This paper is published as part of a *Dalton Transactions* themed issue entitled:

New Talent: Americas

Guest Editors: John Arnold, Dan Mindiola, Theo Agapie,
Jennifer Love and Mircea Dincă

Published in issue 26, 2012 of *Dalton Transactions*

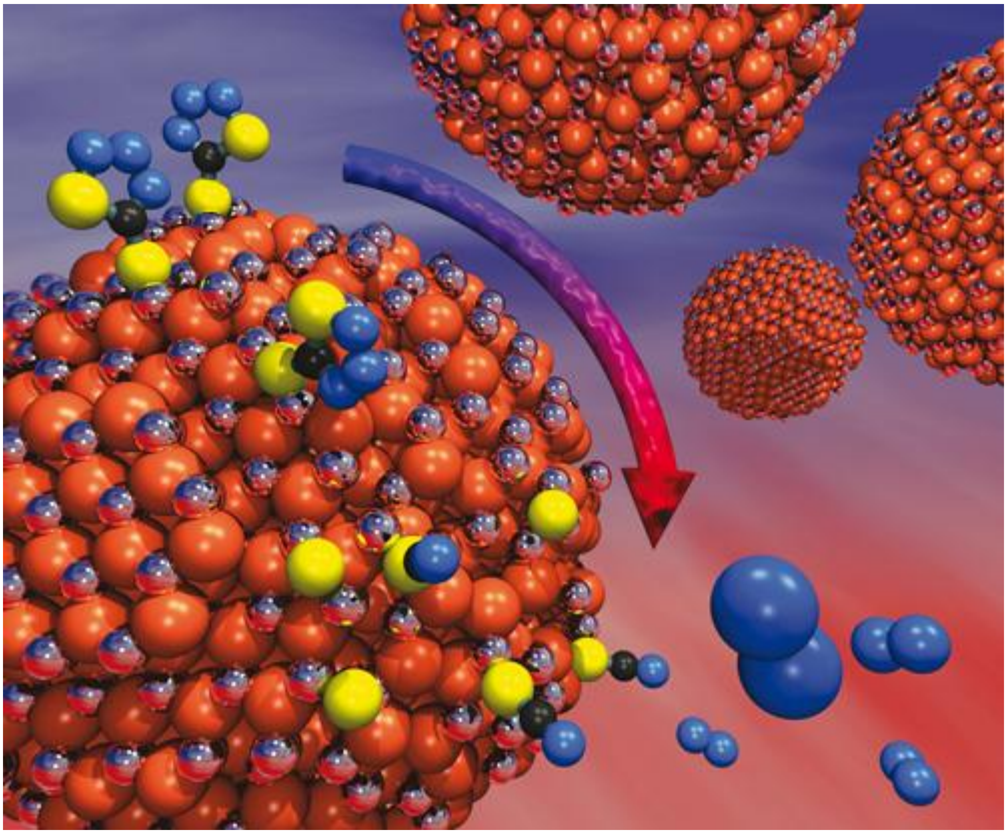


Image reproduced with permission of Richard L. Brutchey

Articles published in this issue include:

Synthesis and reactivity of 2-azametallacyclobutanes
Alexander Dauth and Jennifer A. Love
Dalton Trans., 2012, DOI: 10.1039/C2DT30639E

Perceiving molecular themes in the structures and bonding of intermetallic phases: the role of Hückel theory in an ab initio era
Timothy E. Stacey and Daniel C. Fredrickson
Dalton Trans., 2012, DOI: 10.1039/C2DT30298E

Cycloruthenated sensitizers: improving the dye-sensitized solar cell with classical inorganic chemistry principles
Kiyoshi C. D. Robson, Paolo G. Bomben and Curtis P. Berlinguette
Dalton Trans., 2012, DOI: 10.1039/C2DT30825H

Dalton
Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 7845

www.rsc.org/dalton

COMMUNICATION

Diisocyanoarene-linked pentacarbonylvanadate(I−) ions as building blocks in a supramolecular charge-transfer framework assembled through noncovalent π–π and contact ion interactions†

Tiffany R. Maher, John J. Meyers, Jr., Andrew D. Spaeth, Krista R. Lemley and Mikhail V. Barybin*

