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Electrochemical studies of an oxidatively induced ring slippage in 17-electron (η^3-indenyl)(η^5-indenyl)V(CO)$_2$

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Abstract

Oxidation of (η^5-arene)$_2$V (arene = indenyl, C_5H_5, C_5Me_5) with [$(C_5H_5)_2$Fe][PF_6] under a carbon monoxide atmosphere provides a convenient route to [(η^5-arene)$_2$V(CO)$_2$]$^+$ complexes. The cyclic voltammogram of the indenyl compound shows two reversible one-electron reduction waves. Reduction of 18-electron [(η^5-indenyl)$_2$V(CO)$_2$][PF_6] leads directly to the 17-electron (η^3-indenyl)(η^5-indenyl)V(CO)$_2$. A lower limit for the η^3-to-η^5 ring slip rate constant is estimated to be 10/sec at −32°C. Reductions of the cationic C_5H_5 and C_5Me_5 analogues were irreversible and showed no evidence for ring slipped intermediates.

Introduction

Nucleophilic substitution is a fundamental reaction of organometallic complexes [1–3]. Coordinatively saturated complexes typically react by a dissociative (S_N1) mechanism, which involves ligand loss before coordination of the incoming nucleophile (an 18-16-18-electron sequence). Associative mechanisms have recently been proposed for nucleophilic substitution reactions occurring at 17-electron transition metal complexes. Kinetics studies on organometallic radicals have not only shown dramatic ($> 10^9$) rate accelerations for nucleophilic substitution in comparison to 18-electron complexes, but firmly establish that 17-19-17-electron substitution (S_N2) processes form another important class of organometallic reaction mechanisms [4].

Associative substitution reactions at transition metal complexes that contain cyclopentadienyl ligands may avoid hypervalent 20-electron intermediates by ring slippage [5,6]. Previous work [7] showed that a crystallographically defined slipped ring 17-electron radical, (η^3-Ind)(η^5-Ind)V(CO)$_2$ (**1**, Ind = indenyl) can be isolated from the reaction between (η^5-Ind)$_2$V and carbon monoxide, (presumably via (η^5-Ind)$_2$V(CO)). We were able to convert this slipped ring complex to the cationic bis(η^5-indenyl) complex, [(η^5-Ind)$_2$V(CO)$_2$][PF_6] (**2**) by oxidation of **1** with ferro-

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cenium hexafluorophosphate. There is a lack of thermodynamic and kinetic data on ring slip processes, primarily because the η^3 species are rarely observed. Since a one-electron redox change conveniently drives the η^3- to η^5-ring slippage, we undertook a study of this rearrangement with electrochemical methods. This approach also permits a comparative study of η^5-C_5H_5 and η^5-C_5Me_5 analogues to assess the viability of ring slipped intermediates in these systems.

Results and discussion

Oxidation of 17-electron $(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2$ (**1**) with $[(\eta^5\text{-}C_5H_5)_2Fe][PF_6]$ in tetrahydrofuran (THF) produces 18-electron $[(\eta^5\text{-Ind})_2V(CO)_2][PF_6]$ (**2**) in good yield. Complex **2** forms directly in a one-pot reaction between $(\eta^5\text{-Ind})_2V$ and $[(\eta^5\text{-}C_5H_5)_2Fe)][PF_6]$ under a carbon monoxide atmosphere (presumably **1** forms in situ) [8*]. The X-ray structure of $[(\eta^5\text{-Ind})_2V(CO)_2][BPh_4]$, isolated in low yield via halide abstraction from $(\eta^5\text{-Ind})_2VI$ with $NaBPh_4$ under CO, was reported recently [9] and confirmed that both indenyl ligands were bound in an η^5-fashion. We find that the salts of $[(\eta^5\text{-Ind})_2V(CO)_2]^+$, $[(\eta^5\text{-}C_5H_5)_2V(CO)_2]^+$ and $[(\eta^5\text{-}C_5Me_5)_2V\text{-}(CO)_2]^+$ may be obtained in improved yields by the reaction between the corresponding vanadocenes and $[(\eta^5\text{-}C_5H_5)_2Fe][PF_6]$ under a CO atmosphere.

