

$J = 3.4$  Hz, C=CH), 1.17 (s, 9 H, *t*-Bu);  $^{13}\text{C}$  NMR (50.1 MHz,  $\text{CD}_3\text{NO}_2$ , 0 °C)  $\delta$  243.2 ( $\mu$ -CO), 212.5, 207.4 (CO), 152.0 (C=C=C), 145.6 (d,  $J = 167$  Hz), 127.3 (d,  $J = 161$  Hz) (C=C=C), 93.0 (d,  $J = 183$  Hz), 90.6 (d,  $J = 183$  Hz) ( $\text{C}_6\text{H}_5$ ), 37.6 (C(CH $_3$ ) $_3$ ), 30.0 (q,  $J = 121$  Hz, CH $_3$ ); IR (CH $_2$ Cl $_2$ ) 2042 (s), 2020 (w), 1866 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{21}\text{BF}_4\text{Fe}_2\text{O}_3$ : C, 47.29; H, 4.18. Found: C, 46.95; H, 4.15.

**X-ray Structure Determination of 2.** Crystals for the diffraction study were grown by vapor diffusion of diethyl ether into an acetone solution of 2. A black, rectangular thin plate of dimensions  $0.07 \times 0.34 \times 0.72$  mm was mounted on a glass fiber and coated with epoxy. Collection of the diffraction data was carried out on a Syntex-Nicolet P1 diffractometer equipped with a graphite-monochromated Mo K $\alpha$  source and a modified LT-1 low-temperature device.

Preliminary cell constants and an orientation matrix for a monoclinic (*b* unique) lattice were determined from 10 centered reflections found from a randomly oriented rotation photograph. An axial rotation photograph suggested the possibility of a superposition of a second lattice along the *a* axis. The final orientation matrix and cell constants were calculated from 15 centered high-angle reflections. As a check on the quality of data obtained from the crystal, a full hemisphere of reflections was collected in a shell from  $3^\circ > 2\theta > 30^\circ$ . Three standard reflections, examined after every 53 measurements, showed no signs of decay throughout the data collection. In this hemisphere 6 unique reflections out of a total of 766 unique data were rejected on the basis of discrepancy between equivalents; the merging *R* value for this shell was 0.042. These factors indicated that there was no problem arising from the twinned dimension. A second shell of data from  $30^\circ > 2\theta > 45^\circ$  was collected over a unique quadrant, using the same check reflections.

Data reduction, solution, and refinement of the structure were performed with the SHELXTL structure determination package (Nicolet XRD Corp., Madison, WI). Systematic absences of  $\{h0l\}$  for  $l = 2n + 1$  and  $0k0$  for  $k = 2n + 1$  uniquely define the space group to be  $P2_1/c$ . There were no violations of systematic absences. Absorption corrections were performed by using the method of Hope.<sup>17</sup>

(16) Cole, T. E.; Pettit, R. *Tetrahedron Lett.* 1977, 781-784.

(17) This method (XABS) obtains an empirical absorption tensor<sup>18</sup> from an expression relating  $F_o$  and  $F_c$ : Hope, H.; Moezzi, B., Department of Chemistry, University of California, Davis, CA.

Direct methods were used to locate the positions of the iron, phosphorus, and fluorine atoms. Subsequent difference Fourier maps revealed the location of the remaining non-hydrogen atoms. Attempts to refine all non-hydrogen atoms anisotropically resulted in some of the carbon atom thermal parameters becoming non-positive definite. This was attributed to the inadequacy of the absorption correction. Neither psi scan nor analytical absorption corrections corrected the problem. As a consequence, only the iron, phosphorus, and fluorine atoms were refined anisotropically. All hydrogen atoms were included as fixed contributions at riding, idealized locations with thermal parameters set at 1.2 times that of the bonded carbon atom.

Some disorder in the PF $_6$  counteranion was evident particularly from the large thermal ellipsoids of the fluorine atoms. However, difference Fourier maps failed to suggest a suitable disorder model. The final refinement converged at  $R = 0.083$  and  $R_w = 0.090$ .

The final electron density difference map showed several peaks on the order of  $1 \text{ e}/\text{\AA}^3$ . The positions of these peaks were not associated with the structure and did not define any reasonable solvent molecule. Refinement of the structure using only the low-angle data from  $3^\circ > 2\theta > 30^\circ$  did not reproduce these peaks, suggesting they did not arise from low *Z* scatterers.

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**Registry No.** 1, 82660-14-8; *cis*-2, 106161-95-9; *trans*-2, 106247-69-2; 4, 103691-92-5; 5, 106161-97-1; *cis*-6, 106161-99-3; *trans*-6, 106247-72-7; *cis*-7, 106161-93-7; *trans*-7, 106247-74-9; 9-PF $_6$ , 106247-70-5; 9-BF $_4$ , 106162-01-0; 10-PF $_6$ , 106162-03-2; 11, 106162-04-3; *cis,anti*-12, 106162-05-4; *trans*-12, 106247-75-0; *cis,syn*-12, 106247-76-1; 13, 106162-06-5;  $\text{NET}_4^+\text{HFe}(\text{CO})_4$ , 25879-01-0; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5; phenylacetylene, 536-74-3; *tert*-butylacetylene, 917-92-0.