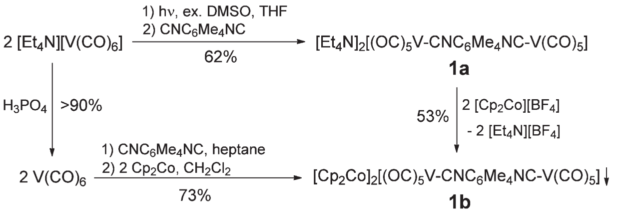
Received 29th February 2012, Accepted 2nd April 2012
DOI: 10.1039/c2dt30488k

Three synthetic routes to the unusual supramolecular complex ($[Cp_2Co]_2[\{(OC)_5V\}_2(\mu\text{-}1,4\text{-}CNC_6Me_4NC)])_\infty$, which was crystallographically characterized, are presented. The dianion $[\{(OC)_5V\}_2(\mu\text{-}1,4\text{-}CNC_6Me_4NC)]^{2-}$ constitutes the first *subvalent* organometallics featuring a diisocyanoarene linker.

Advances in organometallic crystal engineering critically rely on the use of noncovalent phenomena, such as π-stacking, hydrogen bonding, and charge transfer interactions, to assemble novel supramolecular materials.[1] Our recent interest in low-valent, diisocyanoarene-bridged organometallics[2] has led us to explore the possibility of incorporating metallocene and metal carbonyl complexes, which are arguably the two most ubiquitous motifs in organometallic chemistry, into new charge-transfer coordination platforms featuring conjugated linear diisocyanoarene linkers.

The reactivity profile of $V(CO)_6$, the only isolable odd-electron binary metal carbonyl, has been largely limited to one-electron reduction or disproportionation in the presence of donor ligands/solvents to give $[V(CO)_6]^-$.[3] A few interactions of $V(CO)_6$ with phosphines have led to mixed zero-valent substitution products.[4] In addition, Ellis *et al.* have shown that $V(CO)_6$ reacts with excess CNXyl (Xyl = 2,6-dimethylphenyl or xylyl) to afford neutral *trans*-$V(CO)_2(CNXyl)_4$.[5] Herein, we report on an unusual supramolecular ensemble containing a hitherto unknown diisocyanoarene-bridged, *subvalent* bimetallic motif, which is accessible either from $V(CO)_6$ or $[V(CO)_6]^-$. While several group 5 mononuclear species $[M(CO)_5(CNR)]^-$ (R = Me, Ph, Cy, ^{t}Bu, ^{i}Pr, CH_2CO_2Et) have been prepared from the labile complexes $[M(CO)_5L]^-$ by the groups of Ellis ($L = NH_3$)[6] and Rehder (L = DMSO)[7] *via* ligand exchange, no X-ray structural data on such complexes are available.

Treatment of *in situ* generated $[Et_4N][V(CO)_5(DMSO)]$[7] with 0.5 equiv of 1,4-diisocyanodurene (1,4-diisocyano-2,3,5,6-tetramethylbenzene) in THF at ambient temperature afforded a dark red solution, from which air- and moisture sensitive, magenta-coloured $[Et_4N]_2[\{(OC)_5V\}_2(\mu\text{-}CNC_6Me_4NC)]$ (**1a**) was isolated in a *ca.* 60% yield (Scheme 1). The ν_{CO}/ν_{CN} region of the infrared spectrum of **1a** in CH_3CN (Fig. 1) is qualitatively similar to those previously observed for several mononuclear complexes $[Et_4N][M(CO)_5(CNR)]$ M = (V,[6,7] Ta[8]) and constitutes a "classic" example of a pattern expected for a $[M(CO)_5(CNR)]^z$ motif with essentially perfect local C_{4v} symmetry.[9] The ν_{CO} bands at 1951 (m) and 1831 (vs) cm^{-1} correspond to the $A_1{}^{cis}$ and E stretching modes, respectively, of the CO ligands positioned *cis* to the isocyanide groups in **1a**. The remaining allowed ν_{CO} band of A_1 symmetry that arises primarily from stretching of the carbonyl ligands *trans* to the isocyanides is obscured by the very intense E band, as is the case for many other $[V(CO)_5L]^-$ anions not engaged in contact ion interactions with the accompanying cations.[9] The importance of V(dπ) → diisocyanodurene (pπ*) interaction in **1a** is nicely corroborated by a 57 cm^{-1} depression in ν_{CN} upon complexation of the free 1,4-CNC_6Me_4NC linker (ν_{CN} = 2118 cm^{-1} in CH_3CN).



