References

BERTRAND, J. A., ELLER, P. G., FUJITA, E., LIVELY, M. O. & VAN DERVEER, D. G. (1979). *Inorg. Chem.* **18**, 2419–2423.
BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
CAMPANA, C. F., SHEPARD, D. F. & LITCHMAN, W. M. (1981). *Inorg. Chem.* **20**, 4039–4044.
FOLTING, K., COX, M. M., MOORE, J. W. & MERRITT, L. L. (1968). *Chem. Commun.* pp. 1170–1172.
HEMS, R. & MACKAY, M. F. (1975). *J. Cryst. Mol. Struct.* **5**, 227–245.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1976). *Cryst. Struct. Commun.* **5**, 827–831.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
The Universal Crystallographic Computing System–Osaka (1979). The Computation Center, Osaka Univ.

Acta Cryst. (1985). C**41**, 1444–1446

Structure of $(Ph_3P)_2Pt(\mu_2\text{-}CS_2)W(CO)_5$

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Abstract. Bis(triphenylphosphine)platinum-{μ-[(*C,S*-η)-carbon disulfide-S′]}-pentacarbonyltungsten, $C_{42}H_{30}O_5P_2PtS_2W$, $M_r = 1119{\cdot}75$, monoclinic, $P2_1/n$, $a = 14{\cdot}572\,(1)$, $b = 15{\cdot}244\,(2)$, $c = 18{\cdot}897\,(2)$ Å, $\beta = 96{\cdot}663\,(7)°$, $V = 4169{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}78$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 6{\cdot}1$ mm^{-1}, $F(000) = 1904$, $T = 296$ K, $R = 0{\cdot}046$ for 2628 unique reflections. The dinuclear complex $(Ph_3P)_2Pt(\mu_2\text{-}CS_2)W(CO)_5$ consists of a distorted square-planar $(Ph_3P)_2Pt(\eta^2\text{-}CS_2)$ fragment in which a CS_2 ligand is π-bonded through a C=S linkage to a Pt atom, with the second, *exo*-S atom σ-bonded to a W atom. The non-bonded Pt—W distance is 5·55 (1) Å. The W coordination sphere is pseudo-octahedral containing a σ-bonded S atom and five CO ligands.

Introduction. One approach to building organometallic clusters involves the interacton of a metal fragment with the CS_2 moiety of a metal—CS_2 compound which induces fragmentation of the CS_2 ligand to give S and CS ligands. Only a few examples of this behaviour have been cited in the literature; these include (dppe)$Pt(\mu_2\text{-}S)Pt(CS)(PPh_3)$ (Hawling, Walker & Woitzik, 1983) [dppe = bis(1,2-diphenylphosphino)ethane], $(CoCp)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ (Werner & Leonhard, 1979) and $Fe_4(CO)_{12}(\mu_4\text{-}CS)(\mu_3\text{-}S)$ (Broadhurst, Johnson, Lewis & Raithby, 1980). The complex $Pt_2(\mu_2\text{-}CS_2)(PBu_2Ph)_2$, which contains a bridging CS_2 ligand without a metal—metal bond, is stable towards this type of fragmentation of the CS_2 ligand (Farrar, Gukathasan & Morris, 1984). We have found that the title complex, $(Ph_3P)_2Pt(\mu_2\text{-}CS_2)W(CO)_5$ (1), does not undergo this metal-assisted CS_2 fragmentation which is consistent with our belief that the CS_2 ligand must bridge a metal—metal bond before fragmentation can occur. The complex (1) does not exhibit (Fehlhammer, Mayr & Stolzenberg, 1979; Fehlhammer & Stolzenberg, 1980) all of the characteristic IR frequencies normally associated with the bridging CS_2 ligand (Farrar, Gukathasan & Won, 1984) which led us to confirm the structure by a single-crystal X-ray analysis.

