

Crystal and Molecular Structure* of 1,1,1,1-Tetracarbonyl-2,2-bis(η -cyclopentadienyl)-bis(μ -diphenylphosphido)-molybdenumzirconium, [(cp)₂Zr(μ -PPh₂)₂Mo(CO)₄]

Michael G. B. Drew

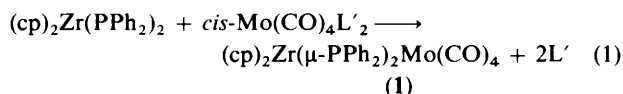
Department of Chemistry, The University, Whiteknights, Reading RG6 2AD

Steven R. Wade, Malcolm G. H. Wallbridge, and Gerald R. Willey

Department of Chemistry, University of Warwick, Coventry CV4 7AL

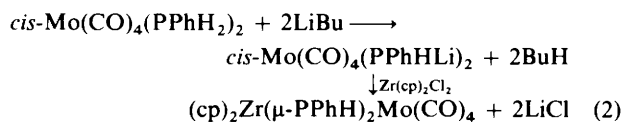
The compound [(cp)₂Zr(μ -PPh₂)₂Mo(CO)₄] (1), where cp = η -C₅H₅, has been prepared and characterised by a single-crystal X-ray diffraction study. The crystals are monoclinic, space group *P*2₁/*c*, *Z* = 4, with *a* = 17.506(9), *b* = 14.607(8), *c* = 14.887(11) Å, and β = 104.0(1)°. 3 715 Independent reflections above background have been measured on a diffractometer and the structure refined to *R* 0.069. The discrete molecules have approximate C_{2v} symmetry. The μ -PPh₂ groups bridge symmetrically across the (cp)₂Zr and Mo(CO)₄ moieties forming an approximately planar four-membered ring [Zr–P–Mo–P–], with the basic geometries about zirconium being tetrahedral and about molybdenum octahedral. The Zr...Mo distance of 3.290(1) Å signifies the presence of a single donor–acceptor bond Mo⁰→Zr^{IV} thereby conferring a formal 18-electron closed-shell electronic configuration upon both metal centres. Dimensions of the bridge are Zr–P 2.618(3) and 2.631(3), Mo–P 2.543(3) and 2.536(3) Å, P–Zr–P 98.5(1), and P–Mo–P 103.1(1)°. The Zr–P–Mo angles are 79.2(1) and 79.1(1)°.

Recent reports from these laboratories^{1,2} and elsewhere^{3,4} describe the synthesis and chemical reactivity of M–L compounds where M = Group 4 metal (Ti, Zr, or Hf) and L = trivalent Group 5 donor PR₂, AsR₂, or SbR₂; R = alkyl or aryl. Utilisation in metal complexation (σ donor) of the formal lone pair of electrons associated with the group L offers a convenient route to bimetallic L-bridged compounds as illustrated in equation (1) (cp = η -C₅H₅; L' = piperidine).



Homo- and hetero-bimetallic systems with a μ -phosphido group have attracted particular attention.⁵ There is a burgeoning interest in such species with regard to their metal–metal bonding characteristics,⁶ and their diverse chemical reactivity associated with disparate metal centres modified by bridging groups.⁷

Compound (1) provides a further example of these systems and herein we report its structural characterisation by X-ray crystallography.† Compounds similar to (1) have been reported, but only characterised spectroscopically, by Stelzer and co-workers,^{8,9} e.g. as in equation (2). The difference in the



* Supplementary data available (No. SUP 56408, 11 pp.); thermal parameters, H-atom co-ordinates, remaining bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, 1, pp. xvii–xx. Structure factors are available from the editorial office.

† Note added in proof. Since this paper was submitted the structure of (1) has been reported independently (L. Gelmini, L. C. Matassa, and D. W. Stephan, *Inorg. Chem.*, 1985, **24**, 2585). These crystals were, however, orthorhombic and contained no solvent of crystallisation. The structures are identical within experimental error.