Scheme 1

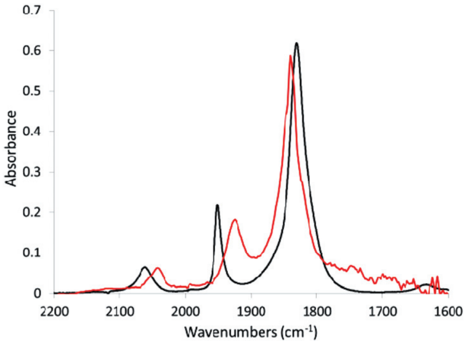


Fig. 1 Infrared spectra of **1a** (black) and **1b** (red) in CH_3CN.

Department of Chemistry, The University of Kansas, 1251 Wescoe Hall Drive, Lawrence, KS 66045, USA. E-mail: mbarybin@ku.edu; Fax: +1-785-864-5396; Tel: +1-785-864-4106

† Electronic supplementary information (ESI) available: Experimental procedures, spectroscopic and analytical data, details of the X-ray and DFT studies. CCDC 862922. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30488k

The electronic spectrum of **1a** in CH_3CN in the visible region (Fig. S3†) features an intense vanadium-to-diisocyanodurene charge transfer absorption (λ_{max} = 489 nm). This charge transfer band exhibits positive solvatochromism[10] and undergoes a 736 cm^{-1} hypsochromic shift upon changing the solvent from CH_3CN to significantly less polar CH_2Cl_2.

The ^{51}V NMR (132 MHz) spectrum of **1a** in CD_3CN at 25 °C shows a singlet resonance at −1903.9 ppm[11] *versus* neat $VOCl_3$. This main peak is accompanied by two ^{13}CO satellite doublets of relative intensities 4 : 1 at −1904.2 ppm with $^1J(^{13}C–^{51}V)$ = 116.8 Hz and −1903.9 ppm with $^1J(^{13}C–^{51}V)$ = 167.5 Hz, respectively, as well as by a weak singlet at −1904.0 ppm due to the $C^{18}O$-containing isotopomer (Fig. S7†). These observations nicely parallel Rehder's earlier findings[12] that the ^{51}V NMR pattern for $[V(CO)_6]^-$ features distinguishable resonances for the minor isotopomers $[V(CO)_5(^{13}CO)]^-$ and $[V(CO)_5(C^{18}O)]^-$. Both of these are slightly shifted upfield from the main peak at −1955 ppm because of the different deshielding effects of the $^{12}C^{16}O$, $^{13}C^{16}O$ and $^{12}C^{18}O$ ligands on the ^{51}V nucleus (Fig. S8†).

Cation metathesis of **1a** with $[Cp_2Co][BF_4]$ in CH_2Cl_2 was driven by precipitation of $[Cp_2Co]_2[\{(OC)_5V\}_2(\mu\text{-}CNC_6Me_4NC)]$ (**1b**) from the reaction mixture (Scheme 1). It is important to note that photolysis of $[Cp_2Co][V(CO)_6]$[13] in the presence of excess DMSO proved sluggish and afforded only a 30% yield of **1b** upon treating the intermediate $[Cp_2Co][V(CO)_5(DMSO)]$ with 0.5 equiv of 1,4-CNC_6Me_4NC (eqn (1)). Our preferred route to compound **1b** involves addition of 1,4-diisocyanodurene to 2 equiv of $V(CO)_6$ in heptane at −70 °C followed by reduction of the presumed thermally unstable, zerovalent intermediate $[\{V(CO)_5\}_2(\mu\text{-}1,4\text{-}CNC_6Me_4NC)]$ with 2 equiv of cobaltocene in CH_2Cl_2 to afford **1b** in a good yield (Scheme 1). Since **1b** is only very sparingly soluble in CH_2Cl_2 or THF, its samples are easily freed from any $[Cp_2Co][V(CO)_6]$ impurity by washing the product with either of these solvents. Employing the above protocol, we also accessed $[Cp_2Co][V(CO)_5(CNXyl)]$ (**2**), which may be viewed as a mononuclear congener of **1b** (eqn (2)).

