

The synthesis and characterization of the vanadium diphosphene complex *trans*-[$\{V(\eta^5-C_5H_5)(CO)_3\}_2(PMes)_2$]

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Abstract

The vanadium diphosphene complex *trans*-[$\{V(\eta^5-C_5H_5)(CO)_3\}_2(PMes)_2$] (**1**) has been synthesized and characterized by X-ray crystallography, ^{31}P NMR and IR spectroscopy. It is the first reported example of a Group 5 transition-metal diphosphene complex. Complex **1** was synthesized as blue-green crystals via the reaction of $Na_2V(\eta^5-C_5H_5)(CO)_3$ and PCl_2Mes and purified by chromatography. It has a centrosymmetric *trans* structure with a planar C(9)VPP'V'C(9)' core. The PP' distance is 2.052(2) Å and the V–P distance is 2.397(1) Å. The structure is discussed in the context of other diphosphene complexes. On the basis of both the structural and IR data of these and the related iron and chromium diphosphene and phosphane complexes it was concluded that a diphosphene bound in an end-on fashion has a π acceptor/ σ -donor ratio similar to, or marginally better than, triarylphosphanes. Although calculations indicate considerable metal–phosphorus back bonding it receives only equivocal support from experimental data.

Introduction

Transition metal complexes containing terminal phosphinidene ligands ($L_xM = PR$, R = alkyl or aryl group) are widely implicated as intermediates in various reactions. Their existence has been proven by various trapping experiments [1] and more recently by X-ray crystallography [2]. The major difficulty in isolating transition metal complexes with a terminal phosphinidene moiety is their tendency to react further. Very often they dimerize, oligomerize and/or act as a donor to another transition metal fragment [3]. Our attempts to isolate a transition complex with a terminal phosphinidene (RP) moiety stabilized by $Fe(CO)_4$ and $Cr(CO)_5$ fragments, even with very bulky substituents on phosphorus were unsuccessful [4,5]. This is due to further reactions at the phosphorus center leading to bridging phosphinidenes and diphosphene complexes.

It occurred to us that the use of even bulkier transition metal moieties might afford terminal phosphinidenes. Accordingly, reactions involving $[\text{Na}_2\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ (in which the metal center may be considered six coordinate) were investigated. The reaction between $[\text{Na}_2\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ with MesPCl_2 resulted in the title compound, the first structurally characterized example of a diphosphene stabilized by a group 5 metal. The only other related work has involved the isolation of $[\{\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\}_2\text{PAr}]$ (**2**); ($\text{Ar} = 2,4,6\text{-t-Bu}_3\text{C}_6\text{H}_2$) via a similar route to **1** [6].

Experimental

All operations were performed under an N_2 atmosphere or in a Vacuum Atmospheres HE-43 dry box. All solvents were distilled from conventional drying agents and degassed twice prior to use. MesPCl_2 [7] and $\text{Na}_2\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$ [8] were prepared according to literature procedures.

Synthesis of trans- $[\{\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}_2(\text{PMes})_2]$

MesPCl_2 (0.33 g, 1.5 mmol) in Et_2O (50 ml) was added dropwise to $\text{Na}_2\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$ (0.48 g, 1.5 mmol) in THF (50 ml) at 0°C . The mixture was stirred overnight, the solvents were removed under reduced pressure and the residue was extracted into hexane (10 ml). Purification by column chromatography (silica gel) gave a yellow band, identified as $\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_4$ on elution with hexane followed by a dark blue green band of **1** on elution with 1/1 hexane/toluene. Crystals of **1** (34% yield) were obtained from hexane at -20°C , m.p. $182\text{--}183^\circ\text{C}$, ^{31}P NMR($\text{C}_6\text{D}_6/\text{THF}$): 426 ppm (broad), IR (Nujol); 1943, 1870, 1734, 1700 cm^{-1} .

X-Ray crystallographic study and structural description

X-ray data was collected on a Syntex P2₁ diffractometer equipped with a locally modified LT-1 device, Mo-K_α radiation and graphite monochromator. Calculations were carried out on a Data General Eclipse computer using the SHELXTL, Version 5, program. The crystals were grown as described above. Upon removal from the Schlenk tube, the crystals were covered with a hydrocarbon oil to protect them from decomposition in air. A single crystal was selected under oil, mounted on a glass fiber using silicone grease, and immediately placed in the low temperature N_2 stream.

