

C(33)	-0.1616 (5)	-0.2633 (7)	0.1615 (6)	5.6 (2)
C(34)	-0.1058 (5)	-0.3033 (6)	0.0953 (6)	4.9 (2)
C(35)	-0.0186 (4)	-0.2937 (5)	0.1122 (5)	3.9 (1)
C(41)	0.0975 (4)	-0.0288 (5)	0.1598 (5)	3.7 (1)
C(42)	0.0886 (7)	0.0516 (6)	0.1059 (6)	6.1 (2)
C(43)	0.1083 (8)	0.0524 (6)	0.0119 (7)	7.5 (3)
C(44)	0.1430 (7)	-0.0263 (6)	-0.0316 (6)	6.1 (2)
C(45)	0.1511 (5)	-0.1043 (5)	0.0252 (5)	4.4 (2)

Table 2. Selected geometric parameters (Å, °)

V(1)—O(1)	1.624 (3)	V(2)—O(4)	1.612 (3)
V(1)—O(2)	1.614 (3)	V(2)—O(5)	1.940 (2)
V(1)—O(5)	2.204 (2)	V(2)—N(2)	2.284 (3)
V(1)—N(1)	2.275 (4)	V(2)—N(31)	2.136 (3)
V(1)—N(11)	2.103 (3)	V(2)—N(41)	2.313 (3)
V(1)—N(21)	2.106 (3)	V(1)···V(2)	3.690 (3)
V(2)—O(3)	1.631 (3)		
O(1)—V(1)—O(2)	106.0 (1)	O(3)—V(2)—O(4)	105.8 (1)
O(1)—V(1)—O(5)	164.9 (1)	O(3)—V(2)—O(5)	100.7 (1)
O(1)—V(1)—N(1)	90.6 (1)	O(3)—V(2)—N(2)	91.1 (1)
O(1)—V(1)—N(11)	93.7 (1)	O(3)—V(2)—N(31)	89.8 (1)
O(1)—V(1)—N(21)	93.1 (1)	O(3)—V(2)—N(41)	162.2 (1)
O(2)—V(1)—O(5)	88.9 (1)	O(4)—V(2)—O(5)	108.3 (1)
O(2)—V(1)—N(1)	163.4 (1)	O(4)—V(2)—N(2)	160.1 (1)
O(2)—V(1)—N(11)	103.6 (1)	O(4)—V(2)—N(31)	94.5 (1)
O(2)—V(1)—N(21)	101.7 (1)	O(4)—V(2)—N(41)	89.4 (1)
O(5)—V(1)—N(1)	74.6 (1)	O(5)—V(2)—N(2)	78.3 (2)
O(5)—V(1)—N(11)	85.4 (2)	O(5)—V(2)—N(31)	151.1 (1)
O(5)—V(1)—N(21)	80.9 (1)	O(5)—V(2)—N(41)	82.7 (1)
N(1)—V(1)—N(11)	75.4 (1)	N(2)—V(2)—N(31)	74.5 (1)
N(1)—V(1)—N(21)	76.2 (1)	N(2)—V(2)—N(41)	72.4 (1)
N(11)—V(1)—N(21)	150.9 (1)	V(1)—O(5)—V(2)	126.2 (1)

H atoms were included at geometrically idealized positions; their coordinates were recalculated after each cycle. The H atoms of the two water molecules were not located.

Data collection, cell refinement and data reduction: *SDP* (Frenz, 1978). Program used to solve structure: *SHELXS86* (VMS version; Sheldrick, 1985). Program used to refine structure: *SDP*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SDP*. The calculations were performed on a VAX computer at the Universität Tübingen.

This work was supported by grants from PADCT, CNPq, FINEP, CAPES, FUNCITEC (Brazil) and VW-Stiftung (Germany).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: MU1137). 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.* (1995). **C51**, 811–813

## Pentacarbonyl-1 $\kappa$ C<sub>2</sub>,2 $\kappa$ <sup>4</sup>C-bis[1,1( $\eta$ <sup>5</sup>-cyclopentadienyl)(dimethylphenylphosphine-2 $\kappa$ P)- $\mu$ -dimethylphosphanido-niobiumtungsten

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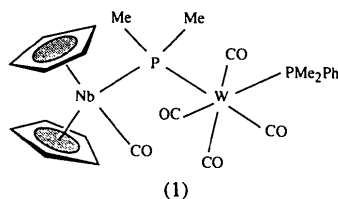
## Abstract