**Supplementary Material Available:** Complete listings of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for 2 (6 pages); a listing of observed and calculated structure factors for 2 (12 pages). Ordering information is given on any current masthead page.

(18) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 1983, A39, 158-166.

## Organometallic Chemistry of Carbon-Nitrogen Multiple Bonds.

### 5. Reactions of Vanadocene with Nitrilium Salts and the Crystal Structure of $\{\text{V}(\eta^5\text{-C}_5\text{H}_5)_2[\eta^2\text{-C}(\text{C}_6\text{H}_5)\text{NCH}_3]\}\text{BF}_4$

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Reactions of vanadocene with nitrilium salts  $[\text{C}_6\text{H}_5\text{C}\equiv\text{NCH}_3]\text{BF}_4$  and  $[\text{CH}_3\text{C}\equiv\text{NCH}_3]\text{BF}_4$  produce adducts that are characterized by small  $^{51}\text{V}$  hyperfine coupling constants (42.1 and 42.9 G, respectively) and C=N stretching absorptions characteristic of iminoacyls.  $\{\text{V}(\eta^5\text{-C}_5\text{H}_5)_2[\eta^2\text{-C}(\text{C}_6\text{H}_5)\text{NCH}_3]\}\text{BF}_4$  was isolated and characterized, by a single-crystal X-ray structure, as an  $\eta^2$ -iminoacyl complex. The dark maroon complex crystallized in the monoclinic space group *Cc* with  $a = 13.872$  (4) Å,  $b = 13.930$  (5) Å,  $c = 9.315$  (4) Å, and  $\beta = 99.33$  (3)°;  $\rho_{\text{calcd}} = 1.44 \text{ g cm}^{-3}$  for  $Z = 4$  and  $M_r$ , 386.13;  $R = 0.040$  and  $R_w = 0.049$  for 1673 data. The V-C and V-N bond distances are 2.054 (4) and 2.030 (4) Å, respectively. The C-N distance is 1.245 (7) Å, which gives a C-V-N angle of 35.2 (2)°. These adducts react with excess nitrilium salt to produce species, which have not been isolated, that have vanadium hyperfine coupling constants  $>60$  G.

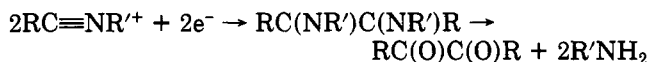
#### Introduction

A number of investigations have shown that iminium salts,  $[\text{R}_2\text{C}=\text{NR}'_2]\text{X}$ , which contain an unsaturated, elec-

trophilic cation, react readily with a variety of organometallic compounds to yield complexes that contain  $\eta^1$ - and  $\eta^2$ - $\text{CR}_2\text{NR}'_2$  moieties.<sup>1</sup> The more highly unsaturated ni-

trilium salts,  $[RC\equiv NR']X$ , are also known.<sup>2</sup> By analogy with the iminium salt results, reactions of nitrilium salts with nucleophilic organometallic species should yield  $\eta^1$ - and  $\eta^2$ -iminoacyl complexes. Although several examples of both types of iminoacyl complex have been prepared,<sup>3</sup> none have been prepared from the direct reaction of a nitrilium salt with an organometallic compound.

We have undertaken an investigation of the use of nitrilium salts in organometallic synthesis. Our objectives are to develop a systematic understanding of the modes of reaction of nitrilium salts with organometallic compounds and, if possible, to develop synthetically useful metal-promoted reactions. For example, an attractive reaction would be the reductive coupling of nitrilium salts to  $\alpha$ -diimines, which would be hydrolyzable to  $\alpha$ -diketones.



Nitrilium cations are isoelectronic and isostructural with acetylenes and might be expected to form structurally analogous metal complexes. Vanadocene is well-known to form monoacetylene complexes<sup>4</sup> so that it seemed like a good candidate for generation of an  $\eta^2$ -nitrilium ion complex. Since vanadocene undergoes facile  $2e$  oxidations, reductive coupling of nitrilium salts was also a possibility. This paper records the results of our initial effort to utilize nitrilium salts in organometallic synthesis.

### Experimental Section

Vanadocene and trimethyloxonium tetrafluoroborate were prepared by literature procedures.<sup>5,6</sup> Vanadocene was freshly sublimed before use in any reaction.