The structure was solved by direct methods in the space group $I2/a$. Some of the crystal data and refinement details are given in Table 1. Atom coordinates with isotropic thermal parameters are provided in Table 2. An absorption correction [9] was applied and all the non-hydrogen atoms were refined anisotropically. Neutral atoms scattering factors and corrections for anomalous dispersions were from the "International Tables for X-Ray Crystallography" [10]. The hydrogens were included using a riding model with C-H of 0.96 \AA and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{iso}}^*(\text{C})$, where U_{iso}^* is the equivalent isotropic thermal parameter.

The *trans*- $[\{\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}_2(\text{PMes})_2]$ molecule has a center of inversion and the structure is illustrated in Fig. 1. The important P-P' distance is $2.052(2)\text{ \AA}$. The phosphorus centers are planar and V-P distance is $2.397(1)\text{ \AA}$. The distance from the center of the C_5H_5 ring to V is 1.924 \AA . Other bond distances and angles are

Table 1

Crystal data and summary of data collection and refinement for **1**^a

Formula	C ₃₄ H ₃₂ O ₆ P ₂ V ₂
<i>f</i> _w	700.48
Crystal system	monoclinic
Space group	<i>I</i> 2/ <i>a</i>
Conditions	<i>hkl</i> , <i>h</i> + <i>k</i> + <i>l</i> = 2 <i>n</i> ; <i>h0l</i> , <i>l</i> = 2 <i>n</i> , <i>h</i> = 2 <i>n</i>
Crystal dims., mm	0.13 × 0.25 × 0.36
Crystal color and habit	well shaped opaque polyhedra
<i>a</i> , Å	14.926(2)
<i>b</i> , Å	10.299(2)
<i>c</i> , Å	21.291(5)
α, deg.	
β, deg.	99.19(2)
γ, deg.	
<i>V</i> , Å ³	3231(1)
<i>Z</i>	4
<i>d</i> calc., g/cm ³	1.44
Linear abs. coeff., cm ⁻¹	7.46
Range of abs. corr. fctrs.	1.08–1.33
Scan speed, deg min ⁻¹	15
Scan width, deg.	1.0
<i>w</i> offset for bkgd., deg.	1.0
2θ range, deg.	0–55
Octants collected + <i>h</i> , + <i>k</i> , ± <i>l</i>	
No. of refl. collected	4056
No. of unique data	3708
<i>R</i> (merge)	0.0247
No. of check refl.	2(0,0,4), (1,1,2)
No. of data used in rfmt.	2463 <i>I</i> > 2σ(<i>I</i>)
No. of variables	208
Data/variable ratio	11.8
<i>R</i> (<i>F</i>)	0.051
<i>R</i> _w (<i>F</i>)	0.048
Largest Δ/σ	0.005
Largest feature on	
Final diff. map eÅ ⁻³	0.41

^a All data were collected on a P2₁ diffractometer with a graphite monochromator using Mo-*K*_α (λ = 0.71069) radiation at 130 K by a ω scan method. Computer programs are from SHELX_{TL}, Version 5, installed on a Data General Eclipse computer. $R = \sum ||F_0| - |F_c|| / \sum |F_0|$ and $R_w = \sum ||F_0| - |F_c|| w^{1/2} / \sum |F_0| w^{1/2}$ with $w = [\sigma^2(F_0)]^{-1}$. Neutral atom scattering factors and corrections for anomalous dispersion are from the "International Tables for X-Ray Crystallography", Kynoch Press, Birmingham, England, 1974, Vol. IV.

given in Table 3. Tables of anisotropic thermal parameters, hydrogen coordinates and structure factors are available on request from the authors.

Results and discussion

The reaction between equimolar quantities of MesPCl₂ and Na₂V(η⁵-C₅H₅)(CO)₃ gave **1** in moderate yield. With the use of the bulkier V(η⁵-C₅H₅)(CO)₃ fragment in this reaction, it was hoped that a terminal phosphinidene might result. It was also

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for *trans*-[$\{\text{V}(\eta^5\text{-C}_5\text{H}_5)_2\}_2\{\text{PMes}\}_2$] (1)

