C(19)	0.3667 (3)	0.2776 (3)	0.4355 (3)	0.046 (1)
C(20)	0.4413 (4)	0.3766 (3)	0.4050 (3)	0.061 (2)
C(21)	0.5735 (4)	0.3754 (3)	0.4254 (3)	0.065 (2)
C(22)	0.6277 (4)	0.2734 (3)	0.4781 (3)	0.057 (2)
C(23)	0.5578 (5)	0.1748 (3)	0.5080 (3)	0.070 (2)
C(24)	0.4281 (4)	0.1758 (3)	0.4866 (3)	0.062 (2)
C(25)†	0.2293 (6)	0.5477 (6)	0.1891 (9)	0.062 (2)
C(26)†	0.1847 (6)	0.4996 (6)	0.1090 (9)	0.059 (2)
C(27)†	0.0388 (6)	0.4676 (6)	0.1693 (9)	0.065 (2)
C(28)†	−0.0067 (6)	0.4959 (6)	0.2865 (9)	0.073 (2)
C(29)†	0.1110 (6)	0.5454 (6)	0.2988 (9)	0.067 (3)
C(25′)†	0.2229 (5)	0.5351 (7)	0.1447 (8)	0.070 (2)
C(26′)†	0.1171 (5)	0.4826 (7)	0.1190 (8)	0.056 (2)
C(27′)†	−0.0073 (5)	0.4685 (7)	0.2240 (8)	0.057 (2)
C(28′)†	0.0216 (5)	0.5122 (7)	0.3147 (8)	0.061 (2)
C(29′)†	0.1639 (5)	0.5534 (7)	0.2657 (8)	0.058 (2)

† Site occupancy of 0.5.

Table 2. *Selected geometric parameters (Å, °) in (1) and a comparison with those of related compounds (2) and (3)*

	(1)	(2)	(3)
Cp—Ni*	1.763 (1)	1.748 (4)	1.748 (4)
Ni—P	2.144 (1)	2.139 (1)	2.136 (1)
Ni—S	2.190 (1)	2.192 (1)	
Cp—Ni—S	132.3 (1)	133.0 (4)	
Cp—Ni—Se			132.3 (2)
Cp—Ni—P	135.3 (5)	136.4 (5)	136.4 (5)
P—Ni—S	92.4 (1)	90.5 (1)	
P—Ni—Se			91.4 (1)

Other selected geometric parameters in (1)

Ni—C(25)	2.146 (6)	Ni—C(26)	2.103 (9)
Ni—C(27)	2.107 (8)	Ni—C(28)	2.153 (5)
Ni—C(29)	2.177 (7)	Ni—C(25′)	2.142 (7)
Ni—C(26′)	2.130 (8)	Ni—C(27′)	2.139 (6)
Ni—C(28′)	2.157 (7)	Ni—C(29′)	2.159 (8)
P—C(1)	1.832 (3)	P—C(7)	1.831 (3)
P—C(13)	1.831 (3)	S—C(19)	1.764 (4)
Cl—C(22)	1.753 (4)		
Ni—P—C(7)	112.0 (1)	Ni—P—C(13)	113.0 (1)
C(1)—P—C(7)	107.0 (1)	Ni—S—C(19)	111.5 (1)
C(1)—P—C(13)	100.6 (1)	C(7)—P—C(13)	104.5 (1)
Ni—P—C(1)	118.3 (1)		

* *Cp* represents the centroid of the cyclopentadienyl group.

In the refinement, the five C atoms of each cyclopentadienyl group were treated as a rigid body, with isotropic atomic displacement parameters and no H atoms attached.

Data collection: *SHELXTL-Plus* (Sheldrick, 1990). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

This work was supported by a grant to JD from the International Foundation for Science (grant No. F/1954-1).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1150). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bruce, M. I., Cifuentes, M. P., Snow, M. R. & Tiekink, E. R. T. (1989). *J. Organomet. Chem.* **359**, 379–399.

Darkwa, J. (1994). *Organometallics*, **13**, 3743–3745.

Darkwa, J., Bothata, F. & Koczon, L. M. (1993). *J. Organomet. Chem.* **455**, 235–240.

