

**Figure 7.** Some orbital splitting patterns for the d orbitals of Cr(CO)<sub>6</sub>, on changing to Cr(CO)<sub>5</sub> and Cr(CO)<sub>5</sub>(amine).

the previous reasoning and whether the experimental result is predictable by a semiquantitative calculation, for example, a calculation of the Fenske-Hall type.

The answer to the first question is really rather simple, in retrospect. The level pattern for Cr(CO)<sub>5</sub> in Figure 7a is correct (and is therefore repeated in Figure 7b). It is also true

that the introduction of a  $\sigma$  donor, NR<sub>3</sub>, into the vacant position of Cr(CO)<sub>5</sub> must raise the energy of the a<sub>1</sub> orbital. The crucial point, however, that even though NR<sub>3</sub> is *potentially* a better  $\sigma$  donor than CO, *other things being equal*, other things are not at all equal. The Cr-C distances, 1.82-1.91 Å, are so much shorter than the Cr-N distances, ca. 2.20 Å, that *in these molecules, CO functions as a stronger  $\sigma$  donor than the amine ligands*. Thus, the introduction of NR<sub>3</sub> into Cr(CO)<sub>5</sub> raises the energy of the a<sub>1</sub> orbital so that it is *less far below* the b<sub>1</sub> orbital, but it does not push it *above* the b<sub>1</sub> orbital, because NR<sub>3</sub> is too far from the metal atom to exert that strong a  $\sigma$  effect. Schematically, then, the behavior of the Cr(CO)<sub>6</sub>-Cr(CO)<sub>5</sub>-Cr(CO)<sub>5</sub>NR<sub>3</sub> series is represented by Figure 7b. This type of pattern is predicted, though not with quantitative correctness, by the Fenske-Hall calculation, as shown in Figure 6.

From the experimental data<sup>13,14</sup> we may say that the actual splitting energies in Figure 7b have approximately the following values:  $E_0 \approx 32\,000\text{ cm}^{-1}$ ;  $E_1 \approx E_1' \approx 5\,000\text{ cm}^{-1}$ ;  $E_2 \approx 11\,000\text{ cm}^{-1}$ ;  $E_2' \approx 4\,000\text{ cm}^{-1}$ ;  $E_3 \approx 16\,000\text{ cm}^{-1}$ ;  $E_3' \approx 23\,000\text{ cm}^{-1}$ . These give an internally consistent pattern, with  $E_1 + E_2 + E_3 \approx E_0$  and  $E_1' + E_2' + E_3' \approx E_0$ .

**Acknowledgment.** We thank the National Science Foundation for financial support and B. J. Baldwin-Zuschke for experimental contributions to this research. B.W.S.K. is the recipient of a NATO postdoctoral fellowship from the Natural Sciences and Engineering Research Council of Canada.

**Registry No.** 1, 15710-39-1; 2, 14740-77-3; 3, 78804-46-3; Cr(CO)<sub>5</sub>NH<sub>3</sub>, 15228-27-0.

**Supplementary Material Available:** Tables of observed and calculated structure factors for both crystals (16 pages). Ordering information is given on any current masthead page.

Contribution from Anorganisch-Chemisches Institut, Technische Universität München, D-8046 Garching, West Germany

## Hydrocarbon-Bridged Vanadocenes<sup>1</sup>

FRANK H. KÖHLER,\* WOLFRAM PRÖSSDORF, and ULRICH SCHUBERT

Received May 27, 1981

Bent vanadocene units have been linked by hydrocarbon bridges. It is shown that the stability of the new compounds depends on the substitution of the Cp rings. Apart from analytical and mass spectroscopic data, characterization is based on NMR spectroscopy. The molecular structure of (C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>VC<sub>6</sub>H<sub>4</sub>V(C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub> has been determined by X-ray analysis. Covering a range of up to 190 ppm for <sup>1</sup>H and 760 ppm for <sup>13</sup>C, NMR spectroscopy has proved to be a sensitive probe for magnetic properties. It is shown that the four electrons per molecule remain essentially unpaired. The stereochemistry derived from NMR data agrees well with X-ray results.

### Introduction

Metal-metal interactions may occur directly via overlapping metal orbitals in simple dimers<sup>2</sup> or in cluster molecules.<sup>3</sup> Most evidence for this comes from structural work, and diamagnetic organometallic compounds have been of prominent interest.<sup>3</sup> A different type of interaction is found when bridging groups prevent direct overlap and metals "know about each other" via transmitting orbitals of the bridge. This may be derived from the magnetism of transition-metal complexes,<sup>4</sup> most of

which do not contain metal-carbon bonds.

However, organometallics bridged by acetylenes should also exhibit metal-metal interactions as pointed out by Kim et al.,<sup>5</sup> although they were not able to prove it. Tsutsui et al.<sup>6</sup> synthesized two bridged tris(cyclopentadienyl)uranium derivatives and carried out solid-state magnetic measurements. They found a remarkably reduced susceptibility for the bridged molecules. Whether this is due to an intermolecular or an

(1) NMR of Paramagnetic Complexes. 24. For part 23 see ref 8.

(2) Templeton, J. L. *Prog. Inorg. Chem.* **1979**, *26*, 211-300.

(3) Vahrenkamp, H. *Angew. Chem.* **1978**, *90*, 403-416; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 379-407.

(4) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173-241.

(5) Kim, P. J.; Masai, H.; Sonogashira, K.; Hagihara, N. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 181-185.