	x	y	z	U^a
V	6491(1)	1349(1)	8595(1)	21(1)
P	7069(1)	1812(1)	7632(1)	20(1)
O(1)	6537(2)	-1349(3)	9203(2)	45(1)
O(2)	5339(2)	-488(3)	7650(1)	41(1)
O(3)	8497(2)	576(3)	9002(1)	41(1)
C(1)	6522(3)	-330(4)	8976(2)	30(1)
C(2)	5785(3)	232(4)	7981(2)	27(1)
C(3)	7764(3)	914(4)	8833(2)	29(1)
C(4)	6618(3)	3234(4)	9157(2)	31(1)
C(5)	6279(3)	2245(4)	9519(2)	36(1)
C(6)	5424(3)	1858(4)	9186(2)	39(2)
C(7)	5236(3)	2602(4)	8626(2)	33(1)
C(8)	5967(3)	3445(4)	8609(2)	29(1)
C(9)	6843(2)	761(3)	6931(2)	20(1)
C(10)	7375(3)	-346(4)	6886(2)	24(1)
C(11)	7215(3)	-1091(4)	6335(2)	25(1)
C(12)	6534(3)	-780(4)	5835(2)	28(1)
C(13)	5977(3)	267(4)	5906(2)	27(1)
C(14)	6105(3)	1042(4)	6448(2)	25(1)
C(15)	8104(3)	-774(4)	7429(2)	28(1)
C(16)	6372(3)	-1581(4)	5235(2)	36(1)
C(17)	5424(3)	2084(4)	6519(2)	32(1)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

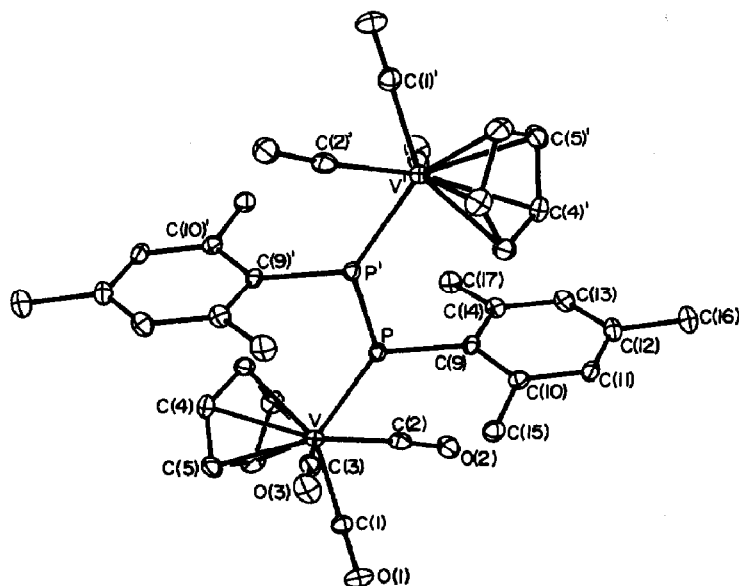


Fig. 1. Computer generated thermal ellipsoid plot of 1.

Table 3

Bond lengths (Å) and bond angles (°) for *trans*-[V(η^5 -C₅H₅)₂(PMes)₂] (1)

V–P	2.397(1)	V–C(1)	1.907(4)
V–C(2)	1.924(4)	V–C(3)	1.939(4)
V–C(5)	2.240(4)	V–C(6)	2.243(5)
P–C(9)	1.830(4)	P–P(A)	2.052(2)
O(1)–C(1)	1.154(5)	O(2)–C(2)	1.158(5)
O(3)–C(3)	1.150(5)	C(4)–C(5)	1.419(6)
C(4)–C(8)	1.410(5)	C(5)–C(6)	1.414(6)
C(6)–C(7)	1.409(6)	C(7)–C(8)	1.399(6)
C(9)–C(10)	1.402(5)	C(9)–C(14)	1.412(5)
C(10)–C(11)	1.389(5)	C(10)–C(15)	1.521(5)
C(11)–C(12)	1.387(5)	C(12)–C(13)	1.385(6)
C(12)–C(16)	1.508(6)	C(13)–C(14)	1.390(5)
C(14)–C(17)	1.503(6)	V–Cp centroid	1.924(5)
P–V–C(1)	123.8(1)	P–V–C(2)	76.7(1)
C(1)–V–C(2)	73.7(2)	P–V–C(3)	78.3(1)
C(1)–V–C(3)	73.9(2)	C(2)–V–C(3)	116.5(2)
P–V–C(5)	142.2(1)	C(1)–V–C(5)	89.9(2)
C(2)–V–C(5)	134.7(2)	C(3)–V–C(5)	97.8(2)
P–V–C(6)	144.9(1)	C(1)–V–C(6)	86.8(2)
C(2)–V–C(6)	99.2(2)	C(3)–V–C(6)	131.4(2)
C(5)–V–C(6)	36.8(2)	V–P–C(9)	122.4(1)
V–P–P(A)	134.3(1)	C(9)–P–P(A)	103.1(1)
V–C(1)–O(1)	179.6(3)	V–C(2)–O(2)	174.9(4)
V–C(3)–O(3)	174.5(4)	C(5)–C(4)–C(8)	107.6(4)
V–C(5)–C(4)	72.9(2)	V–C(5)–C(6)	71.7(3)
C(4)–C(5)–C(6)	107.5(4)	V–C(6)–C(5)	71.5(3)
V–C(6)–C(7)	73.5(3)	C(5)–C(6)–C(7)	108.3(4)
C(6)–C(7)–C(8)	107.9(3)	C(4)–C(8)–C(7)	108.7(4)
P–C(9)–C(10)	120.3(2)	P–C(9)–C(14)	119.6(3)
C(10)–C(9)–C(14)	120.1(3)	C(9)–C(10)–C(11)	118.9(3)
C(9)–C(10)–C(15)	121.8(3)	C(11)–C(10)–C(15)	119.2(3)
C(10)–C(11)–C(12)	121.9(4)	C(11)–C(12)–C(13)	118.3(3)
C(11)–C(12)–C(16)	121.6(4)	C(13)–C(12)–C(16)	120.0(3)
C(12)–C(13)–C(14)	122.1(3)	C(9)–C(14)–C(13)	118.4(3)
C(9)–C(14)–C(17)	122.3(3)	C(13)–C(14)–C(17)	119.2(3)