All manipulations were done under a nitrogen atmosphere in Vacuum Atmospheres glovebox or in oven-dried Schlenk ware. Solvents were distilled under nitrogen from appropriate drying agents before use. Infrared spectra were obtained on a Beckmann IR 4240 spectrophotometer; NMR spectra were obtained with a Varian T-60 spectrometer; EPR spectra were obtained with a

**Table I. Crystal Data for  $\{V(\eta^5-C_5H_5)_2[\eta^2-C(C_6H_5)NCH_3]\}BF_4$**

mol wt	386.13
dimens, mm	$0.50 \times 0.50 \times 0.40$
space group	Cc
cell constants (298 K)	
<i>a</i> , Å	13.872 (4)
<i>b</i> , Å	13.930 (5)
<i>c</i> , Å	9.315 (4)
$\beta$ , deg	99.33 (3)
no. of reflns used to determine cell constants and their $2\theta$ limits, deg	15
	17.05–28.35
<i>Z</i>	4
$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	1.44
$\rho_{\text{exptl}}$ , g cm <sup>-3</sup>	1.42 <sup>a</sup>

<sup>a</sup> By flotation in carbon tetrachloride/*n*-hexane.

Varian E-104 spectrometer with a 9-in. magnet. EPR spectra were analyzed as described by Muller et al.<sup>10</sup>

**Preparation of  $[C_6H_5CNCH_3]BF_4$ .** A 2.3-mL portion of benzonitrile was added to 3 g of trimethyloxonium fluoroborate suspended by stirring in ca. 50 mL of methylene chloride. The flask was fitted with a condenser and heated at reflux under a nitrogen atmosphere for 2 days. The solid that formed was collected, washed with ether, and dried in vacuo; yield, 2.9 g (71%) of a white solid. The <sup>1</sup>H NMR spectrum of this material matched that reported in the literature.<sup>7</sup> IR (Nujol mull):  $\nu_{C\equiv N}$  2380 cm<sup>-1</sup>. The product may be recrystallized from acetonitrile by addition of ether if desired. The preparation may be scaled up without decrease in yield.

**Preparation of  $[CH_3CNCH_3]BF_4$ .** Trimethyloxonium tetrafluoroborate (3 g) was dissolved in ca. 50 mL of acetonitrile and the solution kept at room temperature for 16 h under a nitrogen atmosphere. After this time, the volume was reduced to two-thirds, ether was added to the cloud point, and the mixture was allowed to stand for 1 h. The solid that formed was collected, washed with ether, and dried in vacuo; yield, 1.9 g (65%) of a white solid. The <sup>1</sup>H NMR spectrum of this material matched that reported in the literature.<sup>7</sup> IR (Nujol mull):  $\nu_{C\equiv N}$  2360 cm<sup>-1</sup>. Freshly prepared material may be recrystallized as described above. The salt discolors and becomes sticky upon storage for a few months. The reaction may be scaled up without decrease in yield.

**Preparation of  $\{V(\eta^5-C_5H_5)_2[\eta^2-C(C_6H_5)NCH_3]\}BF_4$ .** An acetonitrile solution of *N*-methylbenzonitrilium tetrafluoroborate, 1.06 g (5.2 mmol) in 6 mL, was added slowly over at least 30 min to a stirred THF solution of freshly sublimed vanadocene, 0.95 g (5.2 mmol). Formation of a maroon solid began almost immediately. The mixture was stirred for 1 h; the solid was then collected, washed with ether, and dried in vacuo; yield, 1.2 g (60%). Anal. Calcd for  $C_{13}H_{13}BF_4NV$ : C, 56.00; H, 4.70; N, 3.63. Found: C, 56.01; H, 4.75; N, 3.59. Note: slow addition of the nitrilium salt is necessary to avoid polymerization of THF. The complex may be recrystallized from methylene chloride by addition of ether. EPR ( $CH_2Cl_2$ ): *g* = 1.995, octet,  $A(^{51}V)$  = 42.1 G. IR (Nujol mull):  $\nu_{CN}$  1745 cm<sup>-1</sup>. IR ( $CH_3CN$ ): 1744 cm<sup>-1</sup>. Crystals suitable for X-ray diffraction were grown at -3 °C from a 3:1 v/v methylene chloride/hexane solution that was prepared by dilution, at room temperature, of a saturated methylene chloride solution of the complex with hexane.

**Reaction of Vanadocene with  $[CH_3CNCH_3]BF_4$ .** This reaction was conducted in the same fashion as described above and yielded a dark brown solid. The EPR spectrum of an acetonitrile solution of this solid indicated that more than one species was present, but the major species exhibited an eight-line pattern with  $A(^{51}V)$  = 60.5 G. Extraction of this solid with methylene chloride yielded a green solution whose EPR spectrum exhibited vanadium hyperfine coupling with  $A(^{51}V)$  = 42.9. This is the spectrum expected for the desired mononitrilium salt complex, but it could not be isolated in pure form.

