

# Low valent carbonylvanadium complexes of the triphosphorus macrocycle 12[ane]P<sub>3</sub>Et<sub>3</sub>

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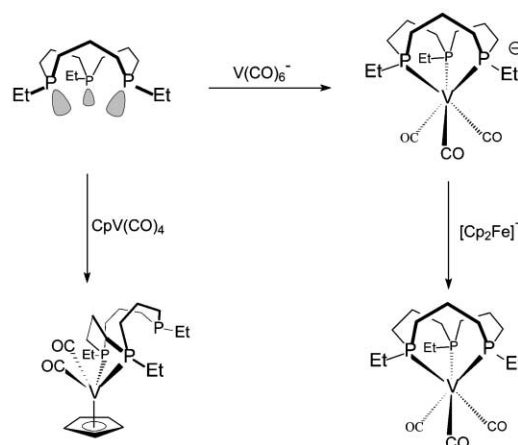
The triphosphorus macrocycle 1,5,9-triethyl-1,5,9-triphosphacyclododecane, 12[ane]P<sub>3</sub>Et<sub>3</sub>, reacts with [V(CO)<sub>6</sub>]<sup>−</sup> under photolytic conditions to produce *fac*-[(12[ane]P<sub>3</sub>Et<sub>3</sub>)V(CO)<sub>3</sub>]<sup>−</sup> (**1**) which has been isolated as its Et<sub>4</sub>N salt. This can be oxidised to the neutral 17 electron complex *fac*-[(12[ane]P<sub>3</sub>Et<sub>3</sub>)V(CO)<sub>3</sub>] (**2**), which has been characterised by EPR spectroscopy. Density functional calculations support the spectroscopic observations and give insight into the bonding. The V(0) compound cannot be further oxidised, but the macrocycle reacts with CpV(CO)<sub>4</sub> thermally or photolytically to produce *cis*-[(η<sup>5</sup>-12[ane]P<sub>3</sub>Et<sub>3</sub>)V(η<sup>5</sup>-Cp)(CO)<sub>2</sub>] (**3**). The diamagnetic compounds have been characterised by IR and multinuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>51</sup>V) NMR spectroscopy.

## Introduction

Vanadium carbonyls stabilised by phosphine donors have long been known.<sup>1</sup> Complexes with η<sup>1</sup>-coordinated phosphines tend to be labile and chelating ligands have been studied in order to enhance the stability of resulting complexes. Not surprisingly, larger chelate ring sizes have been shown to decrease stability<sup>2</sup> and rigid chelating ligands<sup>3</sup> enhance stability. Studies of linear acyclic and tripodal triphosphines have shown these ligands to have variable, in some cases unpredictable, coordination modes and monodentate,<sup>4</sup> bidentate,<sup>4</sup> bridging,<sup>5</sup> and meridional<sup>4</sup> or facial<sup>6</sup> tridentate examples are known, a cyclopentadienyl η<sup>3</sup>-triphosphine carbonyl complex has been shown to exhibit facile fluxionality.<sup>7</sup> Two more recent studies have also demonstrated the utility of tripodal triphosphines in the stabilisation of V(0) and V(1) carbonyls.<sup>8</sup> The ligand used in these studies supports a facially capping coordination mode, but also as is common for tripodal ligands, freedom of backbone bond rotation allows selective dissociation which in this case also enables a bridging configuration, the ligand being bidentate to one metal and monodentate to the other.<sup>8a</sup> We are interested in the study of kinetically robust phosphine complexes and have commented on applications of 12-membered triphosphorus macrocycles based upon the 1,5,9-triphosphacyclododecane core (12[ane]P<sub>3</sub>R<sub>3</sub>) in this context.<sup>9</sup> These ligands are very well suited to facial coordination of metals, and due to the macrocyclic coordination effect they form robust complexes which are more resistant to dissociation than related tripodal ligands. Facially capping ligands also restrict remaining reaction sites to mutually *cis* orientations, a generally advantageous configuration for exploitation of reactivity in applications (*e.g.* in catalysis). We have explored these properties and have recently shown that enhanced reactivity is indeed supported where other more labile metal-tertiary phosphine complexes are known to be ineffective; examples include alkene polymerisations<sup>10</sup> and ring opening metathesis polymerisation.<sup>11</sup> These macrocyclic phosphines also stabilise early transition metal halide complexes;<sup>12</sup> there are, however, few examples of low valent compounds of 12[ane]P<sub>3</sub>R<sub>3</sub> ligands, these being presently restricted to the carbonyls of group 6 metals.<sup>13</sup> As well as stability arising from the macrocyclic coordination effect, the metal-phosphine interaction should be enhanced for softer, lower valence states. In this paper, we report the synthesis of a series of low valent vanadium carbonyl compounds in oxidation states −1, 0 and +1 containing the 12[ane]P<sub>3</sub>Et<sub>3</sub> ligand.