A cathodic scan cyclic voltammogram (CV) of **2** produces the voltammetric response shown in Fig. 1a. The cathodic scan from 0.6 to −2.0 V shows two chemically reversible one electron waves. An initial anodic scan of complex **1** gives redox couple AB ($E^{0\prime}$ − 0.56 V) and an initial cathodic scan gives the redox couple CD ($E^{0\prime}$ − 1.08 V). These are identical to the steady state voltammetric responses observed for compound **2** (Fig. 1b). The two sets of data (summarized in Table 1) suggest reduction of the 18-electron bis(η^5-indenyl) complex **2** gives the 17-electron (η^3-indenyl) complex **1** (redox couple AB), while the oxidation of 17-electron **1** generates 18-electron **2**. The second reduction (redox couple CD) is proposed to give the 18-electron $[(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2]^-$ (**3**). Since the height and shape of the CD wave closely resemble the AB wave, the assignment to another 1-electron redox process is justified. These transformations are outlined in Scheme 1.

$$\underset{(\mathbf{2})\ (18e)}{[(\eta^5\text{-Ind})_2V(CO)_2]^+} \quad \overset{e^-}{\underset{E\ -0.56\ \text{V}}{\longleftrightarrow}} \quad \underset{(\mathbf{1})\ (17e)}{[(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2]}$$

$$\underset{(\mathbf{1})\ (17e)}{[(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2]} \quad \overset{e^-}{\underset{E\ -1.08\ \text{V}}{\longleftrightarrow}} \quad \underset{(\mathbf{3})\ (18e)}{[(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2]^-}$$

(Ind = indenyl)

Despite the chemical reversibility the second reduction of **2** (redox couple CD in Fig. 1 $i_{p_a}/i_{p_c} = 1.09$) in the CV measurements, all attempts to isolate the expected product, $[(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2]^-$ (**3**), were unsuccessful. Sodium naphthalide reductions of **1** (in THF at −80 °C) lead to solutions containing many carbonyl

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* Reference number with asterisk indicates a note in the list of references.

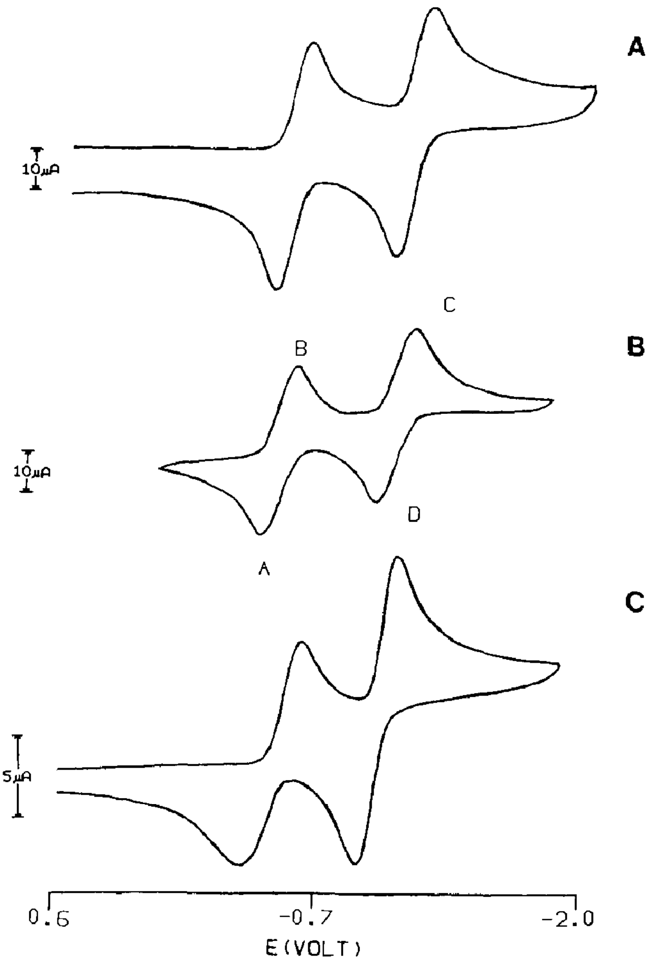

Fig. 1. (A) Cathodic scan cyclic voltammogram of complex **2**. Experimental conditions: $[[(\eta^5\text{-Ind})_2V(CO)_2][PF_6]]$ 1×10^{-3} *M*; [TBATFB] 0.15 *M*; temperature 20 ° C; scan rate 200 mV/s, solvent THF; IR compensated. (B) Steady state cyclic voltammogram of complex **1** attained at repetitive scans. Experimental conditions: Same as above except $[(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2]$ 0.7×10^{-3} *M*; temperature 0 ° C; scan rate 400 mV/s. (C) Low temperature cyclic voltammetric study of complex **1**. Experimental conditions: same as above except: $[[(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2][PF_6]]$ 1×10^{-3} *M*; temperature -40 ° C; scan rate 100 mV/s.