Davies, S. G., McNally, J. P. & Smallbridge, A. J. (1990). *Adv. Organomet. Chem.* **30**, 1–70.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *SHELXTL-Plus. Structure Determination Software Programs.* Release 4.21/V. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1996). **C52**, 2161–2164

An $Mo_2(CO)_4$ (Mo≡Mo) Fragment Stabilized by a Tripod Ligand

Regine Herbst-Irmer[a] and Ernst Egert[b]

[a]*Institut für Anorganische Chemie, Universität Göttingen, Tammannstraße 4, D-37077 Göttingen, Germany, and* [b]*Institut für Organische Chemie, Universität Frankfurt, Marie-Curie-Straße 11, D-60439 Frankfurt am Main, Germany*

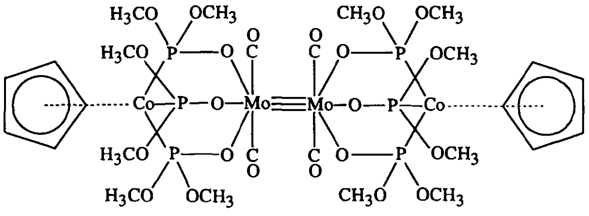
(*Received 3 January 1996; accepted 22 March 1996*)

Abstract

Tetracarbonyl-1κ^2C;2κ^2C-bis[3,4(η^5)-cyclopentadienyl]-hexakis-μ-dimethylphosphito-1:3$\kappa^6O{:}P$;2:4$\kappa^6O{:}P$-dicobaltdimolybdenum(I)(*Mo*—*Mo*), $[Mo(CO)_2\{Co(C_5H_5)(C_2H_6O_3P)_3\}]_2$, a binuclear metal complex of type $L_2Mo_2(CO)_4$ (L is a tripod ligand), shows central Mo≡Mo triple bond lengths of 2.467 (1) and 2.468 (1) Å in the two independent molecules. The structure agrees very well with that of a related tungsten complex. The coordination of the central Mo atoms is distorted octahedral with acute Mo—Mo—C angles. All twelve Mo—O—P—Co fragments are synperiplanar, with Co—P bond lengths ranging from 2.152 (2) to 2.171 (1) Å.

Comment

The (η^5-cyclopentadienyl)tris(dimethylphosphito)cobaltate(1−) anion, which is itself a half-sandwich complex, has a strong tendency to act as an *O*,*O*,*O*-tripod ligand using its three P═O groups and forms stable complexes with many metal ions (Kläui, 1990). Its structure has been studied thoroughly, for example, by crystal structure analysis of its Na and Cs salts (Kläui, Matt, Balegroune & Grandjean, 1991; Englert, Kläui & Weber-Schuster, 1992). We have determined the structure of a binuclear Mo complex, (I), in which two $LMo(CO)_2$ fragments [$L = Co(C_5H_5)(C_2H_6O_3P)_3$] are connected by an Mo≡Mo triple bond.



(I)

The two molecules contained in the asymmetric unit show approximate translation symmetry with $\Delta x \approx 1/2$, $\Delta y \approx 1/4$ and $\Delta z \approx 1/2$. Their structures agree well with that of a very similar $L_2W_2(CO)_4$ complex, with ethoxy instead of methoxy groups, which has been discussed in great detail previously (Kläui, Müller, Herbst & Egert, 1987). The W≡W distance of 2.503 (1) Å in that complex is slightly longer than the Mo≡Mo distances of 2.467 (1) and 2.468 (1) Å in the title compound. The coordination of the central Mo atoms is distorted octahedral with acute Mo—Mo—C angles and each of the three O-atom donors of the tripod ligands is approximately *trans* with respect to the carbonyl ligands and the second Mo atom. The orientation of the carbonyl ligands, which are antiperiplanar with respect to one another, deviates by more than 20° from the ideal 180° torsion angle for the C—Mo—Mo—C fragment. The Mo—O—P—Co fragment, which altogether appears twelve times in the two independent molecules, is always synperiplanar, with a maximum deviation of 11.7 (3)° of the respective torsion angle from the ideal 0° value; the Co—P bond lengths range from 2.152 (2) to 2.171 (1) Å.