The title complex, [NbW(C<sub>2</sub>H<sub>6</sub>P)(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>5</sub>-(C<sub>8</sub>H<sub>11</sub>P)], belongs to a small family of monophosphido-bridged transition metal complexes without both a metal–metal bond and any other bridges. The observed geometries of the Nb (distorted tetrahedral) and W (*cis*-octahedral) centers are as expected with a significantly enlarged Nb—P(1)—W angle of 124.9 (2)°. The methyl groups of the bridging phosphido ligand adopt an *endo* orientation towards the CO (Nb—CO) ligand which compels them to adopt symmetrical positions with respect to the (OC)NbP plane, bisecting that of the cyclopentadienyl rings. Consequently, the C(Nb—CO), Nb, P and W atoms are coplanar.

## Comment

During our studies on the reactivity of phosphido-bridged heterobimetallic compounds derived from bis( $\eta$ <sup>5</sup>-cyclopentadienyl)niobium and Group 6 metal (*M'*) carbonyls of the type [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Nb( $\mu$ -PR<sub>2</sub>CO)*M'*—

(CO)<sub>n</sub>] (Oudet, Kubicki & Moïse, 1994), we observed that an opening of the carbonyl bridge may occur by the action of good electron-donor ligands such as some phosphines. Monobridged  $\mu$ -PR<sub>2</sub> complexes without a metal–metal bond are formed in these reactions. The structure of one of these new monobridged compounds, [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Nb(CO)( $\mu$ -PMe<sub>2</sub>)W(CO)<sub>4</sub>(PMe<sub>2</sub>Ph)] (1), is reported here.



The structures of only two mono-phosphido-bridged heterobimetallic complexes derived from metallocenes without a metal–metal bond or other bridges have been studied previously: [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo(H)( $\mu$ -PPh<sub>2</sub>)Mn(CO)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)] (2) (Barré, Kubicki & Moïse, 1990) and [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ta(H)( $\mu$ -PMe<sub>2</sub>)-Mn(CO)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)] (3) (Bonnet, Kubicki, Lavastre, Leblanc & Moïse, 1990). The value of Nb—P(1)—W in (1) [124.9(2)°] is as expected and is opened as much as the analogous angles in (2) and (3) [Mo—P—Mn 124.47(7), Ta—P—Mn 125.51(1)°]. The M—P—M' angles in bis(cyclopentadienyl) derivatives are therefore much larger than in the phosphido-bridged mono(cyclopentadienyl) complexes [(C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>( $\mu$ -PPh<sub>2</sub>)M(CO)<sub>5</sub>]: M = Cr, Cr—P—Fe = 119.20(5)°; M = Mo, Mo—P—Fe = 118.59(4)° (Shyu, Lin & Wen, 1993); and M = W, W—P—Fe = 118.42(6)° (Shyu, Lin, Dong & Wen, 1993). The W—P(1) bond length in (1) [2.610(4) Å] is rather long but corresponds well to the W—P distances of 2.610(1) and 2.588(1) Å observed in the dibridged anion [(CO)<sub>4</sub>W( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>W(CO)<sub>4</sub>]<sup>2-</sup>

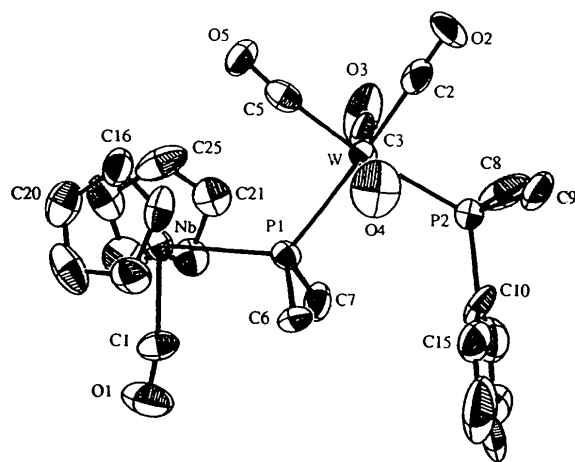


Fig. 1. Molecular structure of (1). Displacement ellipsoids are drawn at the 50% probability level.

(Shyu, Calligaris, Nardin & Wojcicki, 1987). The Nb—P(1) and Nb—C(1) distances [2.668(4) and 2.055(18) Å, respectively] are similar to those found in the niobium(III) terminal-phosphido complex [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Nb(CO)(PrPhP)] (Bonnet, Kubicki, Moïse, Lazzaroni, Salvadori & Vitulli, 1992).