absorptions in the IR spectrum [10*], which on work up yield mixtures of $[(\eta^5\text{-Ind})V(CO)_4]$ and $[V(CO)_6]^-$. Thus, the stability of **3** must be low on the preparative time scale. A similar reaction has been reported [11] where sodium reduction of $[(\eta^5\text{-}C_5H_5)_2V(CO)]$ in the presence of CO yields mainly $[(\eta^5\text{-}C_5H_5)V(CO)_4]$.

The one-electron oxidation of **1** to **2** (redox couple AB) approaches that for a true reversible system since the ΔE_p of 104 mV is close to that of the ferrocene/ferricinium couple under the same conditions (Table 1). This suggests ring slippage occurs rapidly and reversibly on the CV time scale at room temperature. Two reasonable mechanisms for this transformation are depicted in Scheme 2.

Table 1

Electrochemical parameters from cyclic voltammograms [a] of vanadocene derivatives

Compound	E_R [b]	Redox couple	i_{pa}/i_{pc}	ΔE_p [c]
$[Ind_2V(CO)_2][PF_6]$ [d]	−0.56	(+/0)	0.97 [e]	104
	−1.08	(0/−)	1.09	120
$[Cp_2V(CO)_2][PF_6]$	−0.93 [f]	(+/0)	irrev	–
$[Cp^{\star}_2V(CO)_2][PF_6]$	−1.17 [f]	(+/0)	irrev	–
$[Cp_2V(CO)]$	−2.30	(0/−)	0.65	101
$[Cp^{\star}_2V(CO)]$	−2.72	(0/−)	0.64	120
$[Ind_2V]$ [g]	−2.38 [f]	(0/−)	irrev	–
$[Cp_2V]$	−2.72	(0/−)	0.50	162
$[Cp^{\star}_2V]$	– [h]	(0/−)	–	–
$[Cp_2Fe]$	+0.50	(+/0)	1.0	102

[a] 1–2 m*M* solutions in THF with 0.1 *M* TBAHFP as supporting electrolyte unless otherwise noted. Cp = C_5H_5, Cp* = C_5Me_5, Ind = indenyl. [b] $(E_{pa} - E_{pc})/2$ (volts vs. silver wire pseudo-reference electrode). [c] $(E_{pa} - E_{pc})$ (mV), measured at 200 mV/sec. [d] Identical values were obtained starting with $[Ind_2V(CO)_2]$. [e] Measured at 400 mV/sec. [f] E_{pc}. [g] Tetrabutylammonium perchlorate supporting electrolyte. [h] No reduction wave was observed to the solvent limit (ca. −3 V).

$$\begin{tikzcd}
{[(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2]} \arrow[rr, shift left, "-e"] & & {[(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2]^+} \arrow[ll, shift left, "+e"] \\
\textbf{(1)}\ (17e) \arrow[dd, shift right, "k_1"'] & \text{Path A} & \textbf{(4)}\ (16e) \arrow[dd, shift right, "k'_1"'] \\
& \text{Path B} & \\
{[(\eta^5\text{-Ind})_2V(CO)_2]} \arrow[rr, shift left, "-e"] \arrow[uu, shift right, "k_{-1}"'] & & {[(\eta^5\text{-Ind})_2V(CO)_2]^+} \arrow[ll, shift left, "+e"] \arrow[uu, shift right, "k'_{-1}"'] \\
\textbf{(5)}\ (19e) & & \textbf{(2)}\ (18e)
\end{tikzcd}$$

In path A, the oxidation of **1** to the 16-electron $[(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2]^+$ (**4**) precedes the reverse ring slip to yield the 18-electron $[(\eta^5\text{-Ind})_2V(CO)_2]^+$. This requires that the rate constants k'_1 and k'_{-1} be large (> 1/sec) since no build-up of **4** (starting from either **1** or **2**) occurs and the reverse wave behaves well. Since the stable oxidized species is **2**, the **4** $\rightleftharpoons$ **2** equilibrium constant (k'_1/k'_{-1}) must be large (> 100).