**Solution and Refinement of the Structure of  $\{V(\eta^5-C_5H_5)_2[\eta^2-C(C_6H_5)NCH_3]\}BF_4$ .** The crystal chosen for data collection was sealed under nitrogen, in a glass capillary. Crystal

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**Table II. Data Collection and Refinement Details for  $[V(\eta^5-C_5H_5)_2][\eta^2-C(C_6H_5)NCH_3]BF_4$** 

diffractometer	Syntax P2 <sub>1</sub>
monochromator (Bragg 2 $\theta$ angle, deg)	graphite (12.2)
radiation, Å	Mo K $\alpha$ , 0.710 69
takeoff angle, deg	6.75
scan method	$\theta$ -2 $\theta$
scan speed, min/max, deg min <sup>-1</sup>	2.93/29.3
scan width, deg	2.0
no. of std (monitoring freq/no. o reflcns)	3 <sup>b</sup> /97
bkgd/scan time ratio (TR) <sup>a</sup>	1.0
2 $\theta$ limits of data, deg	4 < 2 $\theta$ < 50
$hkl$	- $h, 0, 0$ to $h, k, 0$
no. of data	1745
no. of data used in final refinement ( $F > 3\sigma_F$ )	1673
no. of data/no. of variables	8.45
$\mu$ , cm <sup>-1</sup>	5.44
$R = [\sum  F_o  -  F_c ] / [\sum  F_o ]$	0.040
$R_w = [\sum ( F_o  -  F_c )^2 w^2] / [\sum ( F_o )^2 w^2]$ <sup>d</sup>	0.049

<sup>a</sup> Background counts were measured before (BG1) and at the end (BG2) of the scan. Intensities were determined for the total scan (CT) and background (BG) counts by  $I = CT - TR(BG1 + BG2)$ .  $\sigma_I = [CT + (TR)^2(BG1 + BG2)]^{1/2}$ ;  $F_o = (I/Lp)^{1/2}$ , where  $Lp$  is the Lorentz and polarization correction. <sup>b</sup> Standard reflections were 0,0,4, 0,10,0, and 10,0,0. <sup>c</sup> No absorption corrections were applied. <sup>d</sup>  $w = n/(\sigma_F^2 + mF^2)$ . In the final least-squares cycle  $n = 1.00$  and  $m = 3.27 \times 10^{-3}$ .

data are given in Table I. The structure was solved by standard heavy-atom methods. After location of all non-hydrogen atoms, hydrogen atom positions were calculated by assuming sp<sup>3</sup> or sp<sup>2</sup> geometry of the carbon atoms as appropriate. Thermal parameters of each group of hydrogen atoms were treated as a unit. Isotropic hydrogen atom thermal parameters, positional and isotropic thermal parameters of phenyl group carbon atoms, and positional and anisotropic thermal parameters of all other atoms were subjected to least-squares refinement until convergence. Additional details of data collection and refinement are given in Table II. Scattering factors for both determinations were taken from the usual source;<sup>8</sup> those for all atoms except hydrogen were corrected for real and imaginary anomalous dispersion components with use of the dispersion factors given by Cromer.<sup>9</sup> All computations were carried out by using Sheldrick's SHELX-76 program package with minor local modifications. A listing of non-hydrogen atom positional parameters is given in Table III. Hydrogen atom positional parameters, thermal parameters for all atoms, and structure factor tables are given as supplementary material.

## Results

**Reaction of  $V(\eta^5-C_5H_5)_2$  with Nitrilium Salts.** Vanadocene reacted rapidly with 1 equiv of *N*-methylbenzonitrilium (I) or *N*-methylacetoneitrilium (II) fluoroborate in THF-acetonitrile mixtures. The product of the reaction with I (III) precipitated immediately as a maroon microcrystalline solid that analyzed for vanadocene plus 1 equiv of I. The maroon complex exhibited a single, sharp C=N absorption at 1745 cm<sup>-1</sup>, and its isotropic EPR spectrum consisted of an eight-line pattern with  $g = 1.995$  and  $A(^{51}V) = 42.1$  G. Product III was shown to be the expected  $[V(\eta^5-C_5H_5)_2][\eta^2-C(C_6H_5)NCH_3]BF_4$  by a single-crystal X-ray structure determination (vide infra).

The product obtained from reaction of vanadocene with II was a dark brown precipitate IV whose infrared spectrum contained absorptions at 1760 and 1660 cm<sup>-1</sup>. The EPR spectrum of IV in acetonitrile suggested that the