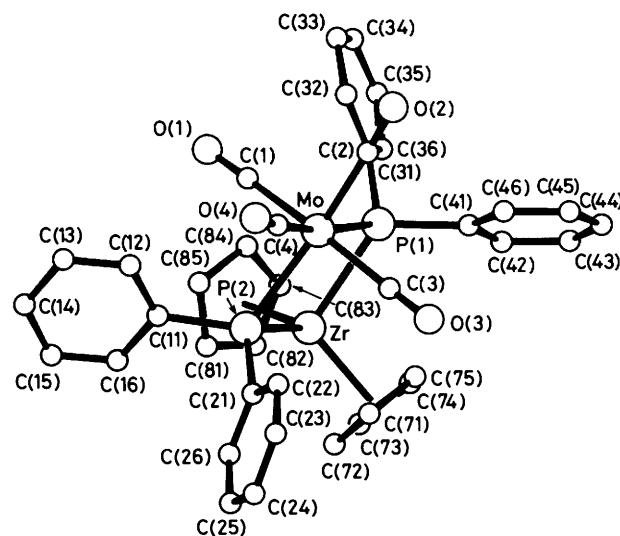


Figure. The structure of (1)

synthetic approaches lies in the sequential order of bond formation. Whereas Stelzer formed Mo–P bonds at the outset and then formed the bridge with the Group 4 metal, we have initially formed Zr–P bonds and subsequently the bridge to Mo.

Discussion

The structure of compound (1) is shown in the Figure together with the atomic numbering scheme. Molecular dimensions are listed in Table 1. The basic skeleton consists of Mo(CO)₄ and Zr(cp)₂ moieties bridged by two diphenylphosphido groups. The ZrP₂Mo bridge is very slightly folded [2.8(1)°]. It is of interest that the Zr–P bonds are essentially equivalent [2.618(3) and 2.631(3) Å]. A structure determination of [Hf(cp)₂(PEt₂)₂]³ clearly indicates the non-equivalence of the diethyl-

Table 1. Molecular dimensions in the metal co-ordination spheres of compound (1); distances in Å, angles in °

| | | | | | | | |
|--------------|------------|----------------|------------|---------------|------------|------------------|------------|
| Mo-Zr | 3.290(1) | Mo-P(1) | 2.543(3) | Zr-C(75) | 2.551(13) | Zr-C(85) | 2.517(13) |
| Mo-C(1) | 2.056(13) | Zr-C(71) | 2.497(15) | Zr-C(81) | 2.491(13) | Zr-P(2) | 2.631(3) |
| Mo-C(2) | 1.991(11) | Zr-C(72) | 2.476(16) | Zr-C(82) | 2.450(13) | Zr-P(1) | 2.618(3) |
| Mo-C(4) | 2.013(12) | Zr-C(73) | 2.468(13) | Zr-C(83) | 2.510(21) | Zr-cg(1) | 2.201(6) |
| Mo-C(3) | 2.000(11) | Zr-C(74) | 2.506(14) | Zr-C(84) | 2.543(15) | Zr-cg(2) | 2.206(6) |
| Mo-P(2) | 2.536(3) | | | | | | |
| C(1)-Mo-C(2) | 90.05(48) | C(3)-Mo-P(2) | 87.67(30) | cg(1)-Zr-P(2) | 105.18(7) | Zr-P(2)-C(21) | 122.44(39) |
| C(1)-Mo-C(4) | 90.01(47) | C(1)-Mo-P(1) | 90.27(35) | cg(2)-Zr-P(1) | 105.41(8) | C(11)-P(2)-C(21) | 98.2(5) |
| C(2)-Mo-C(4) | 84.82(48) | C(2)-Mo-P(1) | 84.73(38) | cg(2)-Zr-P(2) | 105.25(8) | Mo-P(1)-Zr | 79.21(8) |
| C(1)-Mo-C(3) | 176.29(42) | C(4)-Mo-P(1) | 169.55(30) | P(1)-Zr-P(2) | 98.54(9) | Mo-P(1)-C(31) | 117.84(34) |
| C(2)-Mo-C(3) | 92.52(47) | C(3)-Mo-P(1) | 87.30(34) | Mo-P(2)-Zr | 79.09(9) | Zr-P(1)-C(31) | 122.63(34) |
| C(4)-Mo-C(3) | 92.89(47) | P(2)-Mo-P(1) | 103.10(9) | Mo-P(2)-C(11) | 118.01(32) | Mo-P(1)-C(41) | 117.31(40) |
| C(1)-Mo-P(2) | 90.15(32) | cg(1)-Zr-cg(2) | 131.81(4) | Zr-P(2)-C(11) | 122.40(41) | Zr-P(1)-C(41) | 122.96(32) |
| C(2)-Mo-P(2) | 172.16(38) | cg(1)-Zr-P(1) | 105.95(7) | Mo-P(2)-C(21) | 118.08(38) | C(31)-P(1)-C(41) | 98.20(49) |
| C(4)-Mo-P(2) | 87.35(30) | | | | | | |