## Results and discussion

Vanadium carbonyl complexes of tripodal phosphines have previously been prepared by reduction of the V(III) halo-phosphine complexes under CO.<sup>8b</sup> Attempts to reduce the known M(III) complexes of 12[ane]P<sub>3</sub>Et<sub>3</sub> (M = Ti, V)<sup>12</sup> under a CO atmosphere did not yield a metal carbonyl; addition of a small labile phosphine (PMe<sub>3</sub>) to stabilise the unsaturated intermediates did not enable isolation of any carbonyl containing species. Photolysis of solutions of [Et<sub>4</sub>N][V(CO)<sub>6</sub>] in the presence of the macrocycle did however lead to substitution and the complex *fac*-{(12[ane]P<sub>3</sub>Et<sub>3</sub>)V(CO)<sub>3</sub>}[Et<sub>4</sub>N], (**1**), was isolated in good yield (Scheme 1). The <sup>31</sup>P NMR spectrum of (**1**) shows a broad signal at δ<sub>p</sub> = 34.8 ppm (ν<sub>1/2</sub> = 900 Hz) which remains broad on cooling to −40 °C. This is presumably due to unresolved coupling of the <sup>31</sup>P nucleus to <sup>51</sup>V (*I* = 7/2) and is common for V(−1) phosphine complexes. The <sup>51</sup>V nucleus is suited as an NMR probe due to its high abundance and sensitivity and has been used to study phosphine stabilised vanadium carbonyl compounds.<sup>14</sup> The <sup>51</sup>V NMR spectrum of (**1**) shows a quartet at δ<sub>v</sub> = −1691.3 ppm (<sup>1</sup>J<sub>v-p</sub> = 157.8 Hz) due to coupling to three magnetically equivalent phosphines, and is thus consistent with the structure proposed. The metal shielding and hence the chemical shift is influenced by the difference in energy between the HOMO and LUMO,<sup>15</sup> and changing from a strong π-acceptor ligand such as CO to a comparatively weaker phosphine induces a deshielding. The NMR data for (**1**) are



Scheme 1

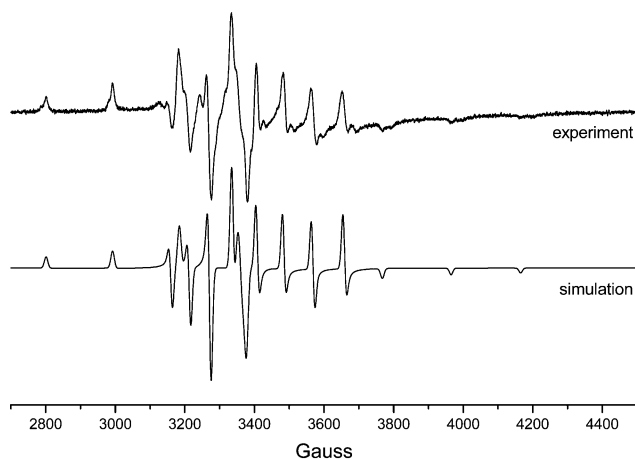
**Table 1** IR spectroscopic and  $^{51}\text{V}$  NMR data for V(-) and V(I) complexes