$$2\,[Cp_2Co][V(CO)_6] \xrightarrow[31\%]{\text{1) h}\nu\text{, ex. DMSO, THF; 2) }CNC_6Me_4NC} \mathbf{1b} \qquad (1)$$

$$V(CO)_6 \xrightarrow[71\%]{\text{1) CNXyl, heptane; 2) }Cp_2Co,\ CH_2Cl_2} \underset{\mathbf{2}}{[Cp_2Co][V(CO)_5(CNXyl)]} \qquad (2)$$

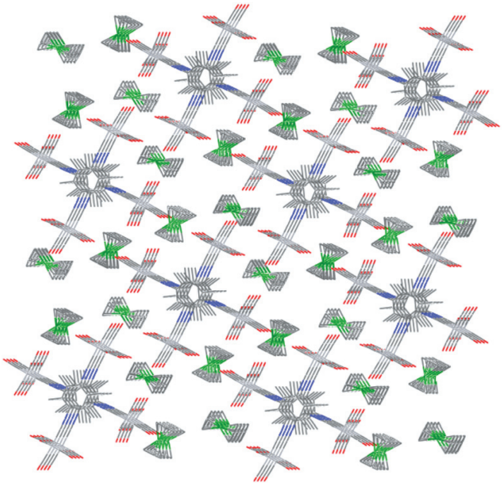


Fig. 2 The supramolecular framework of **1b**.

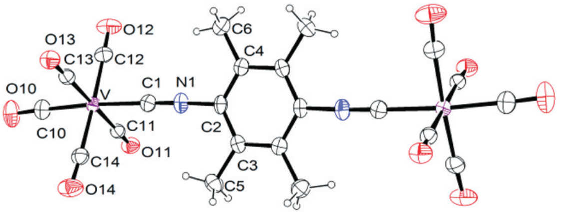


Fig. 3 Molecular structure of the V_2-dianion in **1b** (50% thermal ellipsoids). Selected bond distances (Å) and angles (°): V–C1 2.027(2), V–C10 1.919(3), V–C11 1.967(3), V–C12 1.953(3), V–C13 1.960(3), V–C14 1.959(3), C1–N1 1.173(3), N1–C2 1.388(3), C10–O10 1.174(3), C11–O11 1.145(3), C12–O12 1.155(3), C13–O13 1.146(3), C14–O14 1.148(3), V–C1–N1 178.9(2), C1–N1–C2 177.7(3).

The air- and light sensitive complex **1b** is modestly soluble in acetonitrile and can be recrystallized from $CH_3CN–Et_2O$ to afford dark violet, nearly black microcrystalline solid. The single crystal X-ray analysis of **1b** confirmed its nature as a charge transfer salt between $[\{V(CO)_5\}_2(\mu\text{-}1,4\text{-}CNC_6Me_4NC)]$ and two cobaltocene units.‡ Only a half of the V_2-dianion and one $[Cp_2Co]^+$ cation are crystallographically independent. As illustrated in Fig. 2, the aromatic moieties of the 1,4-diisocyanodurene linker undergo π-stacking aggregation[14] with intercentroid distances between the six-membered rings being 3.58 Å. Such noncovalent π–π interactions form arrays of perfectly staggered $[\{V(CO)_5\}_2(\mu\text{-}1,4\text{-}CNC_6Me_4NC)]^{2-}$ dianions that are insulated from one another by layers of the $[Cp_2Co]^+$ cations. The arrangement of the cobaltocenium ions within the structure of **1b** creates well-defined channels with a solvent accessible volume of 102 $Å^3$ (Fig. 2).[15] These channels appear to be populated by disordered CH_3CN molecules of crystallization.