thought that the use of a metal in a slightly higher oxidation state V(–1), (whereas Fe(–2) and Cr(–2) as [Fe(CO)₄]^{2–} and [Cr(CO)₅]^{2–} were previously used) might lead to greater electrophilicity at the metal which could reduce the donor properties of the phosphorus lone pair and the tendency of the L_nMPR moiety to react further. However, the use of V(η^5 -C₅H₅)(CO)₃ moiety (bulkier and in higher oxidation state than either [Fe(CO)₄]^{2–} and [Cr(CO)₅]^{2–}) did not prevent the dimerization to give **1**.

The title compound, **1**, has a *trans*-planar C(9)VP = P'V'(C9') core with a P–P' distance of 2.052(2) Å. This short distance in combination with the planarity of the core confirms the presence of a P–P double bond. The low ³¹P chemical shift, a singlet at 426 ppm, is also consistent with the double bond formulation. The V–P bond length, 2.397(1) Å is shorter than those normally found in vanadium-phosphane complexes as indicated by the V–P distances 2.486(2) and 2.472(2) Å in

Table 4

The V–P bond distances (Å) and selected IR $\nu(\text{CO})$ cm^{-1} for compounds 1–6

Compound	V–P	IR	Ref.
[($\eta^5\text{-C}_5\text{H}_5$)(CO) ₃ V] ₂ {PMes} ₂] (1)	2.397(1)	1943, 1870(Nuj)	This work
[($\eta^5\text{-C}_5\text{H}_5$)V(CO) ₂] ₂ PAr] (2)	2.255(Av)	1985, 1930 1910, 1855(Hex)	5
[($\eta^5\text{-C}_5\text{H}_5$)V(CO) ₄] (3)	–	2030, 1930(Benz)	12
[($\eta^5\text{-C}_5\text{H}_5$)V(CO) ₃ PPh ₃] (4)	–	1953, 1858(Benz)	12
[($\eta^3\text{-C}_3\text{H}_5$)V(CO) ₄ PPh ₃] (5)	2.486(2)	2052, 2000 1962, 1919 1875, 1819(THF)	10
[($\eta^5\text{-C}_5\text{H}_5$) ₂ V ₂ (CO) ₄ PPh ₃] (6)	2.472(2)	1932, 1871 1819, 1773(Benz)	11

complexes **5** [11] and **6** [12] of Table 4. However, the VP bond is significantly longer than the average value, 2.255 Å, in the phosphinidene complex **2** [5]. The shorter V–P bond in the latter is due to its partial multiple bond character. It is also notable that the PP bond length, 2.052(2) Å, is marginally longer than those in the chromium [5] and iron complexes [4] of dimesityldiphosphene in Table 4. The trend in the M–P distance V–P > Cr–P > Fe–P can be accounted for in terms of increasing metal size and it could also be argued that the vanadium in **1** has a higher effective coordination number than the chromium or iron complexes **6** or **7**.