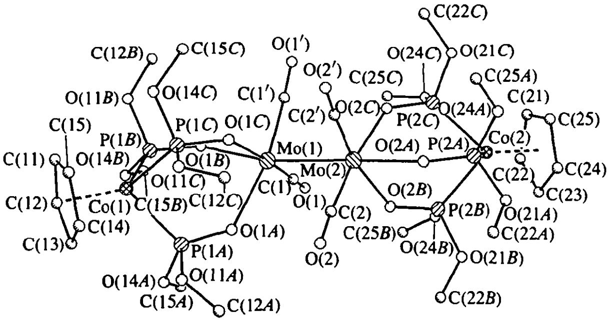


Fig. 1. The structure of molecule 1 of (I) with the atom-numbering scheme. H atoms have been omitted.

Experimental

Crystals of (I) were provided by Professor W. Kläui (Technische Hochschule Aachen, now at the University of Düsseldorf, Germany).

Crystal data

$[Mo(CO)_2\{Co(C_5H_5)(C_2H_6O_3P)_3\}]_2$
$M_r = 1206.2$
Monoclinic
$P2_1/c$
$a = 13.651 (1)$ Å
$b = 23.910 (3)$ Å
$c = 27.883 (2)$ Å
$\beta = 102.44 (1)°$
$V = 8887.2$ Å^3
$Z = 8$
$D_x = 1.803$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10–12.5°$
$\mu = 1.56$ mm^{-1}
$T = 293$ K
Block
0.7 × 0.6 × 0.5 mm
Dark red

Data collection

Stoe–Siemens four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Sheldrick, 1990)
$T_{min} = 0.687$, $T_{max} = 1.000$
16 610 measured reflections
15 775 independent reflections

12 743 observed reflections $[F > 4\sigma(F)]$
$R_{int} = 0.040$
$\theta_{max} = 25°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 28$
$l = -1 \rightarrow 33$
3 standard reflections monitored every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.042$
$wR = 0.049$
$S = 2.08$
12 743 reflections
1009 parameters
H atoms riding, C—H = 0.96 Å
$w = 1/[\sigma^2(F) + 0.0002F^2]$

$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.97$ e Å^{-3}
$\Delta\rho_{min} = -0.78$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Molecule 1				
Mo(1)	0.45701 (3)	0.76080 (1)	0.19896 (1)	0.029 (1)
C(1)	0.5977 (3)	0.7795 (2)	0.2094 (1)	0.041 (1)
O(1)	0.6802 (3)	0.7942 (2)	0.2133 (1)	0.068 (1)
C(1′)	0.4521 (3)	0.8281 (2)	0.2374 (2)	0.043 (1)
O(1′)	0.4508 (3)	0.8706 (2)	0.2576 (1)	0.076 (2)
O(1*A*)	0.4536 (2)	0.7002 (1)	0.1406 (1)	0.044 (1)
P(1*A*)	0.3888 (1)	0.6908 (1)	0.0905 (1)	0.056 (1)
O(11*A*)	0.3447 (4)	0.6280 (2)	0.0874 (2)	0.144 (2)
C(12*A*)	0.3883 (5)	0.5830 (3)	0.1115 (2)	0.085 (3)
O(14*A*)	0.4574 (3)	0.6858 (3)	0.0533 (2)	0.179 (3)
C(15*A*)	0.5518 (6)	0.7071 (3)	0.0581 (3)	0.107 (3)
O(1*B*)	0.4250 (2)	0.8181 (1)	0.1356 (1)	0.042 (1)
P(1*B*)	0.3495 (1)	0.8179 (1)	0.0877 (1)	0.038 (1)
O(11*B*)	0.2776 (3)	0.8704 (1)	0.0867 (1)	0.069 (1)
C(12*B*)	0.2867 (5)	0.9102 (3)	0.1235 (2)	0.087 (3)
O(14*B*)	0.4080 (3)	0.8332 (2)	0.0453 (1)	0.070 (1)
C(15*B*)	0.4957 (4)	0.8659 (3)	0.0556 (2)	0.076 (2)
O(1*C*)	0.2978 (2)	0.7449 (1)	0.1794 (1)	0.043 (1)
P(1*C*)	0.2186 (1)	0.7393 (1)	0.1335 (1)	0.040 (1)
O(11*C*)	0.1594 (3)	0.6835 (2)	0.1362 (1)	0.097 (2)
C(12*C*)	0.1761 (5)	0.6458 (3)	0.1758 (2)	0.088 (2)
O(14*C*)	0.1350 (3)	0.7851 (2)	0.1337 (1)	0.078 (2)
C(15*C*)	0.1067 (5)	0.8021 (3)	0.1779 (2)	0.098 (3)