Complex	$\nu(\text{C}=\text{O})/\text{cm}^{-1}$	Medium	$^{51}\text{V}$ NMR	Ref.
$[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$	1835	Nujol	-1952	
$[\text{Et}_4\text{N}][12[\text{ane}]_3\text{P}_3\text{Et}_3\text{V}(\text{CO})_3]$	1894, 1857	THF	-1695	
$\text{mer}-[\text{V}(\text{CO})_3(\text{tetrphos})]^-^a$	1898, 1810, 1715	THF	-2027	29
$\text{mer}-[\text{V}(\text{CO})_3(\text{pp}_3)]^-^b$	1910, 1815, 1680	THF	-1695	16
$12[\text{ane}]_3\text{P}_3\text{Et}_3\text{Cr}(\text{CO})_3$	1911, 1813	Nujol	—	13
$12[\text{ane}]_3\text{P}_3\text{Et}_3\text{Mo}(\text{CO})_3$	1918, 1815	Nujol	—	13
$\text{CpV}(\text{CO})_4$	2024, 1920	Nujol	-1533	
$(\eta^2-12[\text{ane}]_3\text{P}_3\text{Et}_3)(\text{Cp})\text{V}(\text{CO})_2$	1844, 1765	Toluene	-1034	
$(\eta^1-12[\text{ane}]_3\text{P}_3\text{Et}_3)(\text{Cp})\text{V}(\text{CO})_3$	1950, 1866 <sup>c</sup>			
$\text{CpV}(\text{CO})_3$	1953, 1869, 1875	Nujol		22
$\text{CpV}(\text{CO})_2$	1914, 1813			
$\text{CpV}(\text{CO})$	1831			
$\text{CpV}(\text{CO})_3(\text{dppm})$	1950, 1872, 1845	THF		17(b)
$\text{CpV}(\text{CO})_2(\text{dppm})$	1871, 1808	THF	-974	

<sup>a</sup> tetrphos =  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2$ . <sup>b</sup>  $\text{pp}_3 = \text{P}[(\text{CH}_2)_3\text{PEt}_2]_3$ . <sup>c</sup> Third peak obscured by other bands.

consistent with reported 6-membered chelating tridentate phosphines (e.g.  $\delta_{\text{V}} = -1695$  ppm,  $^1J_{\text{P-V}} = 203$  Hz for  $\text{mer}-[(\text{pp}_3)\text{V}(\text{CO})_3]^-$  ( $\text{pp}_3 = \text{P}[(\text{CH}_2)_3\text{PEt}_2]_3$ ).<sup>16</sup> The  $^{13}\text{C}$  NMR spectrum shows only a broadened singlet at  $\delta_{\text{C}} = 220$  ppm for the carbonyl carbons, the broadening again presumably due to coupling to the vanadium nucleus. The IR spectrum of (**1**) shows two bands of equal intensities in the carbonyl stretching region, indicating three carbonyl ligands in a  $C_{3v}$  facial arrangement. The carbonyl stretching frequencies (1894, 1857  $\text{cm}^{-1}$ ) are in the same range as previously reported triphosphine complexes and are also close to the isoelectronic chromium and molybdenum macrocycle complexes (Table 1). In addition, the negative ion mass spectrum shows the molecular ion and the most intense peak is due to the loss of one CO ligand from the molecular ion.

(**1**) can be oxidised to the V(o) derivative,  $\text{fac}-(12[\text{ane}]_3\text{P}_3\text{Et}_3)\text{V}(\text{CO})_3$  (**2**) by  $[\text{Cp}_2\text{Fe}][\text{PF}_6]$  (Scheme 1) in good yield. In the mass spectrum, an intense peak is observed for the molecular ion minus one CO ligand. The IR spectrum shows the expected 2 bands at 2098 and 1962  $\text{cm}^{-1}$  again indicating a *fac* geometry. The bands have increased in energy, concordant with the decrease in electron density on the metal, and are similar to other reported phosphine stabilised V(o) complexes.<sup>17</sup> The magnetic moment indicates that (**2**) has a low spin  $d^5$  configuration ( $\mu_{\text{eff}} = 2.3 \mu_{\text{B}}$ ), as might be expected for complexes of  $\pi$ -acceptor ligands, and is consistent with other V(o) carbonyls. (**2**) has also been characterised by EPR spectroscopy (Fig. 1).



**Fig. 1** EPR spectrum of  $(12[\text{ane}]_3\text{P}_3\text{Et}_3\text{V})(\text{CO})_3$  (**2**) in  $\text{CD}_3\text{OD}/\text{CD}_3\text{CN}$  at 10 K.  $g_{\parallel} = 1.940$ ,  $g_{\perp} = 1.977$ ,  $A_{\parallel} = 546$  MHz,  $A_{\perp} = 199$  MHz. The weak shoulders in the experimental spectrum are due to a minor impurity in the frozen solution.

