Synthesis, Spectroscopic Properties and Molecular Structure of the Paramagnetic Complex [(η^5-3,5-di-*tert*-butyl-1,2,4-triphosphacyclopentadienyl)(η^5-2,4,5-tri-*tert*-butyl-1,3-diphosphacyclopentadienyl)]vanadium(II)

F. Geoffrey N. Cloke,* Kevin R. Flower, Peter B. Hitchcock and John F. Nixon*

School of Chemistry and Molecular Sciences, University of Sussex, Brighton, UK BN1 9QJ

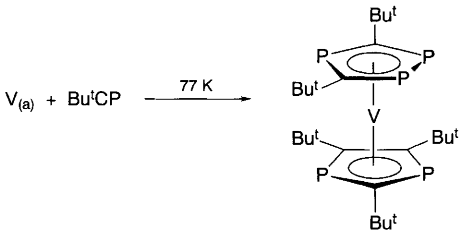
Cocondensation of vanadium vapour with the phosphaalkyne Bu^tCP affords the paramagnetic complex [V(η^5-$P_3C_2Bu^t_2$)(η^5-$P_2C_3Bu^t_3$)], whose molecular structure is determined by a single crystal X-ray diffraction study.

Phosphaalkynes have been shown to undergo oligomerisation reactions at transition metal centres, affording a variety of phosphorus-containing ring systems such as 3,5-di-*tert*-butyl-1,2,4-triphosphacyclopentadienyl, 2,4,5-tri-*tert*-butyl-1,3-diphosphacyclopentadienyl, 1,3-diphosphacyclobutadiene and 1,3,5,7-tetraphosphabarrelene.[1–5] Recently we reported the first direct cocondensation of a metal vapour with phosphaalkynes to afford the homoleptic tris-(η^4-1,3-diphosphacyclobutadiene)molybdenum.[6] Subsequent extension of this synthetic approach led to the preparation of the novel phosphirenyl cation $(PC_2Bu^t_2)^+$ ligated to nickel.[7] Herein, we report that cocondensation of vanadium atoms with Bu^tCP yields the novel paramagnetic pentaphosphavanadocene [V(η^5-$P_3C_2Bu^t_2$)(η^5-$P_2C_3Bu^t_3$)].

Cocondensation of electron-beam generated vanadium atoms with an excess of Bu^tCP at 77 K afforded a product of empirical formula [V($Bu^tCP)_5$] in *ca.* 20–30% yield (*ca.* 1–1.5 g based on vanadium), which mass spectral, analytical,† magnetic and EPR‡ data show to be the paramagnetic pentaphosphametallocene [V(η^5-$P_3C_2Bu^t_2$)(η^5-$P_2C_3Bu^t_3$)] **1**, see Scheme 1. Compound **1** was obtained as orange–brown air-sensitive crystals either by sublimation at 160 °C (10^{-5} mbar) or recrystallisation from pentane at −30 °C.

The single-crystal X-ray diffraction study§ (Fig. 1) confirms the formulation and shows that the ($P_3C_2Bu^t_2$) and ($P_2C_3Bu^t_3$) rings are parallel and eclipsed with the *tert*-butyl groups arranged so as to minimise inter-ring interactions. When compared to the previously reported structures for the analogous iron[8] and chromium[9] compounds, there is a noticeable lengthening of the metal–ring bond distances in **1**: *e.g.* V–C 2.42, Cr–C 2.30, Fe–C 2.20, V–P 2.56, Cr–P 2.45, Fe–P 2.33 and V–R_c 1.97, Cr–R_c 1.81 and Fe–R_c 1.69 Å (where R_c is the ring centroid). These elongations are larger than can be accounted for simply by the change in metal covalent radii (V 1.32, Cr 1.25 and Fe 1.24 Å).[10] It is also interesting to note that this phenomenon can also be seen in the analogous metallocenes [M(η-$C_5H_5)_2$] (M = V, Cr or Fe), where V–R_c 1.92,[11] Cr–R_c 1.79[12] and Fe–R_c 1.66 Å (where R_c = C_5H_5 ring centroid),[13] and has been rationalised in terms of the stepwise reduction in the number of bonding electrons for the open shell molecules.[14]

The solution magnetic moment‡ of 3.54 μ_B for **1** measured by the variable-temperature Evans' method[15] and the bulk susceptibility measurement of 3.58 μ_B are both close to the expected spin-only value for an S = 3/2 system. The EPR spectrtum of **1** (Fig. 2) in toluene at room temperature is broad; however, the frozen solution spectrum at 77 K is reasonably well resolved in the perpendicular region which displays vanadium hyperfine coupling (^{51}V, I = 7/2, 99.75%). The spectrum is consistent with the non-axial symmetry of **1**, but all attempts at accurate simulation, and hence extraction of accurate, fully anisotriopic *A* and *g* values, have been un-



