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Structure of *trans*-Dicarbonyl(η^5-cyclopentadienyl)(phenyl)(triphenylphosphine)molybdenum(II), [$Mo(C_5H_5)(C_6H_5)(CO)_2\{P(C_6H_5)_3\}$]

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Abstract. $M_r = 556{\cdot}5$, triclinic, $P\bar{1}$, $a = 9{\cdot}126\ (4)$, $b = 12{\cdot}417\ (4)$, $c = 12{\cdot}666\ (4)$ Å, $\alpha = 112{\cdot}17\ (3)$, $\beta = 100{\cdot}81\ (3)$, $\gamma = 100{\cdot}00\ (3)°$, $V = 1257{\cdot}5\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}470\ (1)$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}535$ mm^{-1}, $F(000) = 558$, $T = 293$ K, $R = 0{\cdot}063$ for 4805 reflections. The title compound was obtained by photolysis of the corresponding stannyl complex as the first example of a photochemical stannylene elimination. Owing to the steric requirements of the bulky PPh_3 group, the cyclopentadienyl ligand is shifted in the direction of the phenyl ligand. The Mo—C(phenyl) distance of 2·334 (3) Å is an intermediate value between those found in Mo—C(alkyl) and Mo—C(acyl) bonds.

Introduction. Contrarily to an early reference of Manning (1968), stannylmolybdenum complexes, $CpMo(CO)_2(L)SnPh_3$ [$L = PPh_3$, $P(OPh)_3$], are easily obtained by thermal (George, 1972) or photochemical (King & Pannell, 1968) substitution of the parent tricarbonyl moieties. Since only *trans* isomers have been reported in all cases, we repeated the photolysis of $CpMo(CO)_3SnPh_3$ in the presence of PPh_3 and found a second product, which could be separated by recrystallization from CH_2Cl_2/*n*-hexane (Kunze & Sastrawan, 1980). Instead of the expected *cis* isomer, it turned out to be the tin-free σ-phenyl molybdenum complex *trans*-$CpMo(CO)_2(Ph)(PPh_3)$ (1), obtained by Nesmeyanov, Makarova & Ustynyuk (1970) according to other routes. This is the first example of a photolytic stannylene elimination from a stannyl transition-metal complex (*cf.* Grugel, Neumann & Seifert, 1977). The photochemical synthesis of (1) gives much better yields (nearly 60%) than the original procedures of Nesmeyanov *et al.* (6–8%) revealing a novel way for the generation of σ-aryl metal complexes. For definite proof, the X-ray structure of (1) has been analysed.

Experimental. Recrystallization of crude product from CH_2Cl_2/*n*-hexane afforded yellow crystals. Buerger precession photographs (prismatic single crystal, 0·5 × 0·4 × 0·3 mm) indicated triclinic symmetry; 25 reflections used for measuring lattice parameters; intensity data collected on an Enraf–Nonius CAD-4 four-circle diffractometer, ω/θ scan mode, $\theta = 3$–$30°$ (h: −12 to 12, k: −17 to 17, l: 0 to 17), graphite monochromator, two standard reflections $\bar{2}3\bar{4}$ and $\bar{1}3\bar{5}$ with constant intensity; 7536 observed reflections, 4805 unique ($R_{\text{int}} = 0{\cdot}02$) with $|F_o| \geq 2\sigma(|F_o|)$ used in structure analysis; corrections for Lorentz and polarization effects but not for absorption or extinction. Positions of Mo and P from Patterson synthesis, other non-hydrogen atoms from electron density maps; refinement (use of F magnitudes) with anisotropic temperature factors for Mo and P and isotropic for C, O and H, cyclopentadienyl and phenyl rings as rigid groups, H-atom positions calculated [d(C—H) = 1·08 Å]; unit weights; max. electron density in final difference map 1·59 e Å^{-3} near Mo atom (min. 0·5 e Å^{-3}), final $R(wR) = 0{\cdot}063\ (0{\cdot}065)$, max. $\Delta/\sigma = 0{\cdot}03$, scattering factors from Cromer & Mann (1968), Cromer & Liberman (1970). Programs: *SHELX*76 (Sheldrick, 1976) and *PLUTO* (Motherwell, 1978), TR440 computer.