Experimental. (1) was prepared by the reaction of $W(CO)_5(THF)$ and $(Ph_3P)_2Pt(\eta^2\text{-}CS_2)$ following the reported method (Fehlhammer & Stolzenberg, 1980). Yellow crystals were obtained by slow evaporation of an ether/hexane solution. Data collection: crystal $0{\cdot}01 \times 0{\cdot}19 \times 0{\cdot}20$ mm; Enraf–Nonius CAD-4 diffractometer; cell parameters from 24 reflections at $22 < 2\theta < 27°$; 4725 unique reflections with $1 < 2\theta < 45°$ (*hkl* range: *h* 0–15, *k* 0–16, *l* −20–20); three standard reflections checked every 4 h (200, 040, 002), intensity variation 0·02%. Data reduction: Enraf–Nonius structure determination package, *SDP-PLUS* version 4–0; Gaussian absorption correction with crystal bounded by the planes (101), $(\bar{1}01)$, $(10\bar{1})$, $(\bar{1}0\bar{1})$, $(0\bar{1}0)$ and $(13\bar{1})$, relative transmission factors 0·3926 to 0·9024. Structure solution and refinement: solved by automatic direct methods and difference Fourier syntheses using *SHELX*76 (Sheldrick, 1976); full-matrix refinement on *F*; $w^{-1} = \sigma^2(F) + 0{\cdot}0003F^2$; 2628 unique reflections with $F > 6\sigma(F)$; phenyl groups as rigid hexagons with C—C 1·395, C—H 0·95 Å on external C—C—C angle bisectors; anisotropic thermal parameters for Pt, W, S, P and O atoms; scattering factors from *International Tables for X-ray Crystallography* (1974); 196 parameters, $R = 0{\cdot}046$, $wR = 0{\cdot}042$, $(\Delta/\sigma)_{max} = 0{\cdot}02$; largest peak in final difference map 0·84 e Å^{-3} [associated with W—C(4)]; no correction for secondary extinction.

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Table 1. *Atomic positional* ($\times 10^4$) *and thermal parameters*

Estimated standard deviations are given in parentheses and correspond to the least significant digit(s). Positional parameters are given as fractional coordinates; U values are in Å^2. $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq} or U_{iso}
Pt	1725 (1)	1464 (1)	7713 (1)	0·037 (1)
W	−2078 (1)	1081 (1)	7128 (1)	0·054 (1)
S(1)	644 (3)	1357 (3)	6706 (2)	0·049 (3)
S(2)	−590 (3)	1360 (4)	7944 (3)	0·060 (4)
P(1)	3170 (3)	1383 (3)	7318 (3)	0·040 (3)
P(2)	2024 (4)	1582 (4)	8910 (3)	0·051 (3)
O(2)	−2325 (12)	−758 (12)	7843 (11)	0·141 (17)
O(3)	−3055 (12)	2089 (14)	8318 (9)	0·131 (16)
O(4)	−1058 (10)	94 (10)	5969 (8)	0·091 (12)
O(5)	−3982 (11)	627 (11)	6269 (9)	0·095 (13)
O(6)	−1867 (13)	2857 (11)	6279 (9)	0·110 (14)
C(1)	329 (12)	1406 (13)	7546 (10)	0·052 (5)
C(2)	−2198 (16)	−84 (17)	7607 (12)	0·077 (7)
C(3)	−2692 (15)	1713 (15)	7900 (12)	0·068 (7)
C(4)	−1415 (14)	466 (14)	6398 (12)	0·063 (7)
C(5)	−3272 (15)	810 (13)	6573 (11)	0·060 (6)
C(6)	−1931 (15)	2255 (16)	6587 (12)	0·066 (7)
C(111)	3927 (8)	2324 (7)	7421 (6)	0·037 (5)
C(112)	4741 (8)	2359 (7)	7100 (6)	0·065 (6)
C(113)	5278 (8)	3120 (7)	7152 (6)	0·067 (6)
C(114)	5001 (8)	3844 (7)	7525 (6)	0·079 (7)
C(115)	4187 (8)	3808 (7)	7846 (6)	0·071 (7)
C(116)	3650 (8)	3048 (7)	7795 (6)	0·046 (5)
C(121)	3812 (8)	427 (7)	7684 (7)	0·036 (5)
C(122)	4772 (8)	422 (7)	7834 (7)	0·079 (7)
C(123)	5222 (8)	−321 (7)	8133 (7)	0·096 (8)
C(124)	4712 (8)	−1060 (7)	8282 (7)	0·080 (7)
C(125)	3752 (8)	−1055 (7)	8131 (7)	0·077 (7)
C(126)	3302 (8)	−312 (7)	7832 (7)	0·056 (6)
C(131)	3033 (9)	1219 (7)	6361 (7)	0·047 (5)
C(132)	2787 (9)	1949 (7)	5935 (7)	0·071 (7)
C(133)	2601 (9)	1853 (7)	5198 (7)	0·085 (7)
C(134)	2661 (9)	1028 (7)	4888 (7)	0·087 (7)
C(135)	2906 (9)	299 (7)	5314 (7)	0·096 (8)
C(136)	3092 (9)	394 (7)	6051 (7)	0·075 (7)
C(211)	1841 (9)	572 (10)	9385 (8)	0·063 (6)
C(212)	2272 (9)	420 (10)	10072 (8)	0·117 (10)
C(213)	2041 (9)	−319 (10)	10449 (8)	0·143 (12)
C(214)	1379 (9)	−906 (10)	10139 (8)	0·105 (9)
C(215)	947 (9)	−755 (10)	9452 (8)	0·097 (8)
C(216)	1178 (9)	−16 (10)	9075 (8)	0·078 (7)
C(221)	3145 (10)	1969 (9)	9303 (7)	0·071 (7)
C(222)	3299 (10)	2832 (9)	9532 (7)	0·068 (6)
C(223)	4191 (10)	3110 (9)	9778 (7)	0·112 (9)
C(224)	4929 (10)	2525 (9)	9795 (7)	0·132 (11)
C(225)	4776 (10)	1662 (9)	9566 (7)	0·141 (11)
C(226)	3883 (10)	1384 (9)	9320 (7)	0·098 (8)
C(231)	1239 (9)	2379 (9)	9223 (6)	0·045 (5)
C(232)	930 (9)	3061 (9)	8764 (6)	0·074 (7)
C(233)	312 (9)	3681 (9)	8975 (6)	0·104 (9)
C(234)	2 (9)	3618 (9)	9645 (6)	0·104 (9)
C(235)	311 (9)	2936 (9)	10103 (6)	0·110 (9)
C(236)	930 (9)	2316 (9)	9892 (6)	0·086 (8)