Alternatively, a rapid ring slip could give 19-electron $(\eta^5\text{-Ind})_2V(CO)_2$ (**5**), which then becomes oxidized to **2** (path B). This intramolecular 17-19-electron process resembles the 17-19-17-electron reaction sequences proposed for associative nucleophilic attack at 17-electron metal centers. The reversibility of the cyclic voltammograms requires that the rate constants k_1 and k_{-1} be fast (> 1/sec). The **1** $\rightleftharpoons$ **5** equilibrium constant (k_1/k_{-1}) must be small (< 0.01) since the stable form of the reduced species is **1**. Thus, for both paths the rate constants must be fast and the equilibrium must lie heavily in favor of one isomer.

In an effort to "freeze out" the ring slip step, a low temperature study was undertaken. Cyclic voltammograms of **1** or **2** show that wave A becomes broader as the temperature decreases [12*] (Fig. 1c). This suggests that the η^3-to-η^5 ring slip

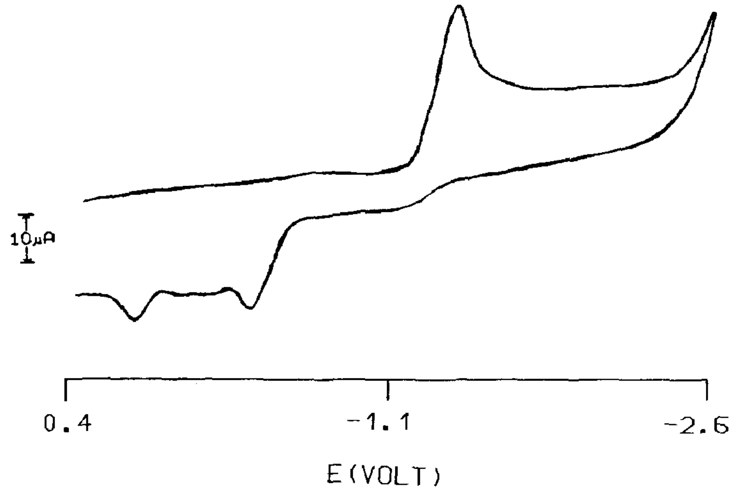

Fig. 2. Cathodic scan cyclic voltammogram of $[(C_5Me_5)_2V(CO)_2][PF_6]$ Experimental conditions: $[[(C_5Me_5)_2V(CO)_2][PF_6]]$ 1×10^{-3} *M*; [TBAHFP] 0.15 *M*; temperature 20 °C; scan rate 400 mV/s; solvent THF; IR compensated.

becomes rate limiting relative to heterogeneous charge transfer. We favor a homogeneous kinetic origin for this behavior because the voltammetric response was independent of the electrode surface with identical voltammograms being obtained with Pt, Hg, and glassy carbon working electrodes. That reduction wave B remains unaffected over the temperature range studied (20 °C to −40 °C) suggests no pre-equilibrium step occurs before reduction of **2**, which is consistent with path B. An accelerated rate of ring slippage in the odd electron complex is consistent with recent observations [13] for CO addition to 17-electron $(H_3C)_4C_2(\eta^5\text{-}C_5H_4)_2Cr(CO)^+$. Double potential step chronocoulometry (DPSCC) [14–19] experiments at −32 °C for the **1**–**2** conversion gave Q_R/Q_F values identical (within experimental error) to those of the ferrocenium/ferrocene standard [20*]. This implies the ring slip rate constant, k_1, is still too large to measure by DPSCC at −32 °C. An estimated lower limit of 10/sec (at −32 °C) for k_1 be given based on the scan limits of the DPSCC experiment. Insolubility of **2** prevents [12*] electrochemical studies from being carried out at temperatures lower than −40 °C.