Co(1)	0.26129 (4)	0.74434 (2)	0.06323 (2)	0.035 (1)
C(11)	0.1515 (3)	0.7843 (2)	0.0095 (1)	0.068 (2)
C(12)	0.2317	0.7666	−0.0119	0.072 (2)
C(13)	0.2407	0.7076	−0.0065	0.097 (3)
C(14)	0.1660	0.6889	0.0183	0.114 (3)
C(15)	0.1109	0.7364	0.0281	0.097 (3)
Mo(2)	0.53266 (3)	0.72868 (1)	0.28286 (1)	0.028 (1)
C(2)	0.4846 (3)	0.6620 (2)	0.2458 (1)	0.038 (1)
O(2)	0.4551 (3)	0.6199 (1)	0.2271 (1)	0.058 (1)
C(2′)	0.3909 (3)	0.7385 (2)	0.2861 (2)	0.040 (1)
O(2′)	0.3096 (3)	0.7414 (2)	0.2912 (1)	0.062 (1)
O(2*A*)	0.5424 (2)	0.6800 (1)	0.3508 (1)	0.042 (1)
P(2*A*)	0.6134 (1)	0.6795 (1)	0.3999 (1)	0.053 (1)
O(21*A*)	0.6430 (4)	0.6163 (2)	0.4130 (2)	0.151 (2)
C(22*A*)	0.5954 (5)	0.5703 (3)	0.3903 (2)	0.087 (3)
O(24*A*)	0.5526 (3)	0.6925 (4)	0.4398 (2)	0.179 (4)
C(25*A*)	0.4556 (6)	0.7068 (4)	0.4320 (3)	0.118 (4)
O(2*B*)	0.6903 (2)	0.7084 (1)	0.2961 (1)	0.040 (1)
P(2*B*)	0.7725 (1)	0.7024 (1)	0.3415 (1)	0.044 (1)
O(21*B*)	0.8065 (4)	0.6394 (2)	0.3463 (1)	0.121 (2)
C(22*B*)	0.7921 (5)	0.5993 (3)	0.3107 (2)	0.081 (2)
O(24*B*)	0.8693 (3)	0.7329 (3)	0.3326 (2)	0.128 (3)
C(25*B*)	0.8955 (5)	0.7470 (3)	0.2913 (3)	0.092 (3)
O(2*C*)	0.5908 (2)	0.7958 (1)	0.3322 (1)	0.047 (1)
P(2*C*)	0.6683 (1)	0.8014 (1)	0.3792 (1)	0.051 (1)
O(21*C*)	0.6163 (3)	0.8295 (2)	0.4187 (1)	0.124 (2)
C(22*C*)	0.5344 (5)	0.8652 (3)	0.4075 (3)	0.126 (3)
O(24*C*)	0.7447 (4)	0.8475 (2)	0.3721 (2)	0.131 (2)
C(25*C*)	0.7443 (6)	0.8802 (3)	0.3323 (3)	0.136 (4)
Co(2)	0.74842 (5)	0.72878 (3)	0.41240 (2)	0.039 (1)
C(21)	0.8264 (3)	0.7787 (1)	0.4679 (2)	0.100 (3)
C(22)	0.8956	0.7535	0.4431	0.075 (2)
C(23)	0.8880	0.6946	0.4475	0.069 (2)
C(24)	0.8141	0.6834	0.4751	0.077 (2)
C(25)	0.7760	0.7354	0.4877	0.105 (4)
Molecule 2				
Mo(3)	1.03973 (3)	0.48319 (1)	0.79301 (1)	0.028 (1)
C(3)	0.9907 (3)	0.4157 (2)	0.7577 (1)	0.037 (1)
O(3)	0.9605 (3)	0.3732 (1)	0.7402 (1)	0.059 (1)
C(3′)	0.8990 (3)	0.4932 (2)	0.7962 (1)	0.039 (1)
O(3′)	0.8168 (3)	0.4958 (2)	0.8008 (1)	0.058 (1)
O(3*A*)	1.0479 (2)	0.4355 (1)	0.8619 (1)	0.042 (1)
P(3*A*)	1.1167 (1)	0.4362 (1)	0.9113 (1)	0.051 (1)
O(31*A*)	1.0553 (3)	0.4572 (3)	0.9504 (2)	0.140 (3)
C(32*A*)	0.9549 (5)	0.4507 (4)	0.9456 (3)	0.126 (4)
O(34*A*)	1.1371 (4)	0.3742 (2)	0.9285 (2)	0.145 (2)
C(35*A*)	1.1084 (5)	0.3263 (3)	0.9005 (2)	0.089 (3)