## Experimental

### Crystal data

[NbW(C<sub>2</sub>H<sub>6</sub>P)(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>5</sub>(C<sub>8</sub>H<sub>11</sub>P)]

*M<sub>r</sub>* = 746.20

Orthorhombic

*Pbca*

*a* = 14.290(3) Å

*b* = 13.571(2) Å

*c* = 27.314(8) Å

*V* = 5297 Å<sup>3</sup>

*Z* = 8

*D<sub>x</sub>* = 1.871 Mg m<sup>-3</sup>

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 10–18°

μ = 4.999 mm<sup>-1</sup>

*T* = 296 K

Rhombic bipyramidal

0.30 × 0.15 × 0.15 mm

Deep red

### Data collection

Enraf–Nonius CAD-4 diffractometer

ω–2θ scans

Absorption correction:

refined from Δ*F*

(*DIFABS*; Walker &

Stuart, 1983)

5653 measured reflections

5192 independent reflections

2360 observed reflections

[*I* ≥ 3σ(*I*)]

*R*<sub>int</sub> = 0.048

θ<sub>max</sub> = 25°

*h* = 0 → 17

*k* = 0 → 16

*l* = -2 → 32

3 standard reflections

frequency: 120 min

intensity decay: 5.5%

### Refinement

Refinement on *F*

*R* = 0.043

*wR* = 0.051

*S* = 2.220

2360 reflections

307 parameters

H-atom parameters not

refined

*w* = 1/[σ<sup>2</sup>(*I*) + (0.051)<sup>2</sup>]<sup>1/2</sup>

(Δ/σ)<sub>max</sub> = 0.24

Δρ<sub>max</sub> = 0.7 e Å<sup>-3</sup>

Δρ<sub>min</sub> = 0.6 e Å<sup>-3</sup>

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<sup>2</sup>)

$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i>
W	0.37398 (5)	0.58129 (4)	0.38582 (2)	2.699 (9)
Nb	0.6280 (1)	0.7720 (1)	0.43782 (5)	2.95 (3)
P(1)	0.5129 (3)	0.7017 (3)	0.3693 (3)	2.86 (8)
P(2)	0.3477 (3)	0.5263 (3)	0.2986 (2)	3.7 (1)
C(1)	0.691 (1)	0.852 (1)	0.3833 (7)	4.2 (4)
C(2)	0.267 (1)	0.498 (1)	0.4015 (6)	3.9 (4)
C(3)	0.461 (1)	0.467 (1)	0.3932 (6)	4.2 (4)
C(4)	0.283 (1)	0.691 (1)	0.3768 (6)	3.3 (3)
C(5)	0.390 (1)	0.606 (1)	0.4576 (6)	3.6 (4)
O(1)	0.731 (1)	0.904 (1)	0.3590 (5)	7.2 (4)
O(2)	0.2031 (9)	0.450 (1)	0.4115 (5)	6.5 (3)
O(3)	0.505 (1)	0.396 (1)	0.3999 (5)	8.5 (4)
O(4)	0.224 (1)	0.751 (1)	0.3721 (6)	7.0 (4)
O(5)	0.395 (1)	0.6121 (9)	0.4990 (4)	6.3 (4)

C(6)	0.467 (1)	0.810 (1)	0.3359 (6)	3.9 (4)
C(7)	0.588 (1)	0.653 (2)	0.3228 (6)	5.3 (5)
C(8)	0.383 (2)	0.403 (1)	0.2852 (7)	7.9 (7)
C(9)	0.226 (1)	0.515 (2)	0.2837 (7)	9.4 (7)
C(10)	0.387 (2)	0.597 (1)	0.2449 (6)	4.3 (4)
C(11)	0.455 (2)	0.564 (2)	0.2140 (8)	6.3 (6)
C(12)	0.486 (2)	0.623 (2)	0.1761 (9)	10.4 (8)
C(13)	0.439 (2)	0.707 (2)	0.1679 (9)	13.4 (6)
C(14)	0.377 (2)	0.746 (2)	0.1976 (9)	12.4 (8)
C(15)	0.350 (1)	0.687 (1)	0.2353 (7)	5.2 (5)
C(16)	0.523 (1)	0.814 (1)	0.5019 (7)	4.2 (4)
C(17)	0.479 (1)	0.847 (1)	0.4606 (6)	3.8 (4)
C(18)	0.537 (1)	0.918 (1)	0.4396 (7)	4.5 (4)
C(19)	0.614 (1)	0.932 (1)	0.4719 (8)	5.7 (5)
C(20)	0.608 (2)	0.864 (1)	0.5086 (7)	5.3 (5)
C(21)	0.669 (1)	0.599 (1)	0.4337 (7)	4.5 (4)
C(22)	0.740 (1)	0.654 (1)	0.4095 (7)	4.5 (4)
C(23)	0.785 (1)	0.714 (2)	0.4437 (8)	5.6 (5)
C(24)	0.739 (1)	0.697 (1)	0.4890 (8)	5.7 (5)
C(25)	0.669 (2)	0.627 (1)	0.4798 (7)	6.0 (5)
Cp(1)†	0.552	0.875	0.476	
Cp(2)	0.720	0.658	0.451	