The molecular structure of the V_2-dianion within **1b** features slightly distorted octahedral coordination around the V(I−) centres (Fig. 3). For **1b**, the C1–N1 distance is 0.010 Å longer while the N1–C2 bond is 0.017 Å shorter compared to corresponding parameters documented for free 1,4-CNC_6Me_4NC.[16] Albeit small, both of the above differences are statistically significant according to the 3σ criterion and reflect significant V (dπ) → CNC_6Me_4NC(pπ*) back-bonding interaction. Due to the *trans*-influence of the isocyanide ligand, which has a greater σ-donor/π-acceptor ratio than CO, the V–C10 bond is notably shorter while the C10–O10 bond is longer than the V–C and C–O distances, respectively, documented for all other V–C–O units in **1b**. The $[Cp_2Co]^+$ cations in **1b** exhibit the Co–C bond lengths of 2.022(3)–2.037(3) Å and the Co–Cp(centroid) distances of 1.63 Å (Fig. S1†), which are typical of other cobaltocenium salts.[17]

While a satisfactory crystallographic analysis of the charge-transfer salt $[Cp_2Co][V(CO)_6]$ proved impossible in the past due to "massive disorder of $[V(CO)_6]^-$ in the crystal",[18] the well-ordered framework of **1b** now allows detailed geometric appreciation of the interionic interactions between the cobaltocenium

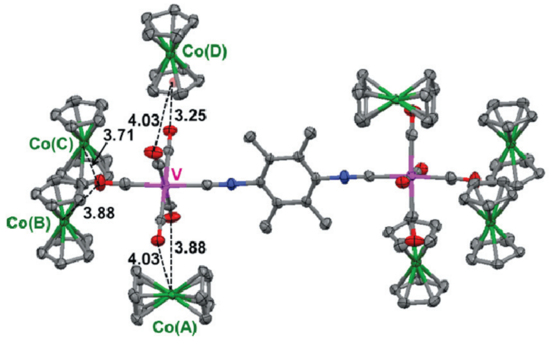


Fig. 4 A fragment of the structure of **1b** showing interionic contacts (in Å). All hydrogen atoms are omitted for clarity.

and carbonylvanadate(I−) ions in the solid state. The X-ray structure of **1b** shows multiple cation–anion contacts at or under 4 Å. These contacts, depicted in Fig. 4, are somewhat shorter than the CO⋯Co (4.29 Å) and CO⋯Cp(centroid) (3.91 Å) nonbonded interactions documented by Kochi and Bockman for the contact ion pair $[Cp_2Co]^+[Co(CO)_4]^-$.[19] Each of the pentacarbonylvanadate(I−) moieties in **1b** displays close interactions with four cobaltocenium units at distances $d_{Co(A)–V}$ = 5.38 Å, $d_{Co(B)–V}$ = 5.53 Å, $d_{Co(C)–V}$ = 5.73 Å, and $d_{Co(D)–V}$ = 6.48 Å (Fig. 4). Interestingly, ultrafast infrared transient absorption spectroscopy experiments by Spears *et al.* revealed two different electron transfer rates for the $Cp_2Co|V(CO)_6$ contact ion pair.[20] These authors' density functional theory (DFT) calculations suggested two distinct stable geometries for $[Cp_2Co]^+|[V(CO)_6]^-$: one with two oxygen atoms lying in the cleft between the two Cp rings at $d_{Co–V}$ = 5.4 Å and the other featuring two oxygen atoms contacting the top of a cyclopentadienyl moiety at $d_{Co–V}$ = 6.1 Å.[20] Very similar interactions are clearly recognizable in Fig. 4 for **1b** ($d_{Co(A)–V}$ = 5.38 Å and $d_{Co(D)–V}$ = 6.48 Å, respectively) and involve the *cis*-CO ligands. In addition, two other cation–anion contacts at $d_{Co(B)–V}$ = 5.73 Å and $d_{Co(C)–V}$ = 5.53 Å place the corresponding $[Cp_2Co]^+$ cations in close proximity of the *trans*-CO ligands (Fig. 4), which experience the greatest extent of back-bonding from the V(I−) centres.