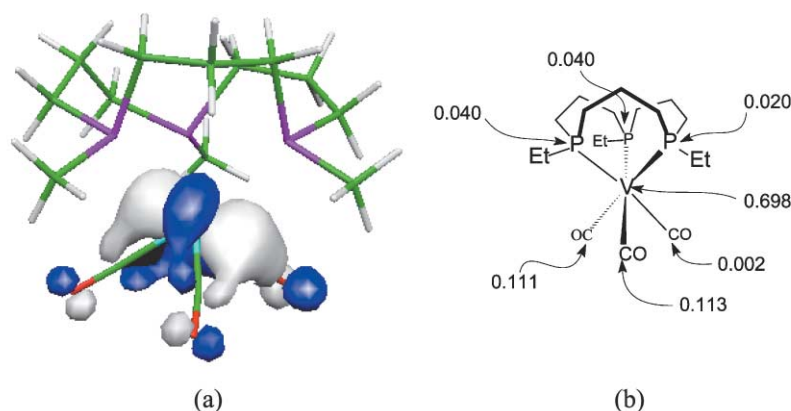
The EPR spectrum is consistent with the assignment of a low spin  $d^5$  system, and simulation of the spectrum reveals that the spin Hamiltonian parameters are  $g_{\perp} = 1.940$ ,  $g_{\parallel} = 1.977$ ,  $A_{\parallel} =$

546 MHz and  $A_{\perp} = 199$  MHz. Previous EPR studies on  $d^1$   $\text{fac}-(12[\text{ane}]_3\text{P}_3\text{Et}_3)\text{V}(\text{O})\text{Cl}_2$ <sup>12</sup> displayed the unmistakable superhyperfine pattern of a triplet of doublets arising from two equivalent  $^{31}\text{P}$  nuclei ( $a_{\text{iso}} = 73$  MHz) and one unique  $^{31}\text{P}$  nucleus with a smaller interaction ( $a_{\text{iso}} = 17$  MHz). There is no evidence for any similar superhyperfine structure in Fig. 1, indicating that a significantly reduced spin density exists on the three  $^{31}\text{P}$  nuclei in (**2**). The line-width of the vanadium peaks (Fig. 1) was ca. 39 MHz, so that any weak interaction with  $^{31}\text{P}$  must be buried under the intrinsic EPR line width (i.e., it will be less than 39 MHz).

The presence of alternative ligands which can  $\pi$ -bond efficiently with the metal may influence the extent to which the unpaired electron interacts with the P nuclei. In these complexes, the proposed structure requires that the phosphine donors coordinate *trans* to the carbonyl ligands. The unpaired electron would presumably reside in a metal orbital (for low spin  $d^5$ ) which is  $\pi$ -symmetric with respect to the M–ligand bonds. Thus the absence of interaction with the P nuclei may be explained if the carbonyls are significantly better  $\pi$ -acids than are the phosphines, which for tertiary alkyl phosphines of this nature is reasonable to assume.

Density functional theory (DFT) calculations support the observation that the unpaired electron density has little or no interaction with the  $^{31}\text{P}$  nuclei. The molecular orbital containing the unpaired electron is represented in Fig. 2, along with the spin densities of the metal and ligating atoms. It is clear that this MO has no overlap with the phosphine atoms or indeed the entire macrocycle, instead having substantial overlap with the  $\pi^*$  orbitals of the CO ligands. This leads in turn to very low spin densities for each phosphorus, which are approximately an order of magnitude less than those on CO, with almost 95% of the spin density residing on the vanadium centre and carbonyl ligands. Both the experimental spectroscopic data and DFT calculations support the view that the bonding between vanadium and phosphorus in this compound contains very little (if any)  $\pi$ -character.

The DFT calculations also allow estimation of the Fermi contact hyperfine coupling on  $^{31}\text{P}$ ; the  $a_{\text{iso}}$  values were estimated as 43.3, 44.9 and 22.4 MHz. Considering the theoretical Fermi contact term for  $^{31}\text{P}$  is 474.79 mT (13306 MHz),<sup>18</sup> a calculated value of only 44 MHz represents a very small spin density on the nucleus. Therefore this calculated value could be easily overestimated, and the real value is less than this but unresolved in the EPR spectrum due to the large linewidth of 39 MHz. Assuming two equivalent  $^{31}\text{P}$  nuclei produce a triplet hyperfine pattern, then the maximum experimental superhyperfine coupling constant will be ca. 20 MHz. It should be noted that the calculated  $^{51}\text{V}$  isotropic coupling (92.7 MHz) is significantly smaller than that observed experimentally ( $a_{\text{iso}} = 236$  MHz). However, a number of authors have reported a systematically



**Fig. 2** Representations of (a) molecular orbital containing the unpaired electron, (b) the spin densities associated with particular atoms in  $(12[\text{ane}]P_3\text{Me}_3)V(\text{CO})_3$ .