• cg = Centroid of cyclopentadienyl group.

phosphide sites with Hf-P distances 2.682(1) and 2.488(1) Å. This is the result of a π -bonding interaction (Hf-P) involving a lone pair of electrons associated with one of the phosphorus centres and is commensurate with an 18-electron formulation at the metal centre. Assuming a similar structure for our starting material $[\text{Zr}(\text{cp})_2(\text{PPh}_2)_2]$ (*X*-ray structure under current investigation), any non-equivalence in the Zr-P bonds clearly disappears on formation of (1).

Donation of a pair of electrons from Mo (filled t_{2g} orbital) into an energetically accessible unoccupied acceptor orbital (a_1) on Zr^{IV} retains the same electronic count and gives rise to a formal polar bond $\text{Mo}^0 \rightarrow \text{Zr}^{\text{IV}}$. The observed Mo...Zr distance of 3.290(1) Å is very similar to the 3.297(1) Å found in $[(\text{cp})_2\text{Zr}(\text{OCMe})(\text{OC})\text{Mo}(\text{CO})(\text{cp})]^{11}$ which incorporates a formal single bond (Zr-Mo) bridged by $\eta^2\text{-OCCH}_3$ (3e) and $\sigma, \eta^2\text{-CO}$ (4e).

Both the Zr-P-Mo angles are identical, and acute at 79.2(1)° and 79.1(1)°; similar angles in the range 65–85° have been observed in a variety of phosphido-bridged 'mixed-metal' systems,^{12–16} where a metal-metal bond has been unequivocally assigned. An accompanying criterion for ostensible metal-metal bonding in such systems is provided by the P...P separation: the stronger the metal(M)...metal(M') interaction the more acute is the subtended M-P-M' angle, and the greater is the non-bonded P...P transverse distance. For example in $[(\eta\text{-C}_3\text{Me}_5)_2\text{Th}(\mu\text{-PPh}_2)_2\text{Ni}(\text{CO})_2]^{17}$ with a formal Th-Ni bond 3.206 Å, the P...P separation is 3.850(5) Å, while in (1) the P...P distance is 3.977(2) Å.

The geometry at the molybdenum atom is relatively unstrained octahedral, the only major distortion being the P-Mo-P angle 103.1(1)° which in itself provides support for a substantial metal...metal interaction. All other deviations from ideal (O_h) are a consequence of this angle; thus the *trans* angles to phosphorus are C(2)-Mo-P(2) 172.2(4)° and C(4)-Mo-P(1) 169.5(3)°. The zirconium atom environment is distorted tetrahedral with a cp(centroid)-Zr-cp(centroid) angle 131.8(1)°, typical of a bent zirconocene fragment^{10,18} and a P(1)-Zr-P(2) angle 98.5(1)°.