† Cp(1) and Cp(2) represent the centroids of the C(16)–C(20) and C(21)–C(25) cyclopentadienyl rings, respectively.

Table 2. Selected geometric parameters (Å, °)

W–Nb	4.679 (2)	W–C(4)	1.99 (2)
W–P(1)	2.610 (4)	W–C(5)	2.00 (2)
W–P(2)	2.524 (5)	Nb–Cp(1)	2.06
W–C(2)	1.95 (2)	Nb–Cp(2)	2.07
W–C(3)	2.00 (2)	Nb–P(1)	2.668 (4)
P(1)–W–P(2)	97.7 (1)	C(2)–W–C(5)	88.3 (6)
P(1)–W–C(2)	176.1 (6)	C(3)–W–C(4)	177.2 (7)
P(1)–W–C(3)	91.9 (5)	C(3)–W–C(5)	87.9 (6)
P(1)–W–C(4)	90.3 (5)	C(4)–W–C(5)	93.8 (6)
P(1)–W–C(5)	88.8 (5)	P(1)–Nb–C(1)	87.3 (5)
P(2)–W–C(2)	85.4 (5)	Cp(1)–Nb–Cp(2)	139.4
P(2)–W–C(3)	87.6 (5)	W–P(1)–Nb	124.9 (2)
P(2)–W–C(4)	90.4 (5)	W–P(1)–C(6)	108.4 (6)
P(2)–W–C(5)	172.1 (4)	W–P(1)–C(7)	110.4 (7)
C(2)–W–C(3)	90.7 (7)	Nb–P(1)–C(6)	106.1 (6)
C(2)–W–C(4)	87.2 (7)	Nb–P(1)–C(7)	105.1 (6)

SDP (Enraf–Nonius, 1985) was used to solve and refine the structure.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: PA1107). 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.* (1995). **C51**, 813–815

## A Mononuclear Manganese(III) Schiff Base Complex, [Mn(C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>)-(C<sub>8</sub>H<sub>7</sub>O<sub>3</sub>)(CH<sub>4</sub>O)]

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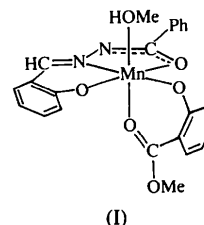
(Received 2 September 1994; accepted 26 October 1994)

## Abstract

In the title compound, [2-( $\alpha$ -hydroxybenzylidenehydrazonomethyl)phenolato(2-)-*N,O,O'*](methanol-*O*)-(methyl salicylato-*O,O'*)manganese(III), [Mn(BHS)-(MS)(CH<sub>3</sub>OH)], the manganese(III) ion is surrounded by an O<sub>5</sub>N coordination sphere. The tridentate 2-( $\alpha$ -hydroxybenzylidenehydrazonomethyl)phenolate (BHS<sup>2-</sup>) ligand (H<sub>2</sub>BHS is the benzoyl hydrazone of salicylaldehyde) binds the metal ion meridionally and the methyl salicylate (MS<sup>-</sup>) ligand is bidentate. The sixth position is occupied by a methanol molecule. There is a significant tetragonal elongation due to a Jahn–Teller effect.

## Comment

Our interest in polynuclear manganese complexes has led us to obtain mononuclear manganese complexes with coordinated solvent molecules. We intend to use these mononuclear complexes as precursors in the synthesis of polynuclear species of desired nuclearity by replacing the solvent molecules with various bridging groups such as oxo, hydroxo, acetato, etc. Herein we report the structure of a new mononuclear manganese(III) complex containing a coordinated methanol molecule, (I).



A view of the [Mn(BHS)(MS)(CH<sub>3</sub>OH)] molecule with the atom-labelling scheme is presented in Fig. 1. The manganese(III) ion has an O<sub>5</sub>N coordination sphere.