Table 2. *Selected bond distances* (Å) *and bond angles* (°)

Pt–P(1)	2·317 (5)	W–S(2)	2·546 (5)
Pt–P(2)	2·262 (5)	W–C(2)	2·01 (3)
Pt–S(1)	2·330 (5)	W–C(3)	2·04 (2)
Pt–C(1)	2·02 (2)	W–C(4)	2·01 (2)
C(1)–S(1)	1·70 (2)	W–C(5)	1·97 (2)
C(1)–S(2)	1·61 (2)	W–C(6)	2·01 (2)
P(1)–Pt–P(2)	104·4 (2)	S(2)–W–C(2)	89·3 (7)
P(1)–Pt–S(1)	106·7 (2)	S(2)–W–C(3)	84·3 (6)
P(2)–Pt–C(1)	103·5 (5)	S(2)–W–C(4)	92·9 (6)
S(1)–Pt–C(1)	45·4 (5)	S(2)–W–C(5)	174·7 (6)
S(1)–C(1)–S(2)	139·5 (12)	S(2)–W–C(6)	91·5 (6)
C(1)–S(2)–W	114·8 (7)		

Discussion. Final atomic coordinates are in Table 1, and bond distances and bond angles in Table 2.* A perspective view of the molecule is presented in Fig. 1. The complex (1) consists of a $(Ph_3P)_2Pt(\eta^2\text{-}CS_2)$ fragment in which the CS_2 ligand is π-bonded through a C=S linkage to the Pt atom, with the second, *exo*-S atom σ-bonded to the W atom. The Pt—W non-bonded distance is 5·55 (1) Å. The angles subtended at the Pt atom are consistent with a highly distorted square-planar coordination geometry and the largest deviation of a least-squares plane containing Pt, P(1), P(2), S(1) and C(1) is 0·09 (2) Å [C(1)]. The W atom is hexacoordinate, bonding to the σ-S(2) atom and five CO ligands with only slight distortions from the normal octahedral geometry. The dihedral angle between a least-squares plane containing the W, S(2), C(3), C(4) and C(5) atoms and the Pt square plane is 23·9 (10)°.

Interestingly the $(Ph_3P)_2Pt(\eta^2\text{-}CS_2)$ dimensions (Mason & Rae, 1970) are essentially unperturbed upon coordination of the $W(CO)_5$ fragment. The Pt—C(1) and Pt—S(1) distances in (1), 2·02 (2) and 2·330 (5) Å respectively, are equivalent to those found in the monomer $(Ph_3P)_2Pt(\eta^2\text{-}CS_2)$, 2·06 (5) and 2·328 (16) Å. The two C—S bond lengths, 1·70 (2) and 1·61 (2) Å, are just significantly different but do not differ statistically from the values reported for the monomer CS_2 complex, 1·72 (5) and 1·54 (5) Å. An S—C—S angle of 139·5 (12)° is also normal.

All other dimensions are within typical ranges with the average P—C(α) and C—O distances and W—C—O angle being 1·81 (1) Å, 1·14 (1) Å and 176·9 (6)° respectively.

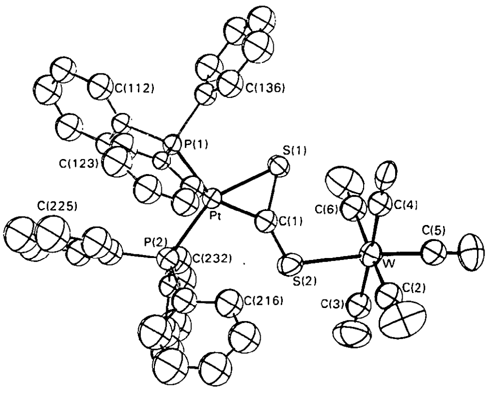

Fig. 1. *ORTEP* drawing (Johnson, 1965) of (1) plotted as 50% probability thermal ellipsoids, with H atoms omitted.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42350 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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References

BROADHURST, P. V., JOHNSON, B. F. G., LEWIS, J. & RAITHBY, P. R. (1980). *J. Chem. Soc. Chem. Commun.* pp. 812–813.