O(3*B*)	1.1976 (2)	0.4621 (1)	0.8071 (1)	0.042 (1)
P(3*B*)	1.2784 (1)	0.4560 (1)	0.8527 (1)	0.046 (1)
O(31*B*)	1.3083 (3)	0.3915 (2)	0.8594 (1)	0.105 (2)
C(32*B*)	1.3030 (5)	0.3538 (2)	0.8211 (2)	0.078 (2)
O(34*B*)	1.3771 (3)	0.4831 (3)	0.8436 (1)	0.129 (3)
C(35*B*)	1.3998 (5)	0.5045 (3)	0.8032 (2)	0.089 (3)
O(3*C*)	1.1000 (2)	0.5506 (1)	0.8416 (1)	0.049 (1)
P(3*C*)	1.1749 (1)	0.5564 (1)	0.8891 (1)	0.055 (1)
O(31*C*)	1.1211 (4)	0.5861 (2)	0.9269 (2)	0.123 (2)
C(32*C*)	1.0292 (5)	0.6133 (4)	0.9145 (3)	0.134 (4)
O(34*C*)	1.2546 (4)	0.6018 (2)	0.8828 (2)	0.132 (2)
C(35*C*)	1.2451 (6)	0.6400 (3)	0.8452 (3)	0.141 (4)
Co(3)	1.25373 (5)	0.48367 (3)	0.92333 (2)	0.043 (1)
C(31)	1.4014 (3)	0.5083 (2)	0.9547 (1)	0.089 (3)
C(32)	1.3928	0.4494	0.9589	0.077 (2)
C(33)	1.3187	0.4384	0.9864	0.085 (2)
C(34)	1.2814	0.4904	0.9992	0.115 (4)
C(35)	1.3325	0.5337	0.9796	0.115 (3)
Mo(4)	0.96314 (3)	0.51454 (1)	0.70897 (1)	0.027 (1)
C(4)	1.1045 (3)	0.5317 (2)	0.7181 (1)	0.039 (1)
O(4)	1.1872 (3)	0.5464 (2)	0.7205 (1)	0.066 (1)
C(4′)	0.9637 (4)	0.5840 (2)	0.7461 (2)	0.046 (2)
O(4′)	0.9664 (3)	0.6269 (2)	0.7654 (1)	0.080 (2)
O(4*A*)	0.9339 (2)	0.5695 (1)	0.6433 (1)	0.042 (1)
P(4*A*)	0.8601 (1)	0.5671 (1)	0.5948 (1)	0.034 (1)
O(41*A*)	0.9207 (2)	0.5745 (1)	0.5518 (1)	0.052 (1)
C(42*A*)	1.0035 (4)	0.6134 (2)	0.5588 (2)	0.070 (2)
O(44*A*)	0.7968 (3)	0.6237 (1)	0.5883 (1)	0.062 (1)
C(45*A*)	0.7893 (5)	0.6600 (3)	0.6269 (2)	0.087 (3)
O(4*B*)	0.9548 (2)	0.4501 (1)	0.6535 (1)	0.041 (1)
P(4*B*)	0.8874 (1)	0.4382 (1)	0.6044 (1)	0.037 (1)
O(41*B*)	0.8380 (3)	0.3776 (1)	0.6043 (1)	0.057 (1)
C(42*B*)	0.8947 (4)	0.3308 (2)	0.6270 (2)	0.068 (2)
O(44*B*)	0.9591 (3)	0.4264 (2)	0.5673 (1)	0.062 (1)
C(45*B*)	1.0495 (4)	0.4571 (3)	0.5702 (2)	0.073 (2)
O(4*C*)	0.8031 (2)	0.5024 (1)	0.6908 (1)	0.043 (1)
P(4*C*)	0.7225 (1)	0.4963 (1)	0.6452 (1)	0.034 (1)
O(41*C*)	0.6568 (3)	0.4436 (2)	0.6512 (1)	0.065 (1)
C(42*C*)	0.6844 (5)	0.4023 (3)	0.6877 (2)	0.087 (3)
O(44*C*)	0.6422 (2)	0.5451 (2)	0.6429 (1)	0.061 (1)
C(45*C*)	0.6062 (4)	0.5601 (3)	0.6859 (2)	0.083 (2)
Co(4)	0.76538 (4)	0.49483 (2)	0.57477 (2)	0.032 (1)
C(41)	0.7430 (2)	0.5045 (2)	0.4991 (1)	0.074 (2)
C(42)	0.6689	0.5352	0.5167	0.060 (2)
C(43)	0.6135	0.4970	0.5394	0.066 (2)
C(44)	0.6533	0.4426	0.5358	0.077 (2)
C(45)	0.7333	0.4473	0.5109	0.090 (2)