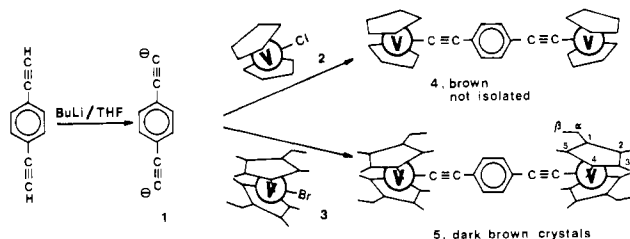
(6) Tsutsui, M.; Ely, N. J. *Am. Chem. Soc.* **1974**, *96*, 3650-3651. Tsutsui, M.; Ely, N.; Gebala, A. *Inorg. Chem.* **1975**, *14*, 78-81.

Table I. Isotropic  $^1\text{H}$  and  $^{13}\text{C}$  Shifts (ppm) at 298 K

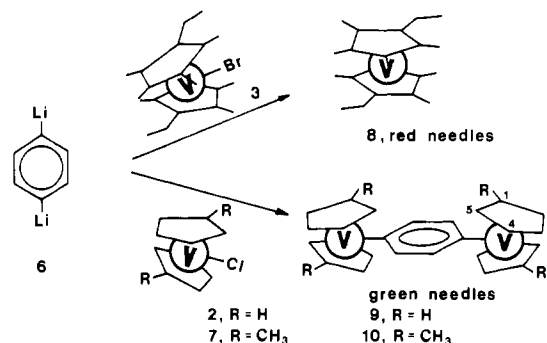
compd	nucleus	solvent	ring positions			$\alpha$ positions			bridge or $o\text{-C}_6\text{H}_5$	$\text{C}_6\text{H}_5$		
			1	2/5 <sup>a</sup>	3/4 <sup>a</sup>	1	2/5 <sup>a</sup>	3/4 <sup>a</sup>		$\beta$ position	<i>m</i>	<i>p</i>
5	$^1\text{H}$	$\text{C}_7\text{D}_8$				-8.5	-16.5	-21.5	0.6	19.2		
	$^{13}\text{C}$	$\text{C}_6\text{H}_6$	223.0	217.2	234.8	-352.4 <sup>d</sup>	-361.8	-361.8	-344.6	-530.4, 20.2 <sup>e</sup>		
11 <sup>b</sup>	$^1\text{H}$	$\text{C}_6\text{D}_6$				-9.6	-18.1	-22.5	0.8	40.2	-17.6	6.0
	$^{13}\text{C}$	$\text{THF-d}_8$		-125.1						52.0		
9	$^1\text{H}$	$\text{C}_7\text{D}_8$								<i>c</i>		
	$^{13}\text{C}$	$\text{THF-d}_8$		187.4						<i>c</i>		
10	$^1\text{H}$	$\text{C}_7\text{D}_8$	-143.2	-124.3		-41.7				50.6		
	$^{13}\text{C}$	$\text{THF-d}_8$	213.3	213.0	163.1	-268.9				<i>c</i>		
12	$^1\text{H}$	$\text{C}_6\text{D}_6$								38.7	11.5	5.7
	$^{13}\text{C}$	$\text{C}_7\text{D}_8$		-128						<i>c</i>	-40.8	-101.5

<sup>a</sup> Tentative assignment; interchange cannot be excluded. For numbering, cf. Schemes I and II. <sup>b</sup> From ref 8. <sup>c</sup> Not observed. <sup>d</sup> Not separated from  $\text{Ca}2\text{-5}$ , splitting due to different reference shifts. <sup>e</sup> Under the assumption that the acetylide carbons as the two nearest neighbors to vanadium are not observed (cf. text), the more shifted signal belongs to the ipso carbons, the other (bigger) one to the remaining bridge carbons.

Scheme I



Scheme II



intramolecular interaction remains unclear.

An advantageous method should be NMR on suitable paramagnetic molecules: (i) impurities accompanying sensitive organometallic compounds are not expected to affect the results since individual rather than bulk properties are measured; (ii) the huge isotropic shifts may serve as sensitive probe for spin pairing; (iii) stereochemical information may be obtained. We wanted to confirm this for organometallic derivatives of the d-block metals with two paramagnetic centers being linked by simple hydrocarbons. Corresponding examples apparently do not exist, probably due to thermal lability of M-C bonds.<sup>7</sup> The present work describes the synthesis of paramagnetic vanadocene derivatives of the type  $\text{Cp}_2\text{V}(\text{C}_m\text{H}_n)\text{VCp}_2$ , their NMR investigation, and X-ray structural results.

## Results and Discussion

**(A) Formation of Compounds.** Vanadocene units may be linked by reacting vanadocene halides with  $\alpha,\omega$ -dimetalated hydrocarbons. We chose *p*-diethynylbenzene as a rather long bridge with fully conjugated carbon framework (see Scheme I).

Reaction with vanadocene chloride (2) yielded brown reaction products showing strongly shifted  $^1\text{H}$  signals. However, we were not able to isolate 4 as a pure solid in agreement with the thermal lability of the corresponding monomer.<sup>8</sup> Peralkylation of the Cp rings stabilized the V-C bond considerably,<sup>8</sup> and with bis(ethyltetramethyl- $\eta^2$ -cyclopentadienyl)vanadium bromide (3) we obtained the bridged compound 5 as brown crystals.

With possible metal-metal interaction in view, we introduced shorter bridges by reaction of vanadocene halides with *p*-dilithiobenzene (6) (see Scheme II). Contrary to the stabilizing effect on vanadium acetylide bonds, the peralkylated halide 3 only yielded the reduction product 8, identified by its characteristic red color and its  $^1\text{H}$  NMR spectrum.<sup>9</sup>

This failure may be attributed to steric hindrance, since 2 and 7 gave the desired bridge compounds 9 and 10 as green needles.