Discussion. Final atomic coordinates are listed in Table 1, bond lengths and angles in Table 2.† Fig. 1 shows the numbering of the atoms of the molecule.

Since only few structural data are reported for σ-bonded organomolybdenum compounds, the closest relationship to (1) is shown by the acetyl complex *trans*-$CpMo(CO)_2(PPh_3)C(O)CH_3$ (Churchill & Fennessey, 1968). The geometry around the Mo atom is

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a full list of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39696 (52 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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about the same in both compounds, the acetyl complex showing slightly enlarged C(acyl)—Mo—P and adjacent C(acyl)—Mo—C(carbonyl) angles owing to the stronger repulsion of the acetyl group. The Mo—C distances to the cyclopentadienyl ring in (1) reveal a similar shift from the central ring position probably owing to the steric repulsion of the PPh_3 group. The two Mo—C(carbonyl) distances show a minor difference from those in the acetyl complex, and the Mo—P distances are equal within error limits.

The phenyl ring intersects the $Mo(CO)_2$ plane perpendicularly. The Mo—C(phenyl) distance of (1) [2·334 (3) Å] adopts an intermediate value between Mo—C(alkyl) [2·38 (2) Å: Bennett & Mason, 1963; 2·383 (10) Å: Bird & Churchill, 1968] and Mo—C(acyl) [2·264 (14) Å: Churchill & Fennessey, 1968; 2·22 (2) Å: Jones & Guggenberger, 1975], as expected with regard to the smaller covalent radius of sp^2 *vs* sp^3 carbon ($\Delta \sim 0{\cdot}03$ Å). A considerable $(d\text{–}p)\pi$ back donation is assumed in the case of σ-acyl metal complexes. Somewhat different are the results of Cotton, Koch & Millar (1978), who report very short Mo—C(phenyl) bond lengths in the range 2·146 (9) to 2·195 (9) Å for the dimeric (2,6-dimethoxyphenyl)-molybdenum complex $Mo_2(dmp)_4$.

Table 1. *Atomic coordinates* (×10⁴) *and* (*equivalent*) *isotropic thermal parameters* (Å² × 10³)

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$ for Mo and P.