**Table III. Final Positional Parameters (with Esd's) for Non-Hydrogen Atoms of  $[V(\eta^5-C_5H_5)_2][\eta^2-C(C_6H_5)NCH_3]BF_4$** 

atom	$x$	$y$	$z$	$U, \text{Å}^2$
V	0.00000	0.20016 (4)	0.00000	0.0419 (4)
N	-0.0036 (5)	0.0879 (3)	-0.0964 (3)	0.044 (2)
C1	-0.1310 (5)	0.1112 (3)	-0.0910 (3)	0.042 (2)
C2	-0.2767 (5)	0.0806 (3)	-0.1375 (3)	0.0420 (9)
C3	-0.2990 (6)	0.0182 (4)	-0.2162 (4)	0.052 (1)
C4	-0.4407 (7)	-0.0049 (5)	-0.2612 (5)	0.060 (1)
C5	-0.5584 (8)	0.0355 (5)	-0.2268 (5)	0.070 (2)
C6	-0.5352 (8)	0.0973 (5)	-0.1471 (5)	0.071 (2)
C7	-0.3972 (6)	0.1209 (4)	-0.1043 (4)	0.061 (1)
C8	0.0671 (6)	0.0172 (5)	-0.1495 (4)	0.062 (3)
C9	0.078 (1)	0.3564 (5)	0.0040 (6)	0.076 (5)
C10	-0.066 (1)	0.3545 (6)	-0.0133 (9)	0.104 (7)
C11	-0.112 (1)	0.3121 (8)	-0.101 (1)	0.117 (8)
C12	0.021 (2)	0.2852 (6)	-0.1382 (6)	0.142 (9)
C13	0.132 (1)	0.3141 (6)	-0.0676 (9)	0.103 (7)
C14	-0.0599 (9)	0.0937 (6)	0.1097 (4)	0.073 (4)
C15	0.0833 (9)	0.0774 (4)	0.1049 (4)	0.065 (4)
C16	0.1631 (7)	0.1599 (6)	0.1366 (4)	0.069 (4)
C17	0.071 (1)	0.2257 (5)	0.1638 (4)	0.077 (4)
C18	-0.072 (1)	0.1862 (7)	0.1458 (5)	0.095 (5)
B	0.0235 (8)	0.1879 (5)	0.6018 (5)	0.061 (4)
F1	-0.0858 (5)	0.1502 (3)	0.6444 (3)	0.088 (3)
F2	0.018 (1)	0.1549 (5)	0.5097 (5)	0.141 (5)
F3	0.0168 (8)	0.2855 (3)	0.6013 (4)	0.111 (4)
F4	0.1518 (5)	0.1573 (5)	0.6545 (6)	0.130 (5)

expected product was present ( $g = 1.994$  and  $A(^{51}V) = 43$  G) but along with a second more abundant species with  $g = 1.993$  and  $A(^{51}V) = 60.5$  G. Attempts to separate these species by recrystallization were unsuccessful. Extraction of IV with methylene chloride yielded a green solution whose EPR spectrum was nearly identical with that of the product from I with  $g = 1.994$  and  $A(^{51}V) = 42.9$  G.

Complex III reacted with additional I, but the results were not straightforward. Examination of acetonitrile solutions containing III and nitrilium salt by EPR spectroscopy indicated that a new species having  $g = 1.992$  and  $A(^{51}V) = 47.4$  G was slowly formed at the expense of III over a period of a few days at room temperature. During this time the maroon solution became orange-red. Less than 0.5 equiv of nitrilium salt was required for complete conversion to the new species. An identical species (by EPR) was obtained by treatment of III with diphenylacetylene in acetonitrile, but not in methylene chloride. Control experiments indicated that exposure of III to acetonitrile alone did not yield the new species. The orange material could not be crystallized, but the oils obtained by removal of solvent exhibited infrared absorptions at ca. 1676 and 1650 cm<sup>-1</sup>.

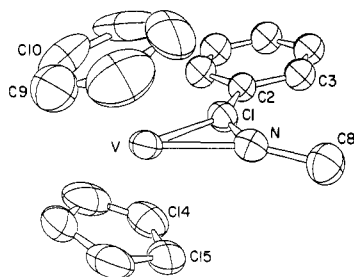
When III was heated at reflux in acetonitrile with at least 1 equiv of I, orange-brown solutions resulted. EPR spectra obtained on these solutions indicated that a new vanadium complex having  $g = 1.982$  and  $A(^{51}V) = 73$  G was present. When greater than 1 equiv of nitrilium salt was used, a green compound crystallized from the reaction mixture. This green complex was shown to be  $[V(\eta^5-C_5H_5)_2(NCCH_3)_2](BF_4)_2$  by analysis and by comparison of its EPR and infrared spectra with those of an authentic sample. The amount of this material formed was roughly proportional to the excess of nitrilium salt that was used. When solvent was removed from these reaction mixtures, their infrared spectra did not contain an absorption for free nitrilium salt, but there were three, nearly equally intense absorptions at 1660, 1625, and 1590 cm<sup>-1</sup>. We were unable to crystallize the vanadium product having  $A(^{51}V) = 73$  G.

**Description of the Structure of  $[V(\eta^5-C_5H_5)_2][\eta^2-C(C_6H_5)NCH_3]BF_4$  (III).** The crystal structure consists of noninteracting  $[V(\eta^5-C_5H_5)_2][\eta^2-C(C_6H_5)NCH_3]^+$  cations

(8) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(9) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(10) Muller, E. G.; Waktins, S. F.; Dahl, L. F. *J. Organomet. Chem.* 1976, 111, 73.