The new compounds 5, 9, and 10 are extremely air sensitive. They are thermally rather stable at room temperature. At 60 °C in solution slow decomposition occurs as evidenced by growing  $^1\text{H}$  signals of the corresponding vanadocenes. This parallels our findings for  $\text{Cp}_2\text{VR}$ .<sup>8</sup> Besides NMR and X-ray analysis, 5, 9, and 10 are characterized by elemental analysis and mass spectroscopy. With the experimental conditions (vide infra) taken into account, which were necessary because of the sensitivity of the compounds, the elemental analysis results are satisfying. Problems are encountered also in the mass spectrometer. While 9 and 10 are rather volatile, giving the parent ions at  $m/e$  438 and  $m/e$  494, 5 had to be heated at 200 °C. At this temperature, decomposition is expected to be fast and  $\text{M}^+$  is found with low intensity. A summary of the major fragments is given in the experimental section.

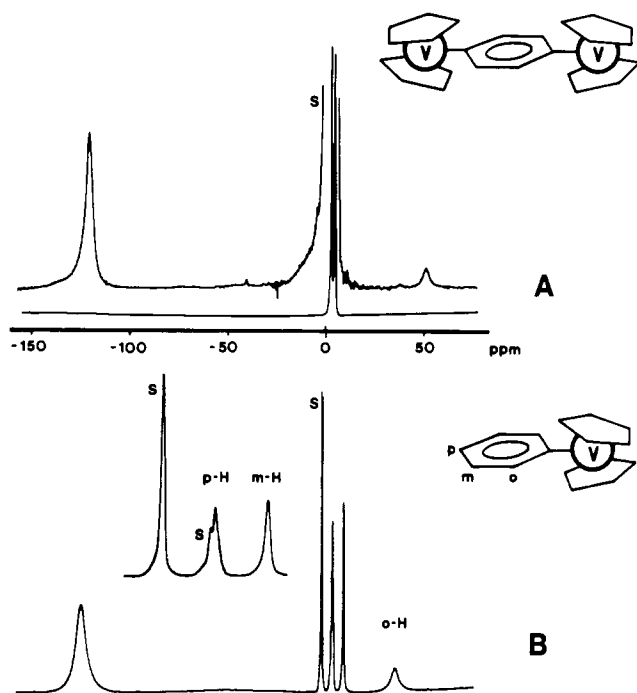
**(B) NMR Investigations.** The bridged compounds 5, 9, and 10 may conveniently be studied by  $^1\text{H}$  NMR spectroscopy. Even nondeuterated solvents may be used if the expected signals have sufficient paramagnetic shifts. In the  $^1\text{H}$  spectrum of 9 (see Figure 1A), the most interesting signal comes from the bridge protons. It appears near 50 ppm (cf. Table II) and should indicate how far both metals influence the unpaired electron spin density within the bridge. If spin pairing occurs in 9, we would expect  $\text{C}_6\text{H}_4$  to be less shifted than the ortho protons of the corresponding monomer  $\text{Cp}_2\text{VC}_6\text{H}_5$  (12).<sup>8</sup> However, Figure 1B and our data in Table I show the opposite behavior. This is verified by the comparison of 10 and 12.

Since each phenylene proton of the bridge compounds 9 and 10 is in a position meta to one vanadium and ortho to the other, their shift should be the sum of the shifts  $\delta^{\text{para}}(\text{H-o}) + \delta^{\text{para}}(\text{H-m}) = 50.2$  as calculated from 12. The agreement is reasonably good<sup>10</sup> and indicates (i) that the equilibrium ar-

(7) (a) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* 1976, 76, 219-242. (b) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* 1976, 76, 243-268. (c) Taube, R.; Dreys, H.; Steinborn, D. *Z. Chem.* 1978, 18, 425-440.

(8) Köhler, F. H.; Hofmann, P.; Prössdorf, W. *J. Am. Chem. Soc.* 1981, 103, 6359.

(9) Köhler, F. H.; Doll, K. H.; Prössdorf, W. *J. Organomet. Chem.*, in press.



**Figure 1.** 200-MHz  $^1\text{H}$  NMR spectra at 302 K: A, **9** dissolved in  $\text{THF-}h_8$ , with upper trace amplified by a factor of 86.6; B,  $(\text{C}_5\text{Me}_4\text{Et})_2\text{VC}\equiv\text{CC}_6\text{H}_5$  (**12**) dissolved in toluene- $d_8$ . S = solvent. The  $\text{C}_6\text{H}_5$  signal of toluene has arbitrarily been chosen as zero (cf. text). Paramagnetic shifts to high field are positive.