FARRAR, D. H., GUKATHASAN, R. R. & MORRIS, S. A. (1984). *Inorg. Chem.* **23**, 3258–3261.

FARRAR, D. H., GUKATHASAN, R. R. & WON, K. (1984). *J. Organomet. Chem.* **275**, 263–271.

FEHLHAMMER, W. P., MAYR, A. & STOLZENBERG, H. (1979). *Angew. Chem. Int. Ed. Engl.* **18**, 626–627.

FEHLHAMMER, W. P. & STOLZENBERG, H. (1980). *Inorg. Chim. Acta*, **44**, L151–L152.

HAWLING, W. M., WALKER, A. & WOITZIK, M. A. (1983). *J. Chem. Soc. Chem. Commun.* pp. 11–12.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MASON, R. & RAE, A. I. M. (1970). *J. Chem. Soc. A*, pp. 1767–1770.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

WERNER, H. & LEONHARD, K. (1979). *Angew. Chem. Int. Ed. Engl.* **18**, 627–628.

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Structure of Dinitratodioxobis(triisobutyl phosphate)uranium(VI) at 139 K*

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Abstract. $[\mathrm{UO_2(NO_3)_2(C_{12}H_{27}O_4P)_2}]$, $M_r = 926{\cdot}64$, triclinic, $P\bar{1}$, $a = 8{\cdot}54\,(1)$, $b = 10{\cdot}298\,(2)$, $c = 11{\cdot}501\,(6)$ Å, $\alpha = 98{\cdot}15\,(3)$, $\beta = 106{\cdot}38\,(7)$, $\gamma = 101{\cdot}86\,(4)°$, $V = 928{\cdot}0$ Å^3, $Z = 1$, $D_x = 1{\cdot}66$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha_1) = 0{\cdot}70926$ Å, $\mu = 39{\cdot}2$ cm^{-1}, $F(000) = 462$, $T = 139$ K, final $R(F) = 0{\cdot}022$ for 2419 reflections. Crystals are composed of discrete centrosymmetric molecules containing a linear uranyl ion equatorially coordinated by two bidentate nitrate ions and two monodentate triisobutyl phosphate molecules. The U=O bond length is 1·758 (3) Å and has a Zachariasen bond strength of 2. Equatorial U—O lengths are 2·371 (4) Å to phosphate and 2·508 (4) and 2·511 (4) Å to nitrato O atoms. All other bond lengths and angles are also within the normal range.

Introduction. Organophosphorus compounds are widely used to extract $\mathrm{U^{VI}}$ from solution in strong acids (Sekine & Hasegawa, 1977), and it is of interest to know the structures of the extraction complexes formed (Burns, 1981, 1983). The most frequently employed neutral extractant, tri-*n*-butyl phosphate (tbp), forms a complex $\mathrm{UO_2(tbp)_2(NO_3)_2}$ that is a liquid at room temperature (Healy & McKay, 1956). However, the analog with triisobutyl phosphate (tibp) crystallizes readily; so we determined its structure because it provides essentially the same chemical information. In spite of its crystallinity at 300 K, there are very large thermal motions of the molecules and a suitably refined structure was obtained only by cooling the crystals to low temperature.

Experimental. Crystals prepared by reacting tibp and $\mathrm{UO_2(NO_3)_2.6H_2O}$ at 343 K and removal of the free $\mathrm{H_2O}$ by vacuum desiccation. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, Mo $K\alpha$ radiation. Isotherm $\mathrm{N_2}$ boil-off cold-stream device for cooling to 139 K. Unit-cell dimensions determined from least-squares refinement using setting angles of 25 reflections in range 35–45° (2θ). Absorption corrections were determined from data of a reflection with χ near 90° whose absorption was measured as a function of φ (Furnas, 1957), plus a superimposed spherical correction based on a radius of 0·15 mm; transmissions ranged from 0·286 to 0·456. Intensities of reflections with $0 \le h \le 9$, $-11 \le k \le 10$, and $-12 \le l \le 11$ were measured to $\sin\theta/\lambda = 0{\cdot}54$ Å^{-1}; all 2419 were observable at the level $I > 2\sigma(I)$. Standard reflection every 2 h varied less than 2%. Structure determined by heavy-

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