Scheme 1

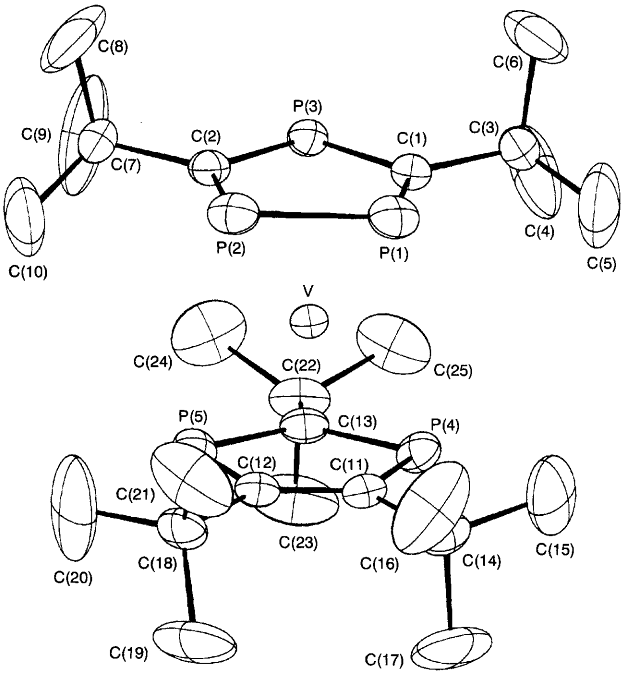


Fig. 1 Molecular structure of [V(η^5-$P_3C_2Bu^t_2$)(η^5-$P_2C_3Bu^t_3$)] **1** (thermal ellipsoids at 50%). Selected bond lengths (Å) and angles (°): V–C(1) 2.421(4), V–C(2) 2.423(4), C–P(1) 2.567(2), V–P(2) 2.567(2), V–P(3) 2.560(2), V–C(11) 2.383(4), V–C(12) 2.391(4), V–C(13) 2.402(4), V–P(4) 2.5216(14), V–P(5) 2.5226(14), V–R_c(1) 1.972, V–R_c(2) 1.977; R_c(1)–V–R_c(2) 179.5 [where R_c(1) and R_c(2) are the ring centroids of the upper and lower rings, respectively].

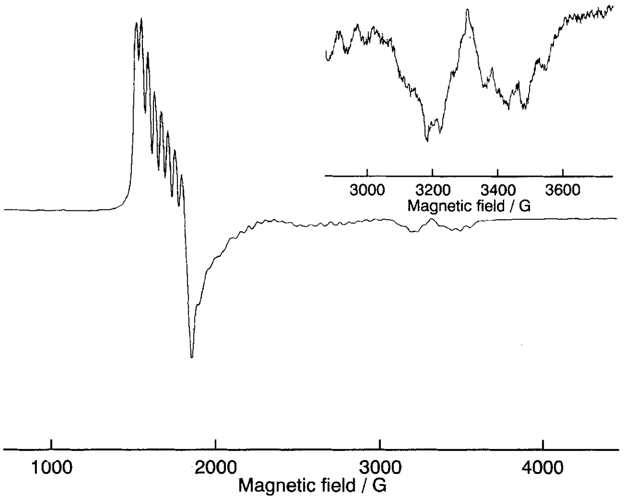


Fig. 2 Frozen solution EPR spectrum of **1**. *Inset*: expansion of low intensity region.

successful; estimated values for the main perpendicular feature are $g = 4.032$ and $A = 40$ G. The weak features in the parallel region of the spectrum may involve both vanadium and phosphorus coupling or possibly a formally forbidden $M_s = 2$ transition, but the present data do not allow us to comment further on this. However, the essential features of the EPR spectrum of **1** are very similar to that of vanadocene,[16] which, together with the magnetic data, imply a $^4A_{1g}(e_{2g}{}^2a_{1g}{}^1)$ ground state for **1** also.

The comparatively high yield of **1** is also noteworthy; the only other paramagnetic phosphametallocene is $[Cr(\eta^5\text{-}P_3C_2Bu^t{}_2)_2]$, obtained by a conventional route in extremely low ($\ll 1\%$ yield).[8] Interestingly, similarly low yields of $[Cr(\eta^5\text{-}P_3C_2Bu^t{}_2)_2]$ (identified by its mass spectrum) were also obtained from the direct reaction of chromium atoms with Bu^{t}CP. The availability of reasonable quantities of **1** will thus allow exploration of the chemistry of an electron-deficient phosphametallocene. Studies in this area are in progress.