**Figure 1.** Perspective drawing of the cation  $\{V(\eta^5\text{-C}_5\text{H}_5)_2[\eta^2\text{-C}(\text{C}_6\text{H}_5)\text{NCH}_3]\}^+$ . Hydrogen atoms are not shown; probability ellipsoids are at the 50% level.

**Table IV.** Selected Interatomic Distances (Å) and Angles (deg) for  $\{V(\eta^5\text{-C}_5\text{H}_5)_2[\eta^2\text{-C}(\text{C}_6\text{H}_5)\text{NCH}_3]\text{BF}_4$

Bond Distances			
V-N	2.054 (4)	C4-C5	1.385 (9)
V-C1	2.030 (4)	C5-C6	1.39 (1)
V-C9	2.292 (7)	C6-C7	1.365 (9)
V-C10	2.236 (8)	C2-C7	1.399 (7)
V-C11	2.237 (7)	C9-C10	1.32 (1)
V-C12	2.228 (7)	C10-C11	1.36 (2)
V-C13	2.299 (7)	C11-C12	1.47 (2)
V-C14	2.259 (6)	C12-C13	1.37 (2)
V-C15	2.298 (5)	C9-C13	1.32 (1)
V-C16	2.298 (5)	C14-C15	1.37 (1)
V-C17	2.289 (6)	C15-C16	1.40 (1)
V-C18	2.240 (7)	C16-C17	1.35 (1)
N-C1	1.245 (7)	C17-C18	1.42 (1)
N-C8	1.451 (7)	C14-C18	1.39 (1)
C1-C2	1.468 (6)		
C2-C3	1.384 (7)		
C3-C4	1.402 (8)		
Bond Angles			
C1-V-N	35.5 (2)	V-N-C8	152.5 (4)
V-C1-C2	150.5 (4)	C8-N-C1	136.3 (5)
V-C1-N	73.3 (3)	N-C1-C2	136.1 (4)
V-N-C1	71.2 (3)		

and fluoroborate anions. A drawing of the cation is given in Figure 1, and a listing of interatomic distances and angles is given in Table IV. The basic structural features of the cation are very similar to those of other  $M(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2$  complexes and particularly to  $\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2[\eta^2\text{-C}(\text{Ph})\text{NC}_6\text{H}_3\text{-2,6-Me}]\}^{30}$  and  $[\text{V}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^2\text{-C}_2(\text{CO}_2\text{CH}_3)_2)]^{11}$  both of which are isoelectronic with the present complex. The V-C1 distance in III is 2.030 (4) Å, and the V-N distance is 2.054 (4) Å. These distances are significantly shorter than the Ti-C and Ti-N distances (2.096 (4) and 2.149 (4) Å, respectively) in  $\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2[\eta^2\text{-C}(\text{Ph})\text{NC}_6\text{H}_3\text{-2,6-Me}]\}^{30}$  and their average (2.042 Å) is less than the average V-C(acetylene) distance in  $[\text{V}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^2\text{-C}_2(\text{CO}_2\text{CH}_3)_2)]^{11}$  (2.09 Å).<sup>11</sup> The C1-N distance in III of 1.245 (7) Å reflects the expected lengthening (from ca. 1.16 Å for a normal C≡N bond) due to  $\pi$ -interactions with the metal. The "bent-back" angles C2-C1-N and C1-N-C8 are 136.1 (4)° and 136.3 (5)°, respectively. The distances between the vanadium and the cyclopentadienyl planes in III are the same at 1.95 Å, and the angle between the V-Cp vectors is 137°. Corresponding M-Cp distances for  $\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2[\eta^2\text{-C}(\text{Ph})\text{NC}_6\text{H}_3\text{-2,6-Me}]\}$  and  $[\text{V}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^2\text{-C}_2(\text{CO}_2\text{CH}_3)_2)]$  are 2.06<sup>30</sup> and 1.96 Å,<sup>11</sup> respectively. The dihedral angle between the V,C1,N and V,Cp,Cp planes in III is 94.6°. The essentially planar arrangement of the five atoms V, C1, N, C2, and C8 is indicated by the low value of the C2-C1-N-C8 torsion angle,

**Table V.** Variation of the Vanadium-51 Hyperfine Coupling Constant in  $\text{VCp}_2\text{L}_2$  Complexes with L-V-L Angle

L (L-L)	L-V-L angle/deg	$a_V/\text{G}$	ref
PhS	94	63	13
S <sub>8</sub>	89	61	14
Cl	87	74	15
PhC(O)CHC(O)Ph	a	75	16
CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub>	78	64	b
tropolonato	a	66	16
MeCO <sub>2</sub> C≡CCO <sub>2</sub> Me	36	43	10
CF <sub>3</sub> C≡CCF <sub>3</sub>	a	45	10b
PhN=NPh	a	45	10b
PhC≡NMe	36	42	c

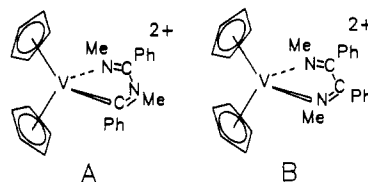
<sup>a</sup> Not available. <sup>b</sup> Petersen, J. L., personal communication. <sup>c</sup> This work.

which is only 1.8°. The V,C1,N and phenyl ring planes are nearly parallel with a dihedral angle between them of only 10°.