In addition to a reversible $Co^{II/III}$ wave, the cyclic voltammograms of **1b** and **2** in CH_3CN feature two vanadium-centered processes $V^{I−/0}$ and $V^{0/I}$, both of which are only partially reversible presumably due to instability of the oxidized vanadium species in CH_3CN (*cf.* fast disproportionation of $V(CO)_6$ in donor solvents[3]). The V(I−) → V(0) oxidation for **1a**,**b** and **2** occurs at substantially lower potentials with respect to the corresponding process for the $[V(CO)_6]^-$ ion (Table 1).[21,22] Also, the V_2-dianion in **1a**,**b** is 60 mV harder to oxidize than the $[V(CO)_5(CNXyl)]^-$ anion in **2**. This is consistent with a lower σ-donor/π-acceptor ratio for the 1,4-diisocyanodurene ligand compared to CNXyl. Indeed, while the LUMOs of 1,4-CNC_6Me_4NC and CNXyl lack contributions from the methyl substituents, the involvement of an additional isocyanide unit (an electron-withdrawing group) in the LUMO of 1,4-CNC_6Me_4NC compared to that of CNXyl, should facilitate the V(dπ) → isocyanoarene (pπ*) interaction (Fig. S2†).

The IR pattern for **1b** in acetonitrile shows broader and more structured bands in the ν_{CO}/ν_{CN} region compared to **1a** (Fig. 1).

Table 1 Half-wave potentials (in volts) for **1a**, **1b**, **2**, and $[V(CO)_6]^{-a}$

	$E_{1/2}$ ($V^{I−/0}$)	$E_{1/2}$ ($V^{0/I}$)	$E_{1/2}$ ($Co^{II/III}$)	Solvent
1a^b	−0.69	−0.38		CH_3CN^b
1b^b	−0.69	−0.39	−1.35	CH_3CN^b
2^b	−0.75	−0.38	−1.35	CH_3CN^b
$[Cp_2Co][V(CO)_6]$	−0.35		−1.32	CH_3CN^b
$[Na(diglyme)_2][V(CO)_6]^c$	−0.36	0.06	—	Acetone^c

^{a} Potentials *vs.* Cp_2Fe/Cp_2Fe^+. ^{b} This work. ^{c} Ref. 21.

The shoulders at 1847 and 1824 cm^{-1}, that accompany a more intense peak at 1839 cm^{-1}, probably correspond to the B_1 and A_1^{trans} ν_{CO} modes, respectively, the former being IR-forbidden under perfect C_{4v} symmetry. This may suggest perturbation of the dianion's C_{4v} geometry[9] in **1b** by contact ion pairing (CIP), *e.g.*, akin to those shown in Fig. 4, even in this polar solvent.

In contrast to **1a**, no significant solvatochromism of the vanadium-to-diisocyanodurene charge transfer absorption (λ_{max} = 484 nm) was documented for **1b** (Fig. S4†), thereby suggesting limited solvent accessibility of the V_2-dianion in **1b** compared to that in **1a**. Interestingly, a relatively weak shoulder at λ_{max} ≈ 738 nm, which is obscured by the low energy tail of the very intense metal-to-diisocyanodurene charge transfer band, was observed for **1b** (Fig. S4†). We tentatively assign this shoulder as a CIP charge transfer band involving the vanadate(I−) anions and the cobaltocenium cations in **1b**. For the $[Cp_2Co]^+[V(CO)_6]^-$ ion pair, such interionic charge transfer occurs at *ca.* 620 nm in CH_2Cl_2 (Fig. S6†).[18] The lower energy of the interionic charge transfer for **1b** *versus* $[Cp_2Co]^+[V(CO)_6]^-$ correlates[18] nicely with ≈300 mV smaller difference between the $E_{1/2}$ redox potentials of the V(I−) donor and the Co(III) acceptor ions documented for the former (Table 1).

In summary, we described the supramolecular ensemble $([Cp_2Co]_2[\{(OC)_5V\}_2(\mu\text{-}1,4\text{-}CNC_6Me_4NC)])_\infty$ held together *via* synergistic π-stacking and $Co^{III}/V^{I−}$ contact ion interactions. We hope that the availability of this unusual platform will offer new opportunities in organometallic crystal engineering.[1] Further studies aimed at detailed understanding of interionic association and photochemistry of **1a**,**b** in solution are in progress.

Acknowledgements

This work was funded by the NSF CAREER award (CHE-0548212) and DuPont Young Professor Award to M.V.B. The authors thank Drs Douglas R. Powell and Victor W. Day for their expert advice in the crystallographic characterization of **1b**.