Least-squares planes show up the essential C_{2v} symmetry of the molecule. The maximum deviation of a contributing atom from plane 1 containing atoms Mo, Zr, C(1), O(1), C(3), O(3), cg(1), cg(2) (cg = centroid of cp) is 0.01 Å, and from plane 2 made up of atoms Mo, Zr, P(1), P(2), C(2), O(2), C(4), O(4) is 0.06 Å (for Zr). The planes are almost perpendicular and intersect each other at 86.8°.

The basic outline of the structure is very similar to that found in $[(\text{cp})_2\text{Ti}(\mu\text{-SMe})_2\text{Mo}(\text{CO})_4]^{19}$ where the central

[Ti-S-Mo-S] four-membered ring is planar with Ti-Mo 3.32 Å. In compound (1) there is a benzene solvent molecule surrounding a centre of symmetry, but no intermolecular contacts of note.

Experimental

The compound $[\text{Zr}(\text{cp})_2(\text{PPh}_2)_2]$ was prepared as described previously¹ and *cis*- $[\text{Mo}(\text{CO})_4\text{L}'_2]$ (L' = piperidine) was obtained from the direct reaction of $[\text{Mo}(\text{CO})_6]$ with excess of piperidine.

Preparation of Compound (1).—The compound $[\text{Zr}(\text{cp})_2(\text{PPh}_2)_2]$ (0.95 g, 1.61 mmol) in tetrahydrofuran (20 cm³) was added dropwise to a stirred slurry of *cis*- $[\text{Mo}(\text{CO})_4\text{L}'_2]$ (0.61 g, 1.61 mmol) in dichloromethane (25 cm³) maintained at 0°C. After stirring the mixture for 12 h at room temperature the solvent was removed to leave a dark yellow solid. The product was washed with *n*-hexane (3 × 30 cm³) and pumped *in vacuo* for several hours at room temperature (0.69 g, 54%) (Found: C, 57.1; H, 3.8. $\text{C}_{38}\text{H}_{30}\text{MoO}_4\text{P}_2\text{Zr}$ requires C, 57.1; H, 3.8%). Recrystallisation (with some difficulty) from benzene-dichloromethane solutions gave pale yellow needle crystals suitable for the *X*-ray structure determination.

Crystallography.—*Crystal data.* $\text{C}_{38}\text{H}_{30}\text{MoO}_4\text{P}_2\text{Zr} \cdot 0.5\text{-C}_6\text{H}_6$, $M = 1190.6$, monoclinic, space group $P2_1/c$, $a = 17.506(9)$, $b = 14.607(8)$, $c = 14.887(11)$ Å, $\beta = 104.0(1)^\circ$, $U = 3693.7$ Å³, $D_m = 1.51(3)$, $Z = 4$, $D_c = 1.51$ g cm⁻³, $F(000) = 1692$, $\lambda = 0.7107$ Å, $\mu = 7.39$ cm⁻¹.

Precession photographs established the preliminary cell constants and space group. A crystal was mounted to rotate around the *a* axis on a Stoe STADI2 diffractometer and data were collected *via* variable-width ω scan. Background counts were 20 s and a scan rate of 0.0333° s⁻¹ was applied to a width of (2.0 + 0.5 sin μ /tan θ). 6436 independent reflections with $2\theta < 50^\circ$ were measured of which 3715 having $I > 3\sigma(I)$ were used in subsequent refinement. The structure was solved from the Patterson function and by subsequent Fourier methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in trigonal positions and those in the same ring were given a common thermal parameter which was refined. The structure was refined using full-matrix least squares. The weighting scheme used was $w = 1/[\sigma^2(F) + 0.003F^2]$ where $\sigma(F)$ was taken from counting statistics. This gave equivalent values of $w\Delta^2$ over ranges of F_o and $\sin\theta/\lambda$. Calculations were performed using SHELX 76²⁰ and local programs on the