Table 2. *Selected geometric parameters (Å, °)*

Molecule 1		Molecule 2	
Mo(1)—Mo(2)	2.467 (1)	Mo(3)—Mo(4)	2.468 (1)
Mo(1)—C(1)	1.932 (4)	Mo(3)—C(3)	1.933 (4)
Mo(1)—C(1′)	1.943 (4)	Mo(3)—C(3′)	1.956 (5)
Mo(2)—C(2)	1.936 (4)	Mo(4)—C(4)	1.935 (4)
Mo(2)—C(2′)	1.970 (5)	Mo(4)—C(4′)	1.956 (5)
Mo(1)—O(1*A*)	2.172 (3)	Mo(3)—O(3*A*)	2.217 (3)
Mo(1)—O(1*B*)	2.203 (3)	Mo(3)—O(3*B*)	2.165 (3)
Mo(1)—O(1*C*)	2.157 (3)	Mo(3)—O(3*C*)	2.153 (3)
Mo(2)—O(2*A*)	2.204 (3)	Mo(4)—O(4*A*)	2.220 (3)
Mo(2)—O(2*B*)	2.159 (3)	Mo(4)—O(4*B*)	2.167 (3)
Mo(2)—O(2*C*)	2.151 (3)	Mo(4)—O(4*C*)	2.154 (3)
Co(1)—P(1*A*)	2.162 (1)	Co(3)—P(3*A*)	2.153 (2)
Co(1)—P(1*B*)	2.158 (1)	Co(3)—P(3*B*)	2.171 (1)
Co(1)—P(1*C*)	2.165 (1)	Co(3)—P(3*C*)	2.156 (1)
Co(2)—P(2*A*)	2.152 (2)	Co(4)—P(4*A*)	2.159 (1)
Co(2)—P(2*B*)	2.167 (1)	Co(4)—P(4*B*)	2.168 (1)
Co(2)—P(2*C*)	2.153 (1)	Co(4)—P(4*C*)	2.167 (1)
Mo(2)—Mo(1)—C(1)	74.3 (1)	Mo(4)—Mo(3)—C(3)	75.0 (1)
Mo(2)—Mo(1)—C(1′)	78.0 (1)	Mo(4)—Mo(3)—C(3′)	77.7 (1)
Mo(1)—Mo(2)—C(2)	74.1 (1)	Mo(3)—Mo(4)—C(4)	74.5 (1)
Mo(1)—Mo(2)—C(2′)	78.0 (1)	Mo(3)—Mo(4)—C(4′)	78.6 (1)
Mo(1)—O(1*A*)—P(1*A*)	135.3 (2)	Mo(3)—O(3*A*)—P(3*A*)	134.4 (2)
Mo(1)—O(1*B*)—P(1*B*)	133.7 (2)	Mo(3)—O(3*B*)—P(3*B*)	134.3 (2)
Mo(1)—O(1*C*)—P(1*C*)	137.5 (2)	Mo(3)—O(3*C*)—P(3*C*)	136.3 (2)
Mo(2)—O(2*A*)—P(2*A*)	134.3 (2)	Mo(4)—O(4*A*)—P(4*A*)	133.3 (2)
Mo(2)—O(2*B*)—P(2*B*)	134.4 (2)	Mo(4)—O(4*B*)—P(4*B*)	135.5 (2)
Mo(2)—O(2*C*)—P(2*C*)	135.9 (2)	Mo(4)—O(4*C*)—P(4*C*)	137.3 (2)
P(1*A*)—Co(1)—P(1*B*)	91.1 (1)	P(3*A*)—Co(3)—P(3*B*)	89.8 (1)
P(1*A*)—Co(1)—P(1*C*)	90.1 (1)	P(3*A*)—Co(3)—P(3*C*)	91.3 (1)
P(1*B*)—Co(1)—P(1*C*)	90.0 (1)	P(3*B*)—Co(3)—P(3*C*)	90.3 (1)
P(2*A*)—Co(2)—P(2*B*)	89.2 (1)	P(4*A*)—Co(4)—P(4*B*)	91.9 (1)
P(2*A*)—Co(2)—P(2*C*)	92.0 (1)	P(4*A*)—Co(4)—P(4*C*)	90.9 (1)
P(2*B*)—Co(2)—P(2*C*)	90.3 (1)	P(4*B*)—Co(4)—P(4*C*)	90.0 (1)