## Discussion

Previous syntheses of iminoacyl complexes have utilized insertion reactions of isocyanides into metal-carbon bonds, oxidative-addition reactions of imidoyl halides, and reactions of metalate anions with imidoyl halides. The present results confirm that nitrilium salts can be used to make an  $\eta^2$ -iminoacyl complex. It should be pointed out that we have failed to obtain characterizable complexes of nitrilium salts with a number of compounds that gave tractable products from reactions with iminium salts, i.e.  $\text{Ni}(\text{PPh}_3)_2\text{C}_2\text{H}_2$ ,  $\text{Na}[\text{FeCp}(\text{CO})_2]$ ,  $\text{Ni}(\text{COD})_2$ , and  $\text{Ni}(\text{CO})_4$ . Iminoacyl products have been obtained from reactions of metalate anions with imidoyl halides, however.<sup>3f,i,l,n,s,t</sup> The absence of similarity between nitrilium and iminium salt reactions is further illustrated by the failure of vanadocene to give a product containing the iminium ion upon reaction with  $[\text{CH}_2=\text{N}(\text{CH}_3)_2\text{Br}]$ . Rather, a blue product that analyzed for  $\text{VCp}_2\text{Br}$  was obtained.

EPR data for other  $\text{VCp}_2\text{L}_2$  complexes (see Table V for some representative data) suggest that there is a rough correlation between the vanadium hyperfine coupling constant and the L-V-L angle.<sup>12</sup> On this basis the species with the 73-G coupling constant almost certainly has two donors bonded with an angle between them that is substantially greater than the angle in a  $\pi$  complex. Presumably the major product formed from vanadocene and II ( $A(^{51}\text{V}) = 60.5 \text{ G}$ ) has a similar structure. Chelate complexes A and B, which involve head-to-tail and head-to-



(12) The magnitude of  $A_{\text{iso}}$  actually reflects the extent of electron delocalization (ref 11b and references cited). There is no reason to expect that there is a linear correlation between the extent of electron delocalization and the L-V-L angle. However, the available data clearly indicate that complexes that contain two monodentate L groups or a bidentate ligand (L-L) that forms a five- or six-membered chelate ring have hyperfine coupling constants greater than 65 G.

(13) As pointed out by a reviewer, participation of the second nitrilium  $\pi$ -orbital in bonding might have a significant effect in some cases. To the extent that this orbital can interact with an empty orbital on the metal, then the M-N bond should be shortened relative to the M-C. Conversely, if this orbital interacts with a filled orbital on the metal, the resulting antibonding interaction should result in a lengthening of the M-N bond relative to the M-C bond.

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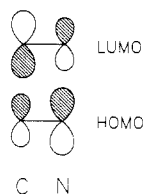
(11) (a) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* 1979, 18, 2282. (b) Petersen, J. L.; Griffith, L. *Inorg. Chem.* 1980, 19, 1852.

Table VI. Selected Data for Structurally Characterized  $\eta^2$ -Iminoacyl Complexes

	M-C/Å	M-N/Å	C-N/Å	$\nu_{\text{CN}}/\text{cm}^{-1}$	ref
TiCp <sub>2</sub> [ $\eta^2$ -C(Ph)NC <sub>6</sub> H <sub>3</sub> -2,6-Me]	2.096 (4)	2.149 (4)	1.280 (6)	1573	3o
{VCp <sub>2</sub> [ $\eta^2$ -C(Ph)NMe]}BF <sub>4</sub>	2.030 (4)	2.054 (4)	1.245 (7)	1745	a
ZrCp <sub>2</sub> (Me)[ $\eta^2$ -C(CHPh <sub>2</sub> )NMe]	2.245 (3)	2.205 (2)	1.262 (3)		19
Zr(OC <sub>6</sub> H <sub>3</sub> -2,6- <i>t</i> -Bu) <sub>2</sub> [ $\eta^2$ -C(Bz)N- <i>t</i> -Bu] <sub>2</sub>	2.228 (3)	2.221 (3)	1.286 (4)	1560	3c
Zr[HB(3,5-Me <sub>2</sub> pz) <sub>3</sub> ](Me)(O- <i>t</i> -Bu)[ $\eta^2$ -C(Me)N- <i>t</i> -Bu]	2.201 (1)	2.194 (8)	1.27 (2)	1542	3e
MoCp(CO) <sub>2</sub> [ $\eta^2$ -C(Me)NPh]	2.106 (5)	2.143 (4)	1.233 (6)	1670	3q
{Mo(CN- <i>t</i> -Bu) <sub>5</sub> [ $\eta^2$ -C(Bz)N- <i>t</i> -Bu]}Br	2.14 (2)	2.17 (2)	1.25	1755	3g
Ru(PPh <sub>3</sub> ) <sub>2</sub> (CO)(Cl)[ $\eta^2$ -C( <i>p</i> -tolyl)N( <i>p</i> -tolyl)]	2.031 (8)	2.123 (7)	1.30 (1)	1654	3r