Table 2. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

| Atom | x | y | z | Atom | x | y | z |
|-------|-----------|-----------|-----------|--------|-----------|-----------|------------|
| Mo | 669(0) | 1 405(1) | 1 724(1) | C(15) | 2 149(9) | -2 150(9) | 3 653(9) |
| C(1) | 869(6) | 397(8) | 845(9) | C(16) | 2 137(8) | -1 195(8) | 3 627(8) |
| O(1) | 963(5) | -151(7) | 359(6) | C(21) | 1 284(8) | 686(8) | 4 233(7) |
| C(2) | -118(7) | 1 982(9) | 686(8) | C(22) | 551(8) | 998(9) | 4 285(9) |
| O(2) | -608(5) | 2 291(7) | 113(6) | C(23) | 361(11) | 1 119(11) | 5 140(11) |
| C(4) | -256(6) | 696(8) | 1 940(8) | C(24) | 1 627(12) | 562(11) | 5 890(9) |
| O(4) | -799(4) | 333(7) | 2 040(7) | C(25) | 914(13) | 901(11) | 5 931(10) |
| C(3) | 550(6) | 2 394(7) | 2 610(8) | C(25) | 1 813(9) | 494(8) | 5 030(8) |
| O(3) | 496(5) | 2 971(7) | 3 116(7) | P(1) | 1 653(2) | 2 441(2) | 1 216(2) |
| Zr | 2 583(0) | 1 550(1) | 2 577(1) | C(31) | 1 736(6) | 2 351(7) | 5(7) |
| C(71) | 3 634(8) | 2 321(13) | 3 773(11) | C(32) | 1 135(7) | 2 001(9) | -683(8) |
| C(72) | 3 245(9) | 2 996(11) | 3 195(10) | C(33) | 1 183(8) | 2 038(11) | -1 605(9) |
| C(73) | 3 116(9) | 1 953(11) | 4 220(9) | C(34) | 1 865(8) | 2 353(11) | -1 816(10) |
| C(74) | 2 402(8) | 2 414(9) | 3 965(9) | C(35) | 2 460(7) | 2 682(8) | -1 134(9) |
| C(75) | 2 464(8) | 3 098(8) | 3 325(8) | C(36) | 2 397(6) | 2 698(8) | -234(8) |
| C(81) | 3 363(8) | 123(9) | 2 589(9) | C(41) | 1 488(7) | 3 691(7) | 1 244(7) |
| C(82) | 3 820(7) | 848(10) | 2 440(12) | C(42) | 754(8) | 4 079(9) | 1 182(9) |
| C(83) | 3 487(10) | 1 200(11) | 1 546(13) | C(43) | 653(11) | 5 020(10) | 1 156(10) |
| C(84) | 2 813(9) | 701(11) | 1 175(9) | C(44) | 1 279(13) | 5 575(10) | 1 191(11) |
| C(85) | 2 738(7) | 49(9) | 1 811(9) | C(45) | 2 020(10) | 5 220(10) | 1 242(10) |
| P(2) | 1 513(2) | 551(2) | 3 092(2) | C(46) | 2 108(8) | 4 276(9) | 1 256(9) |
| C(11) | 1 517(7) | -731(8) | 3 047(7) | C(100) | 435(16) | 4 361(20) | 4 898(20) |
| C(12) | 938(7) | -1 227(8) | 2 476(9) | C(101) | 428(18) | 5 109(26) | 4 420(22) |
| C(13) | 948(8) | -2 160(9) | 2 476(10) | C(102) | -32(25) | 5 933(30) | 4 300(27) |
| C(14) | 1 538(10) | -2 621(9) | 3 071(10) | | | | |

Amdahl V7/A computer at the University of Reading. The final R factor was 0.069 ($R' = 0.076$). Final co-ordinates are given in Table 2.

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