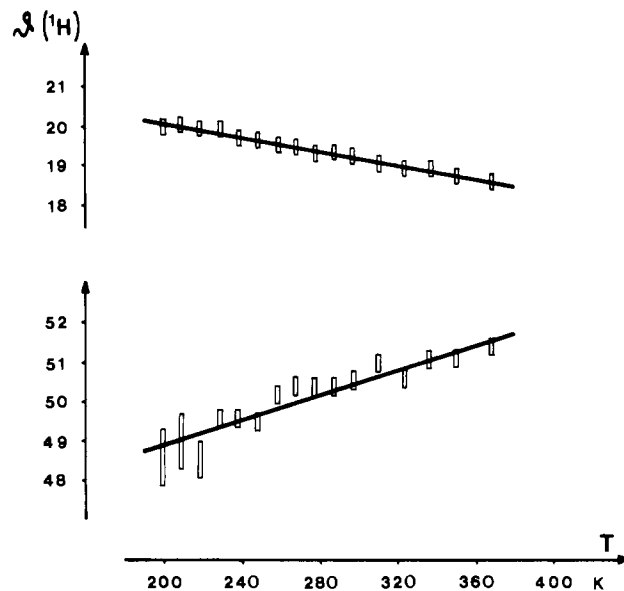
rangement at room temperature of the bent vanadocene units should be far from perpendicular (cf. Figure 3B and part C of the text below) to the phenylene plane as was deduced for **12**<sup>8</sup> and (ii) that if spin pairing occurs it is small. Further evidence comes from the phenylene bridge protons of **5** which, unlike **9** and **10**, are less shifted than  $\delta^{\text{para}}(\text{H-o})$  of the monomer  $(\text{C}_5\text{Me}_4\text{Et})_2\text{VC}\equiv\text{CC}_6\text{H}_5$  (**11**). Contrary to **12**, delocalization in **11** is dominated by the  $\pi$  mechanism so that  $\delta^{\text{para}}(\text{H-m}) + \delta^{\text{para}}(\text{H-o}) = 22.6$  for **11** agrees rather well with  $\delta^{\text{para}}(^1\text{H}) = 19.2$  for the phenylene protons of **5**. Thus, like in **11**, the rotation of the bridge relative to the bent vanadocene units should have a low barrier.

This behavior is also reflected by the  $^{13}\text{C}$  spectra of **9** and **10** which show no signals for the phenylene bridges whereas the Cp rings appear with excellent signal-to-noise ratio (see Table I). Each phenylene bridge carbon is in a position ortho or ipso to vanadium, and likewise these carbons were the only ones which did not yield any signals from the monomer **12**.

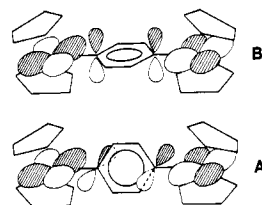
Inspection of the remaining signals of Table I shows that they all are less shifted for the dimers **5** and **9** than for the monomers **11** and **12**. In addition, the  $^{13}\text{C}_5\text{H}_5$  signal in **9** is 9.1 ppm less shifted than that in **12**. This uniform trend suggests a small residual spin pairing in the dimers. It should be noted, however, that steric perturbations of the molecule also influence the  $\delta^{\text{para}}$  as is found in the series of  $\text{Cp}_2\text{VR}$ .<sup>8</sup>

In order to get more information about a small spin pairing across the bridges, we have carried out temperature-dependent  $^1\text{H}$  measurement. Compounds **5** and **10** are sufficiently soluble to give the reduced shifts  $\vartheta = \delta^{\text{para}}T/298\text{ K}^{11}$  in a 168° temperature range. The results for the bridge protons are shown in Figure 2.

Variation of  $\vartheta$  with temperature indicates non-Curie behavior. It is surprisingly small yet outside the error limits.<sup>12</sup>



**Figure 2.** Temperature dependence of the reduced shifts for the bridge protons of **5** (top) and **10** (bottom).



**Figure 3.** Bridge arrangements of **9** relative to the spin-containing  $b_2$  orbitals of the bent vanadocene units.

**Table II.** Distances (pm) and Angles (Deg)

V(1)-C(10)	224.6 (13)	V(2)-C(30)	231.7 (12)
V(1)-C(11)	232.8 (13)	V(2)-C(31)	231.5 (11)
V(1)-C(12)	237.1 (12)	V(2)-C(32)	229.0 (12)
V(1)-C(13)	229.2 (15)	V(2)-C(33)	229.9 (14)
V(1)-C(14)	224.9 (15)	V(2)-C(34)	230.9 (13)
mean	229.7	mean	230.6
V(1)-C(20)	228.3 (11)	V(2)-C(40)	233.8 (12)
V(1)-C(21)	230.5 (13)	V(2)-C(41)	233.6 (14)
V(1)-C(22)	227.9 (13)	V(2)-C(42)	225.8 (14)
V(1)-C(23)	223.8 (15)	V(2)-C(43)	226.7 (11)
V(1)-C(24)	227.0 (12)	V(2)-C(44)	229.4 (13)
mean	227.5	mean	229.9
V(1)-M(1) <sup>a</sup>	198	V(2)-M(3)	196
V(1)-M(2)	195	V(2)-M(4)	197
V(1)-C(1)	212.5 (11)	V(2)-C(4)	215.4 (10)
C(1)-C(6)	141 (2)	C(4)-C(3)	139 (2)
C(1)-C(2)	140 (2)	C(4)-C(5)	140 (2)
C(2)-C(3)	138 (2)	C(5)-C(6)	139 (2)
M(1)-V(1)-M(2)	146.1	M(3)-V(2)-M(4)	146.3
C(1)-V(1)-M(1)	107.1	C(4)-V(2)-M(3)	105.4
C(1)-V(1)-M(2)	106.8	C(4)-V(2)-M(4)	108.3

<sup>a</sup> M represent the centers of the Cp rings.

As shown above, spin pairing in these molecules can be understood as a superposition of delocalized spin densities from different mechanisms. Consequently, it should be modulated by rotation or twisting of the bent vanadocene units relative to the bridge. This is illustrated in Figure 3 where **9** experiences  $\sigma$  delocalization in conformation B and additional  $\pi$  delocalization in A.