Molecule 1	
C(1)—Mo(1)—Mo(2)—C(2)	−116.2 (2)
C(1)—Mo(1)—Mo(2)—C(2′)	156.5 (2)
C(1′)—Mo(1)—Mo(2)—C(2)	157.9 (2)
C(1′)—Mo(1)—Mo(2)—C(2′)	70.6 (2)
Mo(1)—O(1*A*)—P(1*A*)—Co(1)	−2.0 (3)
Mo(1)—O(1*B*)—P(1*B*)—Co(1)	−11.7 (3)
Mo(1)—O(1*C*)—P(1*C*)—Co(1)	3.0 (3)
Mo(2)—O(2*A*)—P(2*A*)—Co(2)	−7.1 (3)
Mo(2)—O(2*B*)—P(2*B*)—Co(2)	−10.6 (3)
Mo(2)—O(2*C*)—P(2*C*)—Co(2)	−1.3 (4)
Molecule 2	
C(3)—Mo(3)—Mo(4)—C(4)	−115.5 (2)
C(3)—Mo(3)—Mo(4)—C(4′)	159.8 (2)
C(3′)—Mo(3)—Mo(4)—C(4)	157.8 (2)
C(3′)—Mo(3)—Mo(4)—C(4′)	73.1 (2)
Mo(3)—O(3*A*)—P(3*A*)—Co(3)	−9.8 (3)
Mo(3)—O(3*B*)—P(3*B*)—Co(3)	−11.1 (3)
Mo(3)—O(3*C*)—P(3*C*)—Co(3)	1.5 (4)
Mo(4)—O(4*A*)—P(4*A*)—Co(4)	−7.3 (3)
Mo(4)—O(4*B*)—P(4*B*)—Co(4)	1.1 (3)
Mo(4)—O(4*C*)—P(4*C*)—Co(4)	3.4 (3)

The cyclopentadienyl rings were idealized and refined as rigid groups. Some of the methoxy groups, especially the O atoms, have high *U* values.

Data collection: profile-fitting program (Clegg, 1981). Cell refinement: profile-fitting program. Data reduction: *XLS* (Sheldrick, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) using direct methods. Program(s) used to refine structure: *XLS* (Sheldrick, 1987). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXTL-Plus*.

The authors thank Professor W. Kläui (Universität Düsseldorf) for kindly providing the sample.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: JZ1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.

Englert, U., Kläui, W. & Weber-Schuster, A. (1992). *Z. Kristallogr.* **200**, 257–264.

Kläui, W. (1990). *Angew. Chem.* **102**, 661–670.

Kläui, W., Matt, D., Balegroune, F. & Grandjean, D. (1991). *Acta Cryst.* C**47**, 1614–1617.

Kläui, W., Müller, A., Herbst, R. & Egert, E. (1987). *Organometallics*, **6**, 1824–1826.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1987). *XLS*. Expanded Version of *SHELX76*. University of Göttingen, Germany.