Notes and references

‡ *Crystal data* for **1b**: $C_{42}H_{32}Co_2N_2O_{10}V_2$, M_w = 944.44, tetragonal, space group $P4_2/n$, black needle, 0.46 × 0.16 × 0.10 mm^3, T = 100(2) K, $a = b$ = 23.719(1) Å, c = 7.1617(8) Å, V = 4029.2(6) Å^3, Z = 4, D_{calc} = 1.557 Mg m^{-3}, μ = 1.319 mm^{-1}, $F(000)$ = 1912, $R_1(I > 2\sigma(I))$ = 0.050, wR_2 (all data) = 0.129, GOF = 1.069 on F^2. CCDC number 862922.

1 D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375.

2 (*a*) M. V. Barybin, *Coord. Chem. Rev.*, 2010, **254**, 1240; (*b*) T. R. Maher, A. D. Spaeth, B. M. Neal, C. L. Berrie, W. H. Thompson, V. W. Day and M. V. Barybin, *J. Am. Chem. Soc.*, 2010, **132**, 15924–15926.
3 X. Liu and J. E. Ellis, *Inorg. Synth.*, 2004, **34**, 96.
4 Selected examples: (*a*) Q. Z. Shi, T. G. Richmond, W. C. Trogler and F. Basolo, *J. Am. Chem. Soc.*, 1984, **106**, 71; (*b*) J. E. Ellis, R. A. Faltynek, G. L. Rochfort, R. E. Stevens and G. A. Zank, *Inorg. Chem.*, 1980, **19**, 1082; (*c*) W. Hieber and E. Winter, *Chem. Ber.*, 1964, **97**, 1037.
5 M. V. Barybin, V. G. Young, Jr. and J. E. Ellis, *J. Am. Chem. Soc.*, 2000, **122**, 4678.
6 J. E. Ellis and K. L. Fjare, *Organometallics*, 1982, **1**, 898.
7 K. Ihmels and D. Rehder, *Organometallics*, 1985, **4**, 1340.
8 M. V. Barybin, W. W. Brennessel, B. E. Kucera, M. E. Minyaev, V. J. Sussman, V. G. Young, Jr. and J. E. Ellis, *J. Am. Chem. Soc.*, 2007, **129**, 1141.
9 M. Y. Darensbourg, *Prog. Inorg. Chem.*, 1985, **33**, 221.
10 C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319.
11 *Cf.* $\delta(^{51}V) = -1901$ ppm for $[Et_4N][V(CO)_5(CN^iPr)]$ in MeCN: ref. 7.
12 D. Rehder, *Coord. Chem. Rev.*, 2008, **252**, 2209.
13 F. Calderazzo, G. Pampaloni, G. Pelizzi and F. Vitali, *Organometallics*, 1988, **7**, 1083.
14 G. W. Coates, A. R. Dunn, L. M. Henling, D. A. Dougherty and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 248.
15 P. Van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 194.
16 M. Zeller, A. D. Hunter and C. L. Perrine, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2003, **59**, o1655.
17 For example: (*a*) J. M. Migliori, W. M. Reiff, A. M. Arif and J. S. Miller, *Inorg. Chem.*, 2004, **43**, 6875; (*b*) C. G. Andrews and C. L. B. Macdonald, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **61**, m2103.
18 .35wJ. K. Kochi and T. M. Bockman, *J. Am. Chem. Soc.*, 1989, **111**, 4669.
19 .35wT. M. Bockman and J. K. Kochi, *J. Am. Chem. Soc.*, 1988, **110**, 1294.
20 (*a*) K. G. Spears and H. Shang, *J. Phys. Chem. A*, 2000, **104**, 2668; (*b*) T. W. Martin, B. J. Homoelle and K. G. Spears, *J. Phys. Chem. A*, 2002, **106**, 1152; (*c*) G. M. Sando and K. G. Spears, *J. Phys. Chem. A*, 2004, **108**, 1290.
21 (*a*) A. M. Bond, R. Colton, P. J. Mahon and G. A. Snook, *J. Phys. Chem. B*, 1998, **102**, 1229; (*b*) A. M. Bond and R. Colton, *Inorg. Chem.*, 1976, **15**, 2036.
22 G. Pampaloni and U. Koelle, *J. Organomet. Chem.*, 1994, **481**, 1.