(10) This agreement further supports our signal assignment of  $(\text{C}_5\text{H}_5)_2\text{V-C}_6\text{H}_5$  (cf. ref 8)

(11) Knorr, R.; Polzer, H.; Bischler, E. *J. Am. Chem. Soc.* **1975**, *97*, 634-644.

(12) Apart from the limited measurement accuracy, an error may be introduced by the diamagnetic reference signal. A difference of  $\pm 1$  ppm from the ideal reference position produces slopes of  $\pm 0.0034$  in a  $\vartheta/T$  diagram.

(13) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729-1742.

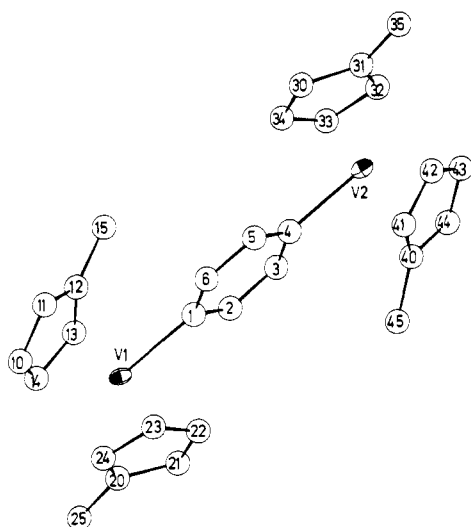


Figure 4. Molecular structure of 10.

Depending on the equilibrium twist angle and the rotational barrier of the dimers,  $\vartheta$  should not necessarily increase but may also decrease with temperature. Both cases seem to be met in Figure 2, though more information from other derivatives must be collected for further details. We may, however, conclude from these data that spin pairing in hydrocarbon-bridged vanadocenes is unimportant in the available temperature range.

(C) **Description of the Molecular Structure of 10.** Since the NMR spectroscopic results suggested that **9** and **10** should have equilibrium conformations at room temperature close to those in Figure 3B, we wished to know details of the solid-state structure of one of these complexes. Of special interest was the question concerning how far ligand bond angles independently reflect the electronic situation which was derived from paramagnetic NMR spectroscopy. We have recently reported<sup>14</sup> the X-ray structure analysis of a related compound,  $(\eta^5\text{-Me}_4\text{EtC}_5)_2\text{VC}\equiv\text{CC}_6\text{H}_2\text{Me}_3$  (**13**).

Bond distances and angles (see Table II) within both halves of the dimeric complex **10** are nearly identical. As can be seen from Figure 4, **10** shows approximate  $D_{2h}$  symmetry if the methyl groups are neglected. The bridging phenylene group lies within one of the mirror planes, and the  $\text{M}(1)\text{-V}(1)\text{-M}(2)$  and  $\text{M}(3)\text{-V}(2)\text{-M}(4)$  planes (M representing the centers of the Cp rings) are nearly perpendicular to the phenylene plane ( $87.4$  and  $85.5^\circ$ ). The conformation of the complex in the solid state therefore corresponds to Figure 3B. According to this symmetry, the Cp rings at each vanadium are staggered. The mean  $\text{V-C}(\text{Cp})$  distance found in **10** ( $229.4$  pm) is of the same magnitude as in other  $\text{V}(\text{III})$  complexes (in **13**,  $230.8$  pm;<sup>14</sup> in  $\text{Cp}_2\text{VCl}$ ,  $227.8$  pm<sup>15</sup>). The bending angle of the vanadocene moieties, however, shows considerable differences: mean  $143.2^\circ$  in **10**,  $149^\circ$  in **13**, and  $139.5^\circ$  in  $\text{Cp}_2\text{VCl}$ . Lauher and Hoffmann have shown<sup>13</sup> that in complexes  $\text{Cp}_2\text{ML}_n$  this angle depends on both the  $\sigma$ - and  $\pi$ -donor ability of the ligand(s) L. On the basis of  $\sigma$  interaction alone as in **10**, one would have to conclude that in the series **13**, **10**, and  $\text{Cp}_2\text{VCl}$  the  $\sigma$ -donor strength decreases with decreasing bending angle. This is supported by MO calculations on  $\text{Cp}_2\text{VC}_6\text{H}_5$  and  $\text{Cp}_2\text{VC}\equiv\text{CC}_6\text{H}_5$ .<sup>8</sup> However, since in **13** and  $\text{Cp}_2\text{VCl}$  there is no  $\sigma$ - $\pi$  separation at any steric arrangement, an additional  $\pi$  con-

Table III. Mass Spectral Data of the Bridged Vanadocenes **5**, **9**, and **10**

assign <sup>a</sup>	<b>5</b>		<b>9</b>		<b>10</b>	
	<i>m/e</i>	intens	<i>m/e</i>	intens	<i>m/e</i>	intens
$\text{M}^+$	822	2.9	438	53.5	494	20.3
$\text{M} - \text{H}^+$			437	35.2	493	63.3
$\text{M} - 2\text{H}^+$			436	100.0	492	35.4
$\text{M} - 3\text{H}^+$					491	100.0
$\text{M} - 4\text{H}^+$					490	18.4
$\text{M} - 5\text{H}^+$					489	39.6
$\text{M} - \text{LV}^+$	622	30.0	322	10.7	364	1.3
$\text{L}_2\text{VB}^+$			257	29.6	285	23.2
$\text{L}_2\text{B}^+$	422	20.9	206	6.1	234	15.0
$\text{L}_2\text{V}^+$	349	44.8	181	87.3	209	83.2
$\text{L}_2\text{V} - \text{H}^+$	348	100.0				
$\text{LV}^+$			116	77.5	130	69.6
$\text{L}^+$	149	19.0	65	1.9	79	4.5
$\text{C}_7\text{H}_7^+$	91	52.4			91	2.4
$\text{C}_6\text{H}_7^+$			90	9.6	90	2.5
$\text{V}^+$	51	3.3	51	8.5	51	30.6

<sup>a</sup> L = corresponding cyclopentadienyl; B = bridge.

tribution to bending must be present in these two molecules. In **13** repulsion of the peralkylated Cp rings has to be considered, too.