We thank the EPSRC for financial support and Mr C. Dadswell for recording the EPR spectrum.

Received, 3rd May 1995; Com. 5/02832I

Footnotes

† $C_{25}H_{45}P_5V$: MS (EI, 70 eV), m/z 551 (M^+, 100%), with the expected isotope pattern. Satisfactory elemental analysis (CH) was obtained.

‡ μ_{eff} (solution, variable-temperature Evans' method 255–295 K) = 3.54 μ_B; μ_{eff} (solid, Johnson Matthey magnetic susceptibility balance, 295 K) = 3.58 μ_B. EPR (toluene, 77 K).

§ *Crystal data*: $C_{25}H_{45}P_5V$, $M = 551.4$, monoclinic, space group $P2_1/n$ (non-standard no. 14), $a = 10.429(5)$, $b = 16.672(5)$, $c = 17.137(5)$ Å, $\beta = 91.84(3)°$, $U = 2978$ Å^3, $Z = 4$, $D_c = 1.23$ g cm^{-3}, $F(000) = 1172$. Monochromated Mo-Kα radiation, $\lambda = 0.71073$, $\mu = 6.7$ cm^{-1}, $T = 293$ K. Data were collected on an Enraf-Nonius CAD 4 diffractometer in the θ–2θ mode using a crystal of *ca.* 0.4 × 0.4 × 0.2 mm. A total of 5244 unique reflections were measured for $2 < \theta < 25°$ and $+h, +k, \pm l$, and used in the refinement based on F^2 using SHELXL-93.[17] The structure was solved by direct methods using SHELXS-86[18] and non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms were included in the riding mode with $U_{iso} = 1.5\,U_{eq}$ for the parent carbon. The final residuals were $R1 = 0.051$ [for 3841 reflections with $I > 2\sigma(I)$] and $wR2 = 0.152$ (for all data). The drawing was prepared using CAMERON.[19] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 P. B. Hitchcock, M. J. Maah and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1986, 737.

2 P. Binger, R. Milczarek, R. Mynott, M. Regitz and W. Rosch, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 644; P. Binger, R. Milczarek, R. Mynott, C. Kruger, Y. H. Tsay, E. Rabbe and M. Regitz, *Chem. Ber.*, 1988, **121**, 637.

3 M. Driess, D. Hu, H. Pritzkow, H. Schaufele, U. Zenneck, M. Regitz and W. Rosch, *J. Organomet. Chem.*, 1987, **334**, C35.

4 J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327; J. F. Nixon, *Coord. Chem. Rev.*, in the press.

5 P. Binger, G. Glaser, B. Gabor and R. Mynott, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 81.

6 F. G. N. Cloke, K. R. Flower, P. B. Hitchcock and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1994, 489.

7 A. G. Avent, F. G. N. Cloke, K. R. Flower, P. B. Hitchcock, J. F. Nixon and D. M. Vickers, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2330.

8 R. Bartsch, P. B. Hitchcock and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1987, 1146.

9 R. Bartsch, P. B. Hitchcock and J. F. Nixon, *J. Organomet. Chem.*, 1988, **356**, C1.

10 J. Emsley, *The Elements*, Clarendon, Oxford, 1989, 52, 96, 210.

11 R. D. Rodgers, J. L. Atwood, D. Foust and M. D. Rausch, *J. Cryst. Mol. Struc.*, 1981, **11**, 183.

12 K. R. Flower and P. B. Hitchcock, *J. Organomet. Chem.*, 1995, in the press.

13 P. Seiler and J. Dunitz, *Acta Crystallogr., Sect. B.*, 1979, **35**, 1069.

14 A. Haaland, *Acc. Chem. Res.*, 1978, **12**, 415.

15 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

16 J. L. Robbins, N. Edlestein, B. Spencer and J. C. Smart, *J. Am. Chem. Soc.*, 1982, **104**, 1882, and references cited therein.

17 G. M. Sheldrick, SHELXL-93, Program for crystal structure refinement, University of Göttingen, Germany, 1993.

18 G. M. Sheldrick, SHELXS-86, Program for the solution of crystal structures, University of Göttingen, Germany, 1985.

19 D. J. Watkin and L. J. Pearce, CAMERON, an interactive graphics editor, University of Oxford, UK, 1993.