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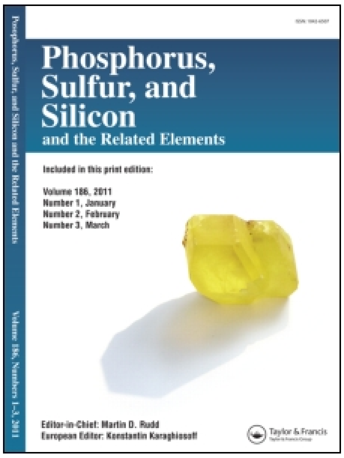

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Phosphorus Complexes Derived from Halfsandwich Vanadium Compounds

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PHOSPHORUS COMPLEXES DERIVED FROM HALFSANDWICH VANADIUM COMPOUNDS

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Abstract The photo-induced decarbonylation of the cyclopentadienyl complexes Cp*V(CO)$_4$ and CpV(CO)$_4$ (Cp* = η^5-$C_5(CH_3)_5$, Cp = η^5-C_5H_5) in tetrahydrofuran solution in the presence of white phosphorus, P_4, has been investigated, and the new carbonyl-containing products have been characterized by ^{1}H, ^{13}C, ^{31}P and ^{51}V NMR spectroscopy. The corresponding thermal decarbonylation in boiling xylene leads to the carbonyl-free tripledeckers $Cp^*_2V_2P_6$ and $Cp_2V_2P_6$; in the case of CpV(CO)$_4$, a tetranuclear product $Cp_4V_4P_6$ is also formed. X-Ray structure analyses have been carried out for the cyclo-P_4 bridged compound $Cp^*(CO)_2V[\mu(\eta^4,\eta^1)$-$P_4]V(CO)_3Cp^*$ and for the pseudocubane $Cp_4V_4(P_3)_2$.

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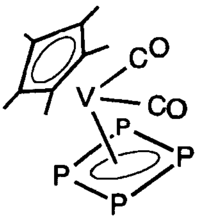
INTRODUCTION

White phosphorus, P_4, is the common source for unsubstituted ("naked") phosphorus ligands, and a large number of transition metal complexes containing P_x units (x = 2-6) has been prepared by thermolysis of carbonylmetal compounds in the presence of P_4 in solution [1,2,3]. In addition, the photo-induced decarbonylation provides the opportunity to isolate carbonyl-containing intermediates [4,5]. In this respect, the halfsandwich Cp*V(CO)$_4$ is expected to be a good model system, both because the voluminous Cp* ring ligand protects the carbonyl hemisphere where the incorporation and conversion of P_x fragments takes place, and because diamagnetic products may be unequivocally identified by their ^{51}V NMR spectra. The only oligophosphorus complex of vanadium known so far is the tripledecker Cp*V[μ,η^6-P_6]VCp*, first synthesized by Scherer et al.[6] via co-thermolysis of Cp*V(CO)$_4$ and P_4 in boiling xylene.

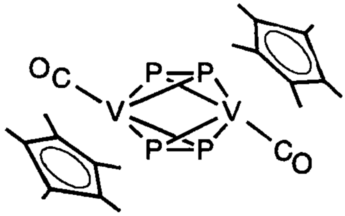
DECARBONYLATION OF Cp*V(CO)$_4$

Both mono- and dinuclear carbonylvanadium complexes (1-4) were formed when a tetrahydrofuran (thf) solution of the permethylated halfsandwich Cp*V(CO)$_4$ was irradiated in the presence of P_4 (V:P = 1:3) at 0°C. Two of the products, 1 and 3, are the expected vanadium analogues of related niobium and tantalum compounds which were obtained by Scherer and coworkers [4,5] in the corresponding photoreactions starting from Cp*Nb(CO)$_4$ [4] and (η^5-$C_5H_3{}^tBu_2$)Ta(CO)$_4$ [5], respectively.



1 (orange)
Cp*V(CO)$_2$(η^4-P_4)

ν(CO) 1982, 1945 cm^{-1}
δ ^{51}V -1034 ppm



3 (green)
Cp*(CO)V[μ(η^2-P_2)$_2$]V(CO)Cp*

ν(CO) 1875 cm^{-1} (hexane)
δ ^{51}V +625 ppm (C_6D_6)

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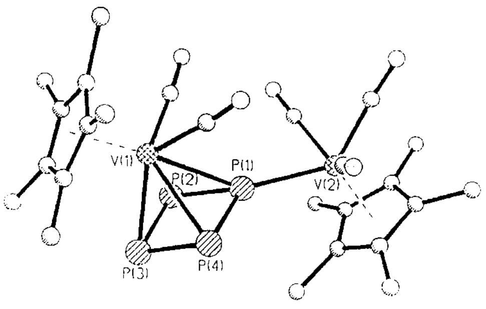
Two additional products were observed in the case of vanadium: a black, paramagnetic material Cp*V(CO)$_2$(P_x) (2) of unknown phosphorus content (x = 3?) and a redbrown dinuclear, P_4-bridged complex 4 in which a [Cp*V(CO)$_3$] fragment is attached to the cyclo-P_4 ring of 1. The molecular geometry of 4 has been determined by an X-Ray structure analysis.