According to Figure 3B, there can be no  $\pi$  overlap between orbitals at the vanadium and the phenylene carbon atoms in the conformation found in crystalline **10**. The  $\text{V}(1)\text{-C}(1)$  and  $\text{V}(2)\text{-C}(4)$  bonds ( $212.5$  ( $11$ ) and  $215.4$  ( $10$ ) pm) therefore should be pure single bonds. In **13**, where two orthogonal  $\pi$  orbitals are available at the carbon bound to vanadium, a length of  $203$  ( $1$ ) pm has been found for the  $\text{V-C}(\text{sp})$  bond.<sup>14</sup> With a difference of about  $5$  pm for the bond radii of  $\text{C}(\text{sp}^2)$  and  $\text{C}(\text{sp})$  taken into account, the shortening of the  $\text{V-C}$  bond in **13**, contrary to **10**, is best explained by  $\pi$  bonding. This was also shown independently by NMR spectroscopy for the corresponding dimer **5**.

From the bond distances of **13**<sup>14</sup> we estimate that the two vanadium atoms in **5** are separated by  $1220$  pm. This value decreases to  $715$  pm in **10**. Nevertheless, spin pairing is unimportant in both dimers. Obviously the shortening of the bridge is almost compensated by the missing  $\pi$  interaction.

## Conclusions

The stability of vanadocene alkyl derivatives is determined by both the nature of the  $\text{V-R}$   $\eta^1$  bond (most probably the steric requirement of R) and the substituents on the Cp ligands. NMR spectroscopy appears to be a powerful method not only to determine the constitution of bridged paramagnetic organometallics but also to analyze the metal-metal interaction across the bridges. In the compounds presented here, this interaction is very small; they must be regarded as possessing four unpaired electrons per molecule. Several reasons may be responsible for this lack of interaction. (1) The bridge ligand contribution to the MOs containing the unpaired electrons is rather small. (2) Only one single  $\sigma$  bond may transmit the interaction (compound **9** and **10**). (3) If an additional  $\pi$  bond acts, the bridge length limits the interaction (compound **5**).

## Experimental Section

All operations were carried out in Schlenk tubes under purified argon and with dried oxygen-free solvents. Melting points were determined in capillaries sealed under argon. For elementary analysis, freshly crystallized and dried samples were sealed under argon in weighed glass tubes which then were broken in the combustion chamber. This procedure turned out to give sufficiently reproducible results for extremely air-sensitive compounds. However, a series of control experiments showed that this leads to errors of ca.  $\pm 1\%$  for the carbon content. Analyses were carried out in the microanalytical laboratory of this institute (we thank M. Barth for helpful advice).

(14) (a) Köhler, F. H.; Prössdorf, W.; Schubert, U.; Neugebauer, D. *Angew. Chem.* **1978**, *90*, 912-913; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 850-851. (b) Schubert, U.; Köhler, F. H.; Prössdorf, W. *Cryst. Struct. Commun.* **1981**, *10*, 245-250.

(15) Fieselmann, B. F.; Stucky, G. D. *J. Organomet. Chem.* **1977**, *137*, 43-54.

Table IV. Atomic Parameters for 10

## (a) Positional Parameters and Isotropic Thermal Parameters for Nonhydrogen Atoms

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
V(1)	0.0992 (4)	0.2387 (1)	0.2409 (1)	C(22)	-0.022 (2)	0.314 (1)	0.166 (1)
C(1)	0.080 (2)	0.1643 (6)	0.1675 (5)	C(23)	-0.180 (3)	0.312 (1)	0.211 (1)
C(2)	0.259 (2)	0.152 (1)	0.130 (1)	C(24)	-0.090 (2)	0.347 (1)	0.260 (1)
C(3)	0.246 (2)	0.1027 (7)	0.0830 (5)	C(25)	0.273 (3)	0.416 (1)	0.283 (1)
C(4)	0.058 (2)	0.0619 (6)	0.0692 (4)	C(30)	-0.016 (2)	-0.122 (1)	0.051 (1)
C(5)	-0.125 (2)	0.0745 (6)	0.1053 (4)	C(31)	0.021 (2)	-0.1456 (6)	-0.0079 (5)
C(6)	-0.112 (2)	0.124 (1)	0.153 (1)	C(32)	0.236 (2)	-0.122 (1)	-0.023 (1)
V(2)	0.0389 (3)	-0.0139 (1)	-0.0049 (1)	C(33)	0.333 (2)	-0.085 (1)	0.027 (1)
C(10)	0.098 (3)	0.216 (1)	0.338 (1)	C(34)	0.178 (2)	-0.085 (1)	0.071 (1)
C(11)	0.036 (3)	0.147 (1)	0.313 (1)	C(35)	-0.132 (3)	-0.191 (1)	-0.045 (1)
C(12)	0.215 (2)	0.1205 (6)	0.2807 (5)	C(40)	-0.032 (2)	0.103 (1)	-0.051 (1)
C(13)	0.381 (3)	0.175 (1)	0.286 (1)	C(41)	-0.231 (2)	0.065 (1)	-0.045 (1)
C(14)	0.304 (3)	0.231 (1)	0.323 (1)	C(42)	-0.223 (2)	-0.001 (1)	-0.074 (1)
C(15)	0.236 (3)	0.045 (1)	0.251 (1)	C(43)	-0.022 (2)	-0.0076 (7)	-0.1030 (5)
C(20)	0.118 (2)	0.3683 (6)	0.2471 (5)	C(44)	0.106 (3)	0.056 (1)	-0.088 (1)
C(21)	0.160 (3)	0.348 (1)	0.188 (1)	C(45)	0.011 (3)	0.179 (1)	-0.031 (1)