Compared to other cyclopentadienyl derived moieties, the η^5-indenyl ligand should show the fastest η^5-to-η^3 ring slip rates because slippage allows the benzene ring to gain aromaticity [21–24]. This acceleration in ring slip rates is commonly referred to as the "indenyl effect." Therefore $[(\eta^5\text{-}C_5H_5)_2V(CO)_2][PF_6]$ (**6**) and $[(\eta^5\text{-}C_5Me_5)_2V(CO)_2][PF_6]$ (**7**) should have slower η^5-to-η^3 ring slips rates on reduction and be amenable to study. The more negative E_{p_c} values for the reductions of **6** and **7** (Fig. 2) conform to what one expects based on the superior donor properties of C_5H_5 and C_5Me_5 as compared to indenyl (Table 1); however, the reductions are irreversible (e.g. Fig. 2) with no evidence for slipped ring analogues of the neutral indenyl complex. No detectable amounts of $(C_5R_5)_2V(CO)_2$ (R = H, Me) could be observed down to −30 °C. For **6**, a reduction wave attributed to $(\eta^5\text{-}C_5H_5)_2V(CO)$, was also observed. This result was confirmed by the reduction of a THF solution of **6** with one equivalent of sodium naphthalide at −80 °C. The IR spectrum (at −80 °C) of the solution exhibited an absorption at 1881 cm^{-1}, identical to that of authentic (η-C_5H_5)$_2$V(CO), in addition to absorptions of other minor unidentified species. The reduction product of **6** must have a half-life of less than 0.1 sec at $-30\,^\circ$C (CV) and less than a minute at $-80\,^\circ$C (IR), which contrasts dramatically with the stability of the isolable indenyl complex. Rather than undergoing an η^5-to-η^3 ring slip, the complexes (C_5R_5)$_2$V(CO)$_2$ (R = H, Me) appear to rapidly lose carbon monoxide as soon as they are generated. These results suggest that ring slip chemistry observed with indenyl ligands may sometimes be exceptional and care should be taken in extrapolating mechanistic conclusions obtained for these systems to complexes containing cyclopentadienyl ligands.

Experimental

Synthetic manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solids were transferred in a nitrogen-filled Vacuum Atmospheres glove box equipped with a Dri-train. All glassware was flame-dried before use except those containing fritted discs, which were dried in a $100\,^\circ$C oven. ^{1}H NMR spectra were obtained on a Varian EM-390 and IR spectra were obtained with either an IBM FTIR/32 or a Perkin–Elmer 1320 IR spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories.

Electrochemical studies were carried out by using a BAS 100 electrochemical analyzer equipped with a Houston Instruments DMP-40 plotter. Most and low temperature experiments were performed using either an IBM voltammetric cell (assembled in an inert atmosphere box and removed as a sealed unit), EG&G PARC 303A hanging mercury drop apparatus, or a vacuum tight three-compartment cell (separated by fine fritted discs) equipped with a glass jacketed thermocouple (Love Controls Corp). The 3-compartment cell was evacuated and flushed with nitrogen three times before inserting the electrodes against a nitrogen flow. Most experiments employed a platinum disc working electrode (IBM Instruments or BAS), a platinum wire auxiliary electrode (IBM Instruments), and a silver wire pseudo-reference electrode. The glassy carbon working electrode used in several experiments was obtained from BAS. Low temperature experiments were performed using a large insulated isopropanol/dry-ice slush bath and the cell temperature could be maintained constant to within $\pm 0.2\,^\circ$C of a specific temperature. A blanket of nitrogen or a mixture of nitrogen and dry carbon monoxide, saturated with solvent at the same temperature, was maintained in the cell by continuous purging.

In a typical electrochemical experiment, tetrabutylammonium tetrafluoroborate (TBATFB) stock solution (0.1 *M* in THF) was added to cover the electrode surfaces and the potential of the working electrode was cycled several times between the initial and final values. With the IBM cell or the EG&G cell, an equal volume of 2–4 m*M* sample solution (in 0.1 *M* TBATFB) was added to the cell (for a final sample concentration of 1–2 m*M*). In the 3-compartment cell, the stock solution was removed from the working electrode compartment and an equal volume of 1–2 m*M* sample solution (in 0.1 *M* TBATFB) was added to ensure the sample solvent level was equal to or less than that of the reference and auxiliary electrode compartments. Cyclic voltammograms (CV) were recorded at several scan rates (with *iR* compensation). Double potential step chronocoulometry (DPSCC) experiments were performed with several step times (τ) after determining the appropriate E_i and E_f values from slow scan CV experiments performed just before the DPSCC experiment. The sample solutions were stirred between each measurement. The cells and the working and auxiliary electrodes were cleaned with aqua regia after each set of experiments. In addition, the platinum disk working electrode surface was polished occasionally with 0.3 micron alumina.

Hydrocarbon and ether solvents were dried over potassium or sodium benzophenone ketyl and distilled under nitrogen. Acetone was distilled from K_2CO_3 under nitrogen. Carbon monoxide (Alfagaz) was passed through an isopropanol/dry-ice trap to remove water. Tetraalkyl ammonium salts (Southwestern Chemical) were electrochemical grade, recrystallized from ethyl acetate/octane, and placed under vacuum (10^{-4} torr) overnight.