	x	y	z	U_{eq}/U_{iso}
Mo(1)	2283 (1)	4703·6 (4)	2479·6 (4)	32·7 (2)
P(1)	3309 (2)	6921 (1)	3386 (1)	32 (1)
C(1)	2538 (4)	7774 (3)	2621 (3)	34 (1)
C(2)	3410 (4)	8908 (3)	2824 (3)	46 (1)
C(3)	2780 (4)	9569 (3)	2268 (3)	52 (2)
C(4)	1278 (4)	9095 (3)	1510 (3)	52 (2)
C(5)	406 (4)	7960 (3)	1308 (3)	48 (1)
C(6)	1036 (4)	7299 (3)	1864 (3)	40 (1)
C(7)	3145 (4)	7686 (3)	4892 (3)	37 (1)
C(8)	2600 (4)	8712 (3)	5263 (3)	43 (1)
C(9)	2434 (4)	9209 (3)	6408 (3)	57 (2)
C(10)	2812 (4)	8681 (3)	7181 (3)	58 (2)
C(11)	3356 (4)	7655 (3)	6810 (3)	61 (2)
C(12)	3522 (4)	7157 (3)	5665 (3)	49 (1)
C(13)	5378 (3)	7422 (3)	3560 (3)	37 (1)
C(14)	5861 (3)	7092 (3)	2528 (3)	51 (1)
C(15)	7435 (3)	7379 (3)	2603 (3)	66 (2)
C(16)	8527 (3)	7997 (3)	3710 (3)	70 (2)
C(17)	8043 (3)	8328 (3)	4742 (3)	66 (2)
C(18)	6469 (3)	8041 (3)	4667 (3)	51 (2)
C(19)	3312 (4)	3233 (3)	1326 (3)	41 (1)
C(20)	4602 (4)	3565 (3)	963 (3)	47 (1)
C(21)	5211 (4)	2681 (3)	274 (3)	52 (2)
C(22)	4530 (4)	1464 (3)	−52 (3)	56 (2)
C(23)	3239 (4)	1132 (3)	312 (3)	54 (2)
C(24)	2631 (4)	2016 (3)	1000 (3)	49 (1)
C(25)	−30 (6)	3212 (4)	1890 (3)	53 (2)
C(26)	899 (6)	3304 (4)	2970 (3)	57 (2)
C(27)	1045 (6)	4457 (4)	3873 (3)	59 (2)
C(28)	206 (6)	5078 (4)	3351 (3)	60 (2)
C(29)	−459 (6)	4308 (4)	2125 (3)	59 (2)
C(30)	2356 (6)	4953 (5)	1065 (5)	40 (1)
O(30)	2299 (5)	5024 (4)	177 (4)	55 (1)
C(31)	4409 (7)	4922 (5)	3327 (5)	43 (1)
O(31)	5659 (6)	5030 (4)	3848 (4)	59 (1)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Mo(1)—P(1)	2·468 (1)	Mo(1)—C(30)	1·941 (6)
Mo(1)—C(19)	2·334 (3)	Mo(1)—C(31)	1·951 (6)
Mo(1)—C(25)	2·335 (5)	P(1)—C(1)	1·825 (3)
Mo(1)—C(26)	2·312 (5)	P(1)—C(7)	1·831 (3)
Mo(1)—C(27)	2·349 (5)	P(1)—C(13)	1·826 (3)
Mo(1)—C(28)	2·393 (5)	C(30)—O(30)	1·154 (7)
Mo(1)—C(29)	2·385 (5)	C(31)—O(31)	1·163 (7)
P(1)—Mo(1)—C(19)	128·9 (1)	C(7)—P(1)—C(13)	103·2 (2)
P(1)—Mo(1)—C(30)	80·3 (2)	P(1)—C(1)—C(2)	120·7 (1)
P(1)—Mo(1)—C(31)	78·2 (2)	P(1)—C(1)—C(6)	119·2 (1)
C(19)—Mo(1)—C(30)	72·6 (2)	P(1)—C(7)—C(8)	123·3 (1)
C(19)—Mo(1)—C(31)	70·0 (2)	P(1)—C(7)—C(12)	116·6 (1)
C(30)—Mo(1)—C(31)	107·2 (2)	P(1)—C(13)—C(14)	117·1 (1)
Mo(1)—P(1)—C(1)	118·9 (1)	P(1)—C(13)—C(18)	122·7 (1)
Mo(1)—P(1)—C(7)	114·7 (1)	Mo(1)—C(19)—C(20)	120·3 (1)
Mo(1)—P(1)—C(13)	113·4 (1)	Mo(1)—C(19)—C(24)	119·7 (1)
C(1)—P(1)—C(7)	103·5 (2)	Mo(1)—C(30)—O(30)	174·7 (5)
C(1)—P(1)—C(13)	101·1 (2)	Mo(1)—C(31)—O(31)	177·9 (5)

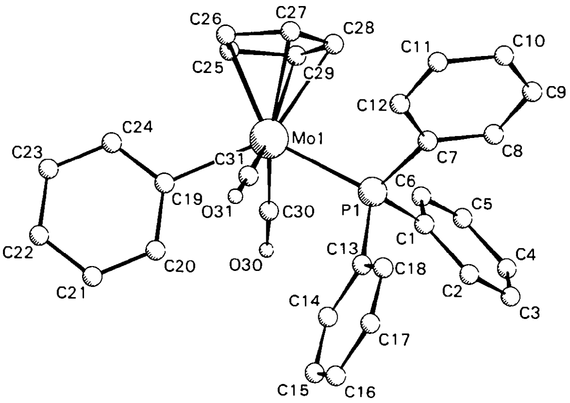

Fig. 1. Perspective view of the title compound with atomic numbering

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