(b) Hydrogen Positions<sup>a</sup>

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(2)	0.3944	0.1796	0.1370	H(41)	-0.3558	0.0847	-0.0215
H(3)	0.3748	0.0956	0.0591	H(42)	-0.3454	-0.0381	-0.0736
H(5)	-0.2626	0.0477	0.0967	H(43)	0.0259	-0.0493	-0.1271
H(6)	-0.2409	0.1306	0.1780	H(44)	0.2564	0.0677	-0.0996
H(10)	0.0133	0.2460	0.3646	H(251)	0.4379	0.3976	0.2771
H(11)	-0.1090	0.1219	0.3177	H(252)	0.2380	0.4106	0.3245
H(13)	0.5267	0.1723	0.2653	H(253)	0.2612	0.4680	0.2733
H(14)	0.3796	0.2771	0.3345	H(351)	-0.0883	-0.1937	-0.0846
H(21)	0.2967	0.3604	0.1661	H(352)	-0.2761	-0.1704	-0.0430
H(22)	-0.0420	0.2950	0.1278	H(353)	-0.1389	-0.2427	-0.0303
H(23)	-0.3304	0.2900	0.2081	H(151)	0.1628	0.0027	0.2861
H(24)	-0.1631	0.3550	0.2980	H(152)	0.3912	0.0321	0.2441
H(30)	-0.1483	-0.1292	0.0742	H(153)	0.1617	0.0416	0.2147
H(32)	0.3079	-0.1301	-0.0611	H(451)	0.0764	0.1932	0.0083
H(33)	0.4802	-0.0621	0.0300	H(452)	-0.1183	0.2107	-0.0354
H(34)	0.1983	-0.0653	0.1105	H(453)	0.1113	0.2038	-0.0598

## (c) Anisotropic Thermal Parameters

atom	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>	atom	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
V(1)	3.5 (1)	1.8 (1)	1.8 (1)	0.3 (1)	0.0 (1)	0.1 (1)	C(4)	1.5 (5)	3.5 (6)	1.3 (4)	0.7 (5)	0.1 (5)	0.4 (4)
C(1)	2.7 (6)	2.7 (5)	2.3 (5)	0.0 (6)	-1.2 (6)	-0.4 (4)	C(5)	2.7 (6)	3.5 (6)	1.6 (5)	0.8 (6)	-0.3 (5)	0.0 (5)
C(2)	3.5 (7)	2.8 (6)	2.5 (6)	-0.7 (6)	0.3 (6)	0.7 (5)	C(6)	3.1 (7)	3.5 (6)	2.9 (6)	0.8 (6)	0.5 (6)	-0.3 (5)
C(3)	2.3 (7)	5.1 (7)	1.4 (5)	0.0 (6)	0.3 (5)	0.5 (5)	V(2)	3.4 (1)	2.3 (1)	1.6 (1)	0.4 (1)	0.2 (1)	0.3 (1)

<sup>a</sup> Isotropic *B* for the hydrogen atoms is 5.0 Å<sup>2</sup>.

**μ-(1,4-Phenylenebis(ethynyl))-bis[bis(ethyltetramethyl-η<sup>5</sup>-cyclopentadienyl)vanadium] (5).** 1,4-Bis(lithioethynyl)benzene was prepared by adding a 2.18 M solution of *n*-butyllithium in hexane (2.47 mL, 5.38 mmol) under vigorous stirring to freshly sublimed *p*-diethynylbenzene (0.34 g, 2.69 mmol) dissolved in 30 mL of diethyl ether and precooled to -40 °C. A white precipitate formed, and the mixture was allowed to warm to room temperature. To this suspension was added bromobis(ethyltetramethyl-η<sup>5</sup>-cyclopentadienyl)vanadium<sup>8</sup> (2.31 g, 5.38 mmol) in diethyl ether (20 mL). The initial blue color changed to green and then to brown during 4 h of stirring at room temperature. Next the solvent was removed and the residue extracted with pentane and filtered. The extract was evaporated to ca. 5 mL, and its components were separated by column chromatography at -15 °C (Al<sub>2</sub>O<sub>3</sub> + 5% H<sub>2</sub>O; length 20 cm; diameter 3 cm). With pentane, red bis(ethyltetramethyl-η<sup>5</sup>-cyclopentadienyl)vanadium<sup>8</sup> was eluted first. Next a brown eluate was obtained with toluene/pentane (1/1) while blue starting material remained on the column. Evaporation of the brown solution gave a black material which was recrystallized (three times) from pentane at -78 °C to yield a dark brown crystal powder of **5**: 0.24 g; 11%; mp 111–112 °C dec. Anal. Calcd for C<sub>54</sub>H<sub>72</sub>V<sub>2</sub>: C, 78.80; H, 8.82. Found: C, 77.39; H, 8.94.