lower value of  $A$  (vanadium) using DFT calculations compared to the experimentally derived values.<sup>19</sup> This discrepancy has been attributed to deviations in the calculated  $A$  values due to spin polarisation and spin contamination effects which are not adequately treated by DFT methods.<sup>20</sup>

Finally, comment should be made on the presence of a small shoulder which is visible in the EPR spectrum of **(2)**. This weak feature is particularly apparent as a shoulder on the parallel components of the EPR spectrum. It appears that this feature arises from a minor contribution from a second  $V(\text{o})$  complex present in the poor quality glass of the frozen solution, and is not part of an associated superhyperfine structure due to  $^{31}\text{P}$ . This conclusion is reasonable since the observed separation between the shoulder and the main vanadium hyperfine lines increases towards higher fields (*i.e.*, second order influences on the  $^{51}\text{V}$  hyperfine pattern of the minor species, as opposed to a superhyperfine pattern on the main vanadium line where the separation would not be expected to increase).

The only other phosphine complexes of  $V(\text{o})$  studied by EPR are  $V(\text{CO})_4(\text{PP})$  where for  $\text{PP} = \text{dppe}$  the spin Hamiltonian parameters were reported as  $g_{\parallel} = 1.9996$  and  $g_{\perp} = 1.9981$  and for  $\text{PP} = \text{dppb}$ ,  $g_{\parallel} = 2.0004$  and  $g_{\perp} = 1.9989$ .<sup>17a</sup> The EPR spectra however were not presented in the paper and no discussion or reference was made to the presence or absence of any  $^{31}\text{P}$  interactions. For a system with a tetragonally distorted octahedral environment, the  $g$  values have the predicted form of  $g_{\perp} > g_{\parallel}$ ; the reported  $g$  values for *cis*- $V(\text{CO})_4(\text{PP})$  are however, difficult to justify since they have the form  $g_{\parallel} \approx 2.0023 > g_{\perp}$ , *i.e.* opposite to that expected for a pseudo octahedral environment and which can only be rationalised based on a low spin  $d^5$  transition metal ion experiencing a tetragonally distorted tetrahedral field. In our case for **(2)**, the  $g$  values have the expected form of  $g_{\perp} > g_{\parallel}$  and the spectrum is consistent with a facially capped octahedral geometry.

**(2)** could not be oxidised further without decomposition, but  $V(\text{i})$  carbonyls are known to be stabilised by cyclopentadienyl ligands. Moreover,  $\text{Cp}V(\text{CO})_x(\text{P})_y$  are also known, where  $\text{P} =$  mono- or bidentate phosphines.<sup>21</sup>  $\text{Cp}V(\text{CO})_4$  proved to be an appropriate starting material to investigate these complexes as the carbonyl ligands are readily substituted both thermally and photolytically in the presence of the macrocycle. The reaction of  $\text{Cp}V(\text{CO})_4$  with  $12[\text{ane}]P_3\text{Et}_3$  caused a colour change from orange to deep red upon UV photolysis and a red/brown powder **(3)** was isolated. Spectroscopic data are collected in Table 1. The  $^{31}\text{P}$  NMR spectrum at room temperature showed a broad peak at  $\delta_{\text{P}} = 53$  ppm ( $\nu_{1/2} = 559$  Hz) and a peak at  $\delta_{\text{P}} = -33.29$  ppm indicative of an unbound phosphine. On cooling to  $-20$  °C these resolve into broad resonances at  $\delta_{\text{P}} = +42$  and  $-39$  ppm ( $\nu_{1/2} = 302$  and  $206$  Hz respectively and thus  $^3J_{\text{P-P}}$  and  $^1J_{\text{P-V}}$  were unresolved). The  $^1\text{H}$  NMR spectrum shows a

