13)	0.0267 (2)
O10	0.5463 (2)	0.59481 (15)	0.89545 (14)	0.0377 (3)
O11	0.11280 (14)	0.31430 (14)	0.86565 (12)	0.0282 (2)
O12	0.07598 (14)	0.02915 (13)	0.38622 (12)	0.0286 (2)

Table 2. Selected geometric parameters (Å, °)

Cr–C8	1.8794 (15)	P–C2	1.8146 (14)
Cr–C9	1.9011 (15)	P–C1	1.9065 (13)
Cr–C10	1.904 (2)	P–C1 ¹	1.9089 (14)
Cr–C12	1.907 (2)	C1–F1	1.3576 (15)
Cr–C11	1.9123 (15)	C1–F2	1.3589 (15)
Cr–P	2.3149 (6)		
C8–Cr–P	177.77 (4)	F1–C1–P	116.53 (9)
C2–P–C1	108.31 (6)	F2–C1–P	110.81 (9)
C2–P–C1 ¹	104.09 (6)	F1–C1–P ¹	112.04 (9)
C1–P–C1 ¹	82.57 (6)	F2–C1–P ¹	114.54 (9)
C2–P–Cr	117.71 (5)	P–C1–P ¹	97.43 (6)
C1–P–Cr	120.60 (4)	C7–C2–C3	119.72 (12)
C1 ¹ –P–Cr	117.54 (4)	C7–C2–P	122.52 (10)
F1–C1–F2	105.75 (10)	C3–C2–P	117.09 (10)

Symmetry codes: (i) -*x*, 1 - *y*, 1 - *z*.

Data collection: *DIF4* (Stoe & Cie, 1991a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick,

1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: FG1186). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 1921–1924

cis-Dibromobis(dimethyl sulfoxide-*S*)-platinum(II) and *trans*-Bis(dimethyl sulfoxide-*S*)diiodoplatinum(II)

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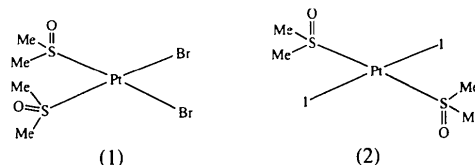
Abstract

The Pt atom has a slightly distorted square-planar coordination in both title compounds, *cis*-[PtBr₂(C₂H₆OS)₂] and *trans*-[PtI₂(C₂H₆OS)₂], with the dimethyl sulfoxide

ligands bonded *via* their S atoms. The bond distances to platinum in the bromo compound are Pt—Br 2.441 (1) and 2.447 (2), and Pt—S 2.254 (2) and 2.245 (2) Å, and in the centrosymmetric iodo complex are Pt—I 2.6111 (9) and Pt—S 2.289 (2) Å.

Comment

With the thioethers dimethyl sulfide and 1,4-thioxane, both the *cis*- and *trans*-[PtCl₂(thioether)₂] isomers can be synthesized and crystallized (Horn, Kumar, Maverick, Fronczek & Watkins, 1990; Kukushkin, Löqvist, Norén, Oskarsson & Elding, 1992; Bugarcic, Löqvist & Oskarsson, 1993). For iodo complexes, however, only a *trans*-thioether compound has been reported previously (Oskarsson, Norén, Svensson & Elding, 1990), indicating that the *trans* configuration might be the preferred isomer for iodide. Also, with sulfoxide ligands, both *cis* and *trans* isomers could be obtained for the dichloro complexes of platinum(II). The *cis* isomer seems to be the thermodynamically more stable complex as the preparation of *trans*-[PtCl₂(dmsO)₂] [dmsO is dimethyl sulfoxide, (CH₃)₂SO] results in rapid isomerization to the *cis* isomer. *trans*-[PtCl₂(dmsO)₂] has been prepared by a bridge-splitting reaction and the *trans*-to-*cis* isomerization rate was followed with ¹H NMR by Annibale, Bonivento, Canovesi, Cattalini, Michelin & Tobe (1985), who claimed that complexes of the type [MX₂L₂] adopt the *trans* configuration when *M* is Pd, but that the *cis* configuration is preferred when *M* is Pt, except for very sterically demanding sulfoxides. Melanson & Rochon (1987, 1988) were able to prepare and determine the structures of both *cis* and *trans* isomers of [PtCl₂(di-*n*-propyl sulfoxide)₂]. The crystal structure of *cis*-[PtCl₂(dmsO)₂] has been reported (Melanson & Rochon, 1975; Shibaeva, 1983), but investigations of the bromo and iodo complexes of [PtX₂(dmsO)₂] have, so far, not resulted in any reported crystal structures, though the structure of *cis*-[PtBr₂(dmsO)₂] was referred to by Kukushkin *et al.* (1991). For *cis* isomers, steric repulsion increases in the series Cl < Br < I and it is of interest to investigate the isomerism of the different halides in [PtX₂(dmsO)₂]. Hence, halides of platinum(II) (X = Cl, Br, I) were dissolved in dimethyl sulfoxide. This resulted in *cis* isomers for Cl and Br, (1), and a *trans* isomer for I, (2), both in the solid state and in solution.



cis-[PtBr₂(dmsO)₂], (1), is isostructural with *cis*-[PtCl₂(dmsO)₂]. The coordination around platinum is distorted square planar and the dimethyl sulfoxide mol-