The trend in the P–P bond lengths requires a more complex explanation which has to be consistent with three observations regarding **1**. These involve (i) the shorter V–P bond, (ii) the slightly longer P–P distance, (iii) much lower CO stretching frequencies in comparison with [V($\eta^5\text{-C}_5\text{H}_5$)(CO)₄] (**3**) [13], and similar CO stretching frequencies to [V($\eta^5\text{-C}_5\text{H}_5$)(CO)₃PPh₃] (**4**) [13] (Table 3). The data must also be considered in light of calculations on hypothetical systems [14] such as [{Cr(CO)₅]₂(P₂H₂)] which indicate considerable interaction between filled metals *d*-orbitals and the unfilled *b_g*, π^* -orbitals of the ligand as well as the σ interaction involving the ligand *a_g* orbitals.

The shorter V–P bond in **1** compared to the phosphane complex **4** may be partly accounted for in terms of good σ -donor characteristics and the low steric requirements of this particular diphosphene ligand. It should also be kept in mind that phosphorus has a lower coordination number in the diphosphene complex **1** than in a normal phosphane complex such as **4**. In addition, the hybridization in the lone pair orbital in a diphosphene is close to sp^2 whereas in a phosphane it varies between almost purely *s* character and sp^3 . These factors may contribute to the observed shorter V–P distance. These considerations aside, it could be argued that strong back donation from the metal *d*-orbital to the P–P π^* (*b_g*) orbital would also result in a short V–P bond and consequently a longer P–P bond. However, the P–P distance is only slightly lengthened compared to the distances in free diphosphenes [15]. However, some lengthening is to be expected since the coordination number at phosphorus is increased from two to three. In addition, the much lowered CO frequencies in the complex **1** indicate significantly increased back bonding from the

Table 5

Structural and IR ν CO Data for complexes, 1, 6, 8 and Related Chromium and Iron Phosphane Complexes

Complexes	P=P (Å)	M-P (Å)	IR (cm ⁻¹)	Ref.
<i>trans</i> -[$\{(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3\}_2(\text{PMes})_2$] (1)	2.052(2)	2.397(1)	1943, 1870 (Nujol)	This work
<i>trans</i> -[$\{\text{Cr}(\text{CO})_5\}_2(\text{PMes})_2$] (6)	2.037(7)	2.329(4)	2077, 2003, 1967 (Nujol)	4
<i>trans</i> -[$\{\text{Fe}(\text{CO})_4\}_2(\text{PMes})_2$] (7)	2.029(Av)	2.189(Av)	2075, 1992 1973 (Nujol)	3
[Cr(CO) ₅ PPh ₃]			2066, 1988 1942 (CCl ₄)	15
[Cr(CO) ₅ {P(OPh) ₃ }]			2080, 2000 1960 (CCl ₄)	15
[Fe(CO) ₄ PPh ₃]			2059, 1984, 1946 (Cetane)	16
[Fe(CO) ₄ {P(OMe) ₃ }]			2063, 1991 1961, 1949 (Cetane)	17

metal to the remaining carbonyls when a CO is substituted by the end-on bonded diphosphene. This in turn indicates that bonding to the diphosphene involves a much lower π -acid/ σ -donor ratio than that seen for CO. Indeed, if the carbonyl stretching frequencies in **1** are taken to be a rough guide (Table 4) the diphosphene has comparable bonding characteristics to PPh₃. In the case of the chromium diphosphene complex the CO stretching frequencies (see Table 5) fall between those of Cr(CO)₅PPh₃ [16] and Cr(CO)₅{P(OPh)₃} [16] while for the iron diphosphene the CO frequencies are about 10 cm⁻¹ higher than those found for Fe(CO)₄PPh₃ [17] and Fe(CO)₄P(OMe)₃ [18]. It is also notable that the P-P distances in the chromium and iron diphosphene complexes are only marginally longer than those in free diphosphenes.

The above discussion may be summarized as follows: (i) the P-P bond length in a diphosphene ligand increases slightly upon complexation to a transition metal and the increase is greatest in the case of **1**; (ii) the M-P distances are marginally shorter than those seen in other metal phosphane complexes; (iii) the ν (CO) frequencies in metal carbonyl complexes of diphosphenes indicate that π -acceptor/ σ -donor ratio for diphosphenes is relatively low and is comparable to tri-arylphosphanes in the case of **1**. In the light of these data we conclude that the major interaction between diphosphenes and metal carbonyls involves an interaction of the σ -type, and that π -back bonding from the metal is a minor contribution. Thus, although from symmetry considerations and MO calculations on an idealized chromium system the extent of back donation is quite large (0.3 e to the empty b_g 'antibonding' level), the currently available structural and spectroscopic data for diphosphene complexes offer only limited support for this conclusion.

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