singlet at  $\delta_{\text{H}} = 4.8$  ppm indicating a freely rotating Cp ligand relative to the NMR timescale, again any fine structure due to Cp protons was unresolved upon cooling. The  $^{51}\text{V}$  NMR spectrum consists of a broadened triplet at  $\delta_{\text{V}} = -1034.7$  ppm with  $^1J_{\text{P-V}} = 173.6$  Hz, which is similar to that for reported vanadium(*i*) phosphine complexes.<sup>21</sup> An intense ion corresponding to the loss of one CO ligand from the molecular ion was also observed in the mass spectrum, along with a weaker ion corresponding to the loss of both CO ligands. The same complex is obtained thermally. The reaction was followed by IR spectroscopy; two bands due to an intermediate ( $\nu_{\text{CO}} = 1950, 1866$   $\text{cm}^{-1}$ ) initially appeared and decayed as equally intense bands attributable to the product ( $\nu_{\text{CO}} = 1844, 1765$   $\text{cm}^{-1}$ ) grew. From these data it is possible to infer that the macrocycle is acting as a bidentate ligand with two carbonyl groups *cis* to each other and we propose a formulation, *cis*-( $\eta^2$ - $12[\text{ane}]P_3\text{Et}_3$ )-( $\eta^5$ -Cp) $V(\text{CO})_2$ , for **(3)** (Scheme 1). The intermediate is presumably the mono-substituted phosphine adduct, ( $\eta^1$ - $12[\text{ane}]P_3\text{Et}_3$ )-( $\eta^5$ -Cp) $V(\text{CO})_3$ , where the expected third  $\nu_{\text{CO}}$  absorption is obscured by other bands.

The non-phosphine containing vanadium dicarbonyl complex  $[\text{Cp}V(\text{CO})_2]$  has been prepared in a Nujol matrix,<sup>22</sup> and comparison of the IR stretches shows that the metal is binding more strongly to the remaining carbonyls, indicating that CO is a better  $\pi$ -acceptor than the phosphine, as expected. The CO stretches for **(3)** are similar to those reported with bidentate phosphines.<sup>21</sup>

## Conclusions

The triphosphorus macrocycle forms stable complexes starting from vanadium carbonyl precursors in which the macrocycle acts as a facially capping tridentate ligand for the simple carbonyls and as a bidentate chelating ligand for the cyclopentadienyl carbonyl. The diamagnetic compounds have been characterised by multinuclear NMR, and this has proved unequivocally their structure. Oxidation of the  $V(-\text{i})$  compound has enabled us to characterise a rare example of a  $V(\text{o})$  carbonyl complex by EPR spectroscopy. Spectroscopic and DFT calculations indicate the tertiary phosphine macrocycle to be a very poor  $\pi$ -acceptor in these compounds. Preliminary investigations also show that the heavier group 5 metals show similar reactivity.

## Experimental

All reactions were carried out in an atmosphere of dry nitrogen or argon passed through a CrO (supported on silica) column using standard Schlenk techniques or in a Vacuum Atmospheres glove box. All solvents were dried by refluxing

over standard drying agents and distilled immediately prior to use. The petroleum ether (petrol) used had a boiling point of 40–60 °C. The compounds 12[ane]P<sub>3</sub>Et<sub>3</sub><sup>9</sup> and [Et<sub>4</sub>N][V(CO)<sub>6</sub>]<sup>23</sup> were prepared by literature methods. All other chemicals were obtained from commercial sources and used as received, except CpV(CO)<sub>4</sub> which was sublimed before use. UV photolyses were carried out using a Hanovia 125 W mercury discharge lamp (254 nm). NMR spectra were recorded on a Bruker DPX-400 instrument at 400 MHz (<sup>1</sup>H) and 100 MHz (<sup>13</sup>C) or a Jeol FX-90Q at 36.23 MHz (<sup>31</sup>P) or a Jeol Lamda Eclipse 300 at 121.65 MHz (<sup>31</sup>P), 300.52 MHz (<sup>1</sup>H), 75.57 MHz (<sup>13</sup>C) and 78.91 MHz (<sup>51</sup>V). <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are relative to solvent resonances, <sup>31</sup>P chemical shifts are relative to 85% external H<sub>3</sub>PO<sub>4</sub> (δ = 0 ppm) and <sup>51</sup>V chemical shifts are relative to external VOCl<sub>3</sub> (δ = 0 ppm). Magnetic moments were determined by the Evans' method<sup>24</sup> or by the Gouy method on a Johnson Matthey magnetic susceptibility balance; an experimental diamagnetic correction was measured for 12[ane]P<sub>3</sub>Et<sub>3</sub> and applied. Mass spectra (APCI, with NH<sub>3</sub>) were recorded on a VG Platform II Fisons mass spectrometer. Infrared spectra were recorded on a Perkin Elmer 1600 or a Nicolet 510 FT-IR spectrometer in solution using KBr solution cells. The EPR spectrum was recorded on a CW X-band Bruker ESP 300E series spectrometer, operating at 12.5 kHz field modulation in a Bruker EN 801 cavity. All spectra were recorded at 10 K using an Oxford instruments ESR 900 continuous flow He cryostat. EPR simulations were carried out using the Bruker Simfonia program.