Vanadocene [25,26], decamethylvanadocene [27], carbonylbis(cyclopentadienyl)-vanadium [28,29], carbonylbis(pentamethylcyclopentadienyl)vanadium [30], bis(indenyl)vanadium[7,31] and dicarbonyl(η^3-indenyl)(η^5-indenyl)vanadium [7] were prepared by literature procedures. Ferrocenium hexafluorophosphate was prepared by metathesis of $[(C_5H_5)_2Fe][FeCl_4]$ (Alfa) with $(NH_4)(PF_6)$ (Aldrich) in water, recrystallized from acetone/hexanes, and dried under vacuum overnight.

Preparation of dicarbonylbis(indenyl)vanadium(III) hexafluorophosphate. Dry CO was bubbled into a slurry of 100 mg (0.36 mmol) of $(\eta^5\text{-Ind})_2V$ in 30 ml of THF for 10 min. This mixture was treated with a slurry of 100 mg (0.32 mmol) of $[(C_5H_5)_2Fe][PF_6]$ in 30 ml of THF, stirred for 40 min, and filtered. The residue was extracted with THF until the filtrate was nearly colorless. The red filtrate was cooled to $-80\,°C$ and pentane was added to precipitate a red crystalline product. The supernatant was discarded and the red matted flakes were rinsed with 1×15 ml of pentane (23°C) to yield 102 mg (59% yield) of the title compound. ^1H NMR (acetone-d_6): δ 7.5 (m, 8H), 6.5 (d, J 3Hz, 4H), 5.5 (t, J 3 Hz, 2H); IR (THF): ν(CO) 2039 (s), 1993 (s) cm^{-1}; IR (Nujol mull): 3135 (w), 2037 (s), 1983 (s), 1532 (w), 1297 (w), 1251 (w), 1220 (w), 1160 (w), 1059 (w), 1038 (w), 937 (w), 862 (sh), 835 (s), 762 (m), 734 (sh), 557 (s) cm^{-1}. Anal. Found: C, 49.82; H, 3.23. $C_{20}H_{14}F_6O_2PV$ calcd.: C, 49.81; H, 2.93%.

Preparation of dicarbonylbis(cyclopentadienyl)vanadium(III) hexafluorophosphate. A solution of 200 mg (1.1 mmol) of $(C_5H_5)_2V$ in 50 ml of THF was exposed to a dry CO atmosphere and treated with a THF slurry of $[(C_5H_5)_2Fe][PF_6]$. The reaction mixture was stirred for an hour and then filtered. The residue was extracted with THF until it was nearly gone (a total of ca. 500 ml of THF was used). The solvent was removed under vacuum until a saturated solution was obtained and two volumes of pentane were added slowly to the solution to precipitate a shiny yellow product. Recrystallization from acetone/pentane gave fluffy mica-like clumps of yellow crystals in 37% yield (152 mg). ^1H NMR (acetone-d_6): δ 5.93: IR (THF): ν(CO) 2045 (s), 1995 (s) cm^{-1}. The IR carbonyl absorptions are identical to those seen in other salts of this cation [28,29,32].

Preparation of dicarbonylbis(pentamethylcyclopentadienyl)vanadium(III) hexafluorophosphate. A suspension of 126 mg (0.39 mmol) of $(C_5Me_5)_2V$ in 30 ml of acetone under a CO atmosphere was stirred for 10 min and treated with a slurry of 124 mg (0.37 mmol) of $[(C_5H_5)_2Fe][PF_6]$ in 10 ml of acetone. The reaction mixture was stirred until the dark blue color of the ferrocenium cation dissipated. The solution was filtered and concentrated under reduced pressure to 5 ml. Addition of pentane completed the precipitation of orange crystals. The supernatant was discarded and the residue was placed under vacuum for 3 h. The product was exhaustively extracted into THF and the resulting filtrate was concentrated to saturation. Cooling the solution to −80 °C and slowly adding pentane resulted in 136 mg (67% yield) of fine yellow platelets. ^{1}H NMR (acetone-d_6): δ 1.99; IR (THF): ν(CO) 1998 (s), 1943 (s) cm^{-1}. The mull IR spectrum is identical to that reported in the literature [33].

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