Sheldrick, G. M. (1990). *SHELXTL-Plus*. Release 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1996). C**52**, 2164–2166

trans-Diazidobis[1,2-bis(diethylphosphino)-ethane-*P*,*P*′]iron(II)

Leslie D. Field,* Adrian V. George,* Stuart R. Pike, Irmi E. Buys and Trevor W. Hambley

Divisions of Inorganic and Organic Chemistry, University of Sydney, New South Wales, Australia 2006

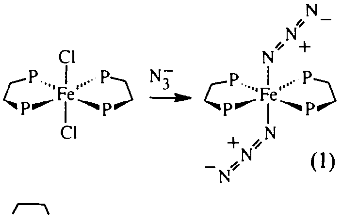
(*Received 8 February 1995; accepted 29 June 1995*)

Abstract

The title structure, $[Fe(N_3)_2(C_{10}H_{24}P_2)_2]$, has been studied and was found to consist of neutral molecules with the Fe atom located at a centre of symmetry. The Fe—P bond lengths [2.258 (1) and 2.268 (1) Å] are indicative of low-spin Fe^{II}. The Fe—N_{azido} distance is 2.008 (4) Å.

Comment

As part of a project investigating the synthesis of iron tetraphosphines having acetylido, azido and nitrile ligands, a series of diazido complexes of the type $[Fe(PP)_2(N_3)_2]$ [where PP is 1,2-bis(dimethylphosphino)ethane (dmpe), 1,2-bis(diethylphosphino)ethane (depe) or 1,2-bis(dipropylphosphino)ethane (dprpe)] were synthesized and their properties examined (Buys, Field, George, Hambley & Pike, 1995). These bis(diazido)–iron(II) complexes can easily be converted to the corresponding iron–bis(acetylide) complexes by reaction with the corresponding acetylene. The title compound, $[Fe(depe)_2(N_3)_2]$, (1), was synthesized by substitution of the chloride in $[FeCl_2(depe)_2]$ with azide in alcohol solution.



(1)

P⌒P = $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$

The crystal structure of (1) (Fig. 1) shows the three N atoms of each azide group to be approximately linear, with an Fe—N—N angle of 139.1 (4)°. This is significantly larger than the corresponding angle found in related structures, for example, 132.3 (3)° for Fe—N—N in $[Fe(dmpe)_2(N_3)_2]$ (Buys, Field, George, Hambley & Pike, 1995), 121.8 (4)° for Fe—N—N in $[Fe(tpp)(N_3)]$ (where tpp is tetraphenylporphyrin) (Zhang, Hallows, Ryan, Jones, Carpenter & Sweigart, 1994), 116.7 (7)° for Ru—N—N in $[Ru(en)_2(N_2)(N_3)]^+$ (Davis & Ibers, 1970), 132.9 (3)° for Ru—N—N in $[Ru(N_3)_2(depe)_2$ (Buys, Field, George, Hambley & Purches, 1995), 125.4 (5)° for Cu—N—N in $[Cu\{Et_2NCH_2CH_2N(H)CH_2CH_2NEt_2\}_2(Br)(N_3)]$ (Ziolo, Allen, Titus, Gray & Dorio, 1972) and 121.4 (6)–129.9 (5)° for Mo—N—N in $[Mo(N_3)_4(NO)(H_2NO)]$ (Weighardt, Backes-Dahmann, Swiridoff & Weiss, 1983). The N—N bond lengths are 1.170 (5) and 1.155 (6) Å for (Fe—)N_1—N_2 and (N—)N_2—N_3, respectively, which compare well with values of 1.179 (5) and 1.162 (5) Å for the corresponding bond lengths in $[Fe(dmpe)_2(N_3)]$ (Buys, Field, George, Hambley & Pike, 1995), and values of 1.180 (5) and 1.170 (5) Å in $[Ru(depe)_2(N_3)_2]$ (Buys, Field, George, Hambley & Purches, 1995). The N—N bond lengths in HN_3 are 1.240 (3) and 1.134 (3) Å (Amkle & Dailey, 1950), and 1.150 (16) Å in N_3^- (Frevel, 1936). The azide groups in (1) are tilted in opposite directions in the crystal.

Acta Crystallographica Section C
ISSN 0108-2701 © 1996