#### *fac*-(12[ane]P<sub>3</sub>Et<sub>3</sub>)V(CO)<sub>3</sub>[Et<sub>4</sub>N] (1)

[Et<sub>4</sub>N][V(CO)<sub>6</sub>] (0.05 g, 0.17 mmol) was dissolved in toluene (20 cm<sup>3</sup>) and a solution of 12[ane]P<sub>3</sub>Et<sub>3</sub> (0.05 g, 0.16 mmol) in toluene (5 cm<sup>3</sup>) was added. The resultant solution was irradiated for 20 minutes after which an orange precipitate in a yellow solution was obtained. The solid was filtered and dried *in vacuo*. Yield = 0.07 g (71%). (Found: C, 54.1; H, 8.9; N, 2.2%. C<sub>26</sub>H<sub>53</sub>NO<sub>3</sub>P<sub>3</sub>V requires: C, 54.64; H, 9.28; N, 2.45%). IR (THF): 1894 (s), 1857 (s). <sup>31</sup>P{<sup>1</sup>H} NMR, δ ppm (CD<sub>3</sub>CN, 20 °C): +34.82 (br,  $\nu_{1/2}$  = 900 Hz). <sup>51</sup>V NMR, δ ppm (CD<sub>3</sub>CN, 20 °C): -1691.3 (q) <sup>1</sup>J<sub>P-V</sub> = 157.8 Hz. <sup>13</sup>C NMR, δ ppm (CD<sub>3</sub>CN, 20 °C): 220.0 (br) CO, 26.43 (dd) (<sup>1</sup>J<sub>P-C</sub> = 15.7 Hz, <sup>3</sup>J<sub>P-C</sub> = 9.2 Hz), PCH<sub>2</sub>CH<sub>2</sub>; 18.80 (m), PCH<sub>2</sub>CH<sub>2</sub>; 9.6 (d) (<sup>2</sup>J<sub>P-C</sub> = 15.7 Hz) PCH<sub>2</sub>CH<sub>3</sub>; 6.61 (s) PCH<sub>2</sub>CH<sub>3</sub>; 51.45 (s) NCH<sub>2</sub>CH<sub>3</sub>; 4.72 (s) NCH<sub>2</sub>CH<sub>3</sub>. <sup>1</sup>H NMR, δ ppm (CD<sub>3</sub>CN, 20 °C): 0.6–1.9 overlapping multiplets (macrocycle protons + CH<sub>3</sub>CH<sub>2</sub>N); 3.15 (q) ( $J_{H-H}$  = 7.2 Hz) (CH<sub>3</sub>CH<sub>2</sub>N). *m/z* (negative ion APCI) 441.2 [M<sup>+</sup>, 10%], 413.2 [M – CO, 100%].

#### *fac*-(12[ane]P<sub>3</sub>Et<sub>3</sub>)V(CO)<sub>3</sub> (2)

[Et<sub>4</sub>N][(12[ane]P<sub>3</sub>Et<sub>3</sub>)V(CO)<sub>3</sub>] (0.05 g, 0.1 mmol) and [Cp<sub>2</sub>Fe][PF<sub>6</sub>] (0.03 g, 0.1 mmol) were dissolved in THF (10 cm<sup>3</sup>) and MeCN (5 cm<sup>3</sup>) and stirred overnight. This was filtered to give a yellow solution and the solvent removed *in vacuo*. The yellow solid was washed with petrol (3 × 30 cm<sup>3</sup>) and recrystallised from THF/petrol at -35 °C. Yield = 0.03 g (61%). (Found: C, 48.6; H, 7.3%. C<sub>18</sub>H<sub>33</sub>O<sub>3</sub>P<sub>3</sub>V requires: C, 48.98; H, 7.48%). IR (MeCN): 2098 (m), 1962 (m) cm<sup>-1</sup>.  $\mu_{\text{eff}}$  = 2.3  $\mu_{\text{B}}$ . *m/z* (APCI) 413.2 [M – CO, 100%].