head coupling of 2 equiv of I, respectively, would have L-V-L angles in the proper range, and either one should have infrared spectral properties similar to those of the unknown species. Compounds of type A are formed in reactions of imidoyl halides with certain organometallic compounds.<sup>3s,f,l,17</sup> These species are apparently formed by intermolecular reactions of  $\eta^1$ -iminoacyl groups with free imidoyl halide. Coupling of imidoyl chlorides to  $\alpha$ -diimines by anionic nickel (0) species has also been reported but the reaction appears to proceed by a radical reaction and does not involve an iminoacyl complex.<sup>18</sup> An example of coupling of coordinated  $\eta^2$ -iminoacyl moieties to give an  $\alpha$ -diimine (or 1,4-diaza-1,3-butadiene) was recently reported.<sup>3a</sup> We currently have no model to account for the species with the ca. 47-G hyperfine coupling constant that is formed upon treatment of III with less than equivalent amounts of nitrilium salt or with diphenylacetylene.

The shortening of the  $\pi$ -donor to metal distances in III compared to those in {Ti( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>[ $\eta^2$ -C(Ph)NC<sub>6</sub>H<sub>3</sub>-2,6-Me]} and [V( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>( $\eta^2$ -C<sub>2</sub>(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>)] can be attributed to the effect of the formal charge on the vanadium atom in III, which results in the normal tightening of bonding interactions. All of the eight structurally characterized,  $\eta^2$ -iminoacyl complexes but one have M-N distances that are equal to, or greater than, the M-C distances (Table VI). Consideration of the asymmetry of the HOMO and LUMO of the nitrilium ion, i.e.



would predict that if  $\sigma$ -bonding ( $p_\pi$  donation) predominates, the M-N distance should be shorter than the M-C distance, whereas if the  $\pi$ -bonding ( $p_\pi^*$  back-bonding) interaction was more important, then the M-C distance

should be the shortest. This analysis assumes that there are no steric interactions between iminoacyl substituents and ancillary ligands in the complex and that the  $\pi$ -orbital that is perpendicular to the M,C,N plane does not play a significant role.<sup>13</sup> The data in Table VI suggest that the  $\pi$ -back-bonding interaction is very important to the bonding of the  $\eta^2$ -iminoacyl ligand in at least seven of the eight compounds listed in Table VI. The relatively large difference in Ti-N and Ti-C distances in {Ti( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>[ $\eta^2$ -C(Ph)NC<sub>6</sub>H<sub>3</sub>-2,6-Me]} is probably a result of steric interactions between the cyclopentadienyl hydrogens and the methyl groups of the 2,6-dimethylphenyl substituent. ZrCp<sub>2</sub>(CH<sub>3</sub>)[ $\eta^2$ -CH<sub>3</sub>NCCH(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>] is the only compound in Table VI that has a M-C distance that is longer than the M-N distance. It is quite possible that this exception results from steric interactions between the diphenylmethyl group and the cyclopentadienyl rings since the ORTEP drawing of the complex shows that the phenyl rings are pointing toward the cyclopentadienyl groups.<sup>13,19</sup>

The difference in the Ru-C and Ru-N distances in Ru(PPh<sub>3</sub>)<sub>2</sub>(CO)(Cl)( $\eta^2$ -*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NCC<sub>6</sub>H<sub>5</sub>-*p*-CH<sub>3</sub>) is very large at 0.09 Å. There do not appear to be any significant steric interactions between either *p*-tolyl group and any other ligand. This large difference suggests that the  $\pi$ -back-bonding interaction is much stronger than the  $\sigma$ -donor interaction in this complex.<sup>13</sup> As the  $\pi$ -interaction increases and the  $\sigma$  decreases, the bonding approaches the limiting structure of an  $\eta^1$ -iminoacyl.

Finally, it is worth noting that there is no apparent correlation of the C-N bond distances with the M-C and M-N distances for the complexes listed in Table VI. And although there is a substantial variation in C-N stretching absorption for these complexes, there does not seem to be a correlation with any structural parameter.

**Acknowledgment.** This work was supported in part by NSF Grant CHE78-18584.

**Supplementary Material Available:** Tables of anisotropic and isotropic thermal parameters and hydrogen atom positional parameters (2 pages); a listing of structure factor tables (7 pages). Ordering information is given on any masthead page.

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