V(1)-P(1)	258.2(1) pm
V(1)-P(2)	257.5(1)
V(1)-P(3)	250.9(1)
V(1)-P(4)	256.9(1)
V(2)-P(1)	237.2(1)
P - P	214.7 av.

FIGURE 1 Molecular structure of Cp*(CO)$_2$V[μ(η^4,η^1)-P_4]V(CO)$_3$Cp* (4)

Complexes 1-4 are air-sensitive and soluble in polar solvents such as CH_2Cl_2 and thf. The tripledecker Cp*V[μ,η^6-P_6]VCp* (5) [6] is not formed in the photoreaction, although all compounds 1-4 are converted to 5 upon prolonged thermal treatment either with or without P_4. Apparently, the tripledecker 5 is the thermodynamically stable end-product in the system Cp*V$(CO)_4$/P_4. The EI- and FD mass spectra of 2 indicate the exclusive formation of 5 upon ionization of 2.

DECARBONYLATION OF CpV$(CO)_4$

In contrast to the permethylated halfsandwich Cp*V$(CO)_4$, the unsubstituted complex CpV$(CO)_4$, upon irradiation in the presence of P_4 in thf solution, gave only the binuclear, P_4-bridged product Cp$(CO)_2$V[μ(η^4,η^1)-P_4]V$(CO)_3$Cp (4a). On the other hand, co-thermolysis of CpV$(CO)_4$ and P_4 in boiling xylene produced a mixture of the tripledecker CpV[μ,η^6-P_6]VCp (5a) and a new pseudocubane cluster $Cp_4V_4(P_3)_2$ (6a). According to the X-Ray structure analysis, 6a may be described as a combination of two interpenetrating CpV[μ,η^3-P_3]VCp units.

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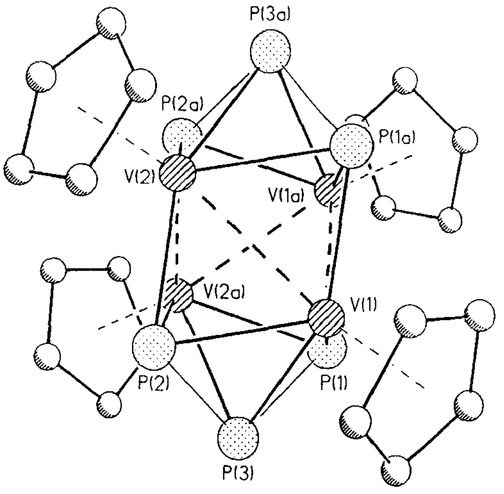
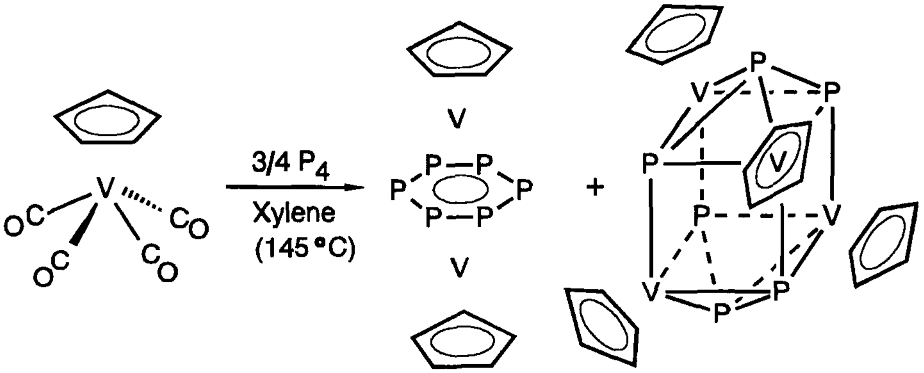


V(1)-P(1)	245.4(1) pm
V(1)-P(2)	244.2(1)
V(1)-P(3)	243.2(1)
V(1)-P(1a)	235.2(1)
V(1)-P(2a)	410.7(1)
P(1)-P(2)	354.2(1)
P(1)-P(3)	217.8(1)
P(2)-P(3)	217.9(1)
P(1)-P(3)-P(2)	108.80(9)°

FIGURE 2 Molecular structure of $Cp_4V_4(P_3)_2$ (6a)

The steric demand of the five-membered cyclopentadienyl ring ligand apparently determines whether the tetranuclear pseudocubane cluster can be formed in addition to the tripledecker (Scheme I):

SCHEME I



Ring Ligand	Yield	
η^5-C_5H_5 (Cp)	23.8%	51.6%
η^5-C_5H_4Me (Cp')	28.3%	21.3%
η^5-C_5H_7 (indenyl)	22.4%	—
η^5-C_5Me_5 (Cp*)	39.0%	—

A similar influence of the ring substituents has been noted in the series of vanadium-chalcogen complexes [7]: Decarbonylation of $Cp^*V(CO)_4$ in the presence of sulfur leads to dinuclear products $Cp^*V[S_n]VCp^*$ ($n = 5,4$) which remain dinuclear upon desulfuration by P^nBu_3 to give $Cp^*V[(\mu\text{-}S)_3]VCp^*$ [7], whereas the $Cp'V[S_n]VCp'$ ($n = 4$) analogue is converted to the vanadium-sulfide clusters $Cp'_4V_4(\mu_3\text{-}S)_4$ and $Cp'_5V_5(\mu_3\text{-}S)_5$ by sulfur abstraction [8].

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