#### *cis*-( $\eta^2$ -12[ane]P<sub>3</sub>Et<sub>3</sub>)( $\eta^5$ -Cp)V(CO)<sub>2</sub> (3)

*Method 1.* CpV(CO)<sub>4</sub> (0.10 g, 0.44 mmol) and P<sub>3</sub>Et<sub>3</sub> (0.12 g, 0.41 mmol) were dissolved in toluene (60 cm<sup>3</sup>) and heated to reflux for 2 days. The resulting dark green solution was cooled and filtered through a pad of celite to give a brown solution. This was concentrated to ~5 cm<sup>3</sup> and petrol (5 cm<sup>3</sup>) added. On cooling to -35 °C, a brown solid precipitated which was filtered and dried *in vacuo*. Yield = 0.11 g (55%). (Found: C, 54.0; H, 7.2%. C<sub>23</sub>H<sub>38</sub>O<sub>3</sub>P<sub>3</sub>V requires: C, 54.54; H, 7.51%). IR (toluene,

cm<sup>-1</sup>): 1844 (vs), 1771 (vs). <sup>31</sup>P{<sup>1</sup>H}, δ ppm (C<sub>6</sub>D<sub>6</sub>): 53, -34. <sup>1</sup>H, δ ppm (C<sub>6</sub>D<sub>6</sub>): 4.8 (s) (Cp); 0.6–1.9 overlapping multiplets (macrocycle protons). <sup>13</sup>C, δ ppm (C<sub>6</sub>D<sub>6</sub>, 20 °C): 195.2, br, CO; 30.1, t (<sup>1</sup>J<sub>P-C</sub> = 8 Hz), chelate ring: PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PCH<sub>2</sub>CH<sub>3</sub>; 23.1, s, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PCH<sub>2</sub>CH<sub>3</sub>; 31.3, (<sup>1</sup>J<sub>P-C</sub> = 34 Hz), PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PCH<sub>2</sub>CH<sub>3</sub>; 18.4, s, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PCH<sub>2</sub>CH<sub>3</sub>; 30.1, pendant ring: V-PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PCH<sub>2</sub>CH<sub>3</sub>, coincident with  $\alpha$ -chelate carbon; 20.0, m, V-PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PCH<sub>2</sub>CH<sub>3</sub>; 31.3, dd (<sup>1</sup>J<sub>P-C</sub> = 16 Hz, <sup>3</sup>J<sub>P-C</sub> = 9 Hz), V-PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PCH<sub>2</sub>CH<sub>3</sub>; 18.4, d (<sup>1</sup>J<sub>P-C</sub> = 8 Hz), V-PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PCH<sub>2</sub>CH<sub>3</sub>; 11.5, d (<sup>1</sup>J<sub>P-C</sub> = 15 Hz), V-PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PCH<sub>2</sub>CH<sub>3</sub>; 88.6, s,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>. <sup>51</sup>V, δ ppm (C<sub>6</sub>D<sub>6</sub>, 20 °C): -1034.7 ppm (t) <sup>1</sup>J<sub>P-V</sub> = 173.6 Hz. *m/z* (APCI) 478.3 [M<sup>+</sup> – CO, 100%], 450.3 [M – 2(CO), 25%].

*Method 2.* CpV(CO)<sub>4</sub> (0.22 g, 0.96 mmol) and 12[ane]P<sub>3</sub>Et<sub>3</sub> (0.30 g, 0.98 mmol) were dissolved in toluene (40 cm<sup>3</sup>) and the solution irradiated for 75 min. The resulting dark red solution was concentrated to ~5 cm<sup>3</sup> and petrol added. On cooling, a brown precipitate was collected, washed with petrol (2 × 5 cm<sup>3</sup>) and dried *in vacuo*. Yield = 0.46 g (67%).

#### DFT Calculations

Theoretical calculations were carried out using the Gaussian98 suite of programs<sup>25</sup> running on the UKCCF's Columbus facility. Starting from the crystallographically determined geometry of an analogous Mo complex,<sup>13</sup> the geometry of (12[ane]-P<sub>3</sub>Me<sub>3</sub>)V(CO)<sub>3</sub> was optimised without symmetry restrictions at the Unrestricted Hartree-Fock level using the LANL2DZ basis set and effective core potential (ECP)<sup>26</sup> (ethyl groups in the parent compound were substituted for methyl to reduce flexibility). Subsequent frequency calculations using the smaller LANL1MB basis set/ECP confirmed that this facially capping arrangement is a true minimum. Molecular orbitals and electronic properties were then calculated using UB3LYP/6-311G\*<sup>27</sup> methods at this geometry. The MO diagram in Fig. 2 was generated with the Molekel program<sup>28</sup> using a 0.20 au isodensity surface.

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