**μ-1,4-Phenylene-bis[bis(η<sup>5</sup>-cyclopentadienyl)vanadium] (9).** From *p*-dibromobenzene (0.68 g, 2.9 mmol) a solution of *p*-dilithiobenzene in THF (20 mL) was prepared according to ref 16 and kept at -40

°C. This solution was passed through a cooled frit and directly added to (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>VCl (1.26 g, 5.8 mmol) in diethyl ether (20 mL) cooled to -60 °C. After the cooling bath was removed, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>VCl disappeared gradually to give a green reaction mixture. This was stirred for 20 h at room temperature, the solvent was removed, and the residue was extracted several times with toluene. The crude product which was obtained after filtration and evaporation of toluene under reduced pressure was recrystallized (four times) from THT at -78 °C to yield small green needles of **9**: 0.77 g; 61%; mp 184–185 °C. Anal. Calcd for C<sub>26</sub>H<sub>24</sub>V<sub>2</sub>: C, 71.23; H, 5.52. Found: C, 70.44; H, 5.66.

**μ-1,4-Phenylene-bis[bis(methyl-η<sup>5</sup>-cyclopentadienyl)vanadium] (10).** The procedure was essentially the same as that described for **9**, except pentane was used for recrystallization. From *p*-dibromobenzene (1.4 g, 5.93 mmol) and (C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>VCl<sup>17</sup> (2.38 g, 9.73 mmol) green needles of **10** (0.97 g, 40%), mp 113–114 °C, were obtained. Anal. Calcd for C<sub>30</sub>H<sub>32</sub>V<sub>2</sub>: C, 72.87; H, 6.52. Found: C, 72.98; H, 6, 68.

**Physical Measurements.** The mass spectra (Table III) were obtained with a Varian MAT 311 A instrument with data system. Ionization was accomplished by electron impact (70 eV) at 50 °C (Except for **5**; at 200 °C). We thank Drs. F. R. Kreissl and W. Üdelhofen for assistance.

The NMR spectra were recorded on a Bruker CXP 200 spectrometer with B-ST 100/700 temperature controller. Details such as instrumental parameters, sample tubes, and temperature measurement were similar to those reported previously<sup>8</sup> except that both

(16) Schöllkopf, U. In "Methoden der Organischen Chemie"; Müller, E., Ed.; G. Thieme: Stuttgart, 1970; Vol. 13/1, p 148.

(17) Köhler, F. H.; Prössdorf, W. *Chem. Ber.* **1978**, *111*, 3464–3471.

$^{13}\text{C}$  and  $^1\text{H}$  spectra were run in 10-mm tubes.

The isotropic shifts (low-field shifts negative) were obtained by measuring the shift relative solvent signals (benzene,  $^1\text{H}$   $\delta$  7.3; toluene,  $\text{C}^1\text{H}_3$   $\delta$  2.3,  $^{13}\text{C}_3$   $\delta$  20.3; THF,  $^{13}\text{C}$ - $\beta$   $\delta$  26.0) and calculating it relative to the signal of a similar diamagnetic compound. For the bent vanadocene units ferrocene signals were taken ( $(\text{C}_5\text{H}_5)_2\text{Fe}$ ,  $^1\text{H}$   $\delta$  4.1,  $^{13}\text{C}$   $\delta$  67.8;  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Fe}$ ,  $\text{C}_5^1\text{H}_4$   $\delta$  4.0,  $\text{C}^1\text{H}_3$   $\delta$  1.8 and ref 18;  $(\text{C}_5\text{Me}_4\text{Et})_2\text{Fe}$ , cf. ref 9 and 19) while the aromatic signals of *p*-diethynylbenzene ( $^1\text{H}$   $\delta$  7.4;  $^{13}\text{C}1/4$   $\delta$   $\sim$ 120,  $^{13}\text{C}2,3,5,6$   $\delta$   $\sim$ 128 analogous to ref 20) and benzene were chosen as standard signals for the bridge protons.

The variable-temperature results were subjected to a least-squares fit analysis which also gave the data of Table II except 9 where the 298 K shifts were calculated with the assumption of an unimportant deviation from the Curie law. Digital accuracy for  $^1\text{H}$  and  $^{13}\text{C}$  was 0.17 and 0.35 ppm, respectively.

**Crystal Measurements.** Cell dimensions were obtained on a Syntex P2<sub>1</sub> four-circle diffractometer by centering and subsequent refinement of 15 high-angle reflections from different parts of the reciprocal space at room temperature:  $a = 607.9$  (4),  $b = 1755.5$  (9),  $c = 2277.2$  (15) pm. The space group  $P2_12_12_1$  was inferred from systematic extinctions.

(18) Köhler, F. H.; Matsubayashi, G. *J. Organomet. Chem.* **1975**, *96*, 391-397.

(19) Feitler, D.; Whitesides, G. M. *Inorg. Chem.* **1976**, *15*, 466-468.

(20) Formáček, V.; Desnoyer, L.; Kellerhals, H. P.; Keller, T.; Clerc, J. T. " $^{13}\text{C}$  Data Bank"; Bruker-Physik: Karlsruhe, 1976; Vol. 1, pp 46, 47.

With  $Z = 4$ , the calculated density is 1.35 g/cm<sup>3</sup>. Intensity measurements were collected between  $2^\circ \leq 2\theta \leq 48^\circ$  (2212 independent reflections) with use of Mo  $K\alpha$  radiation ( $\lambda = 71.069$  pm, graphite monochromator). After Lorentz and polarization corrections (no absorption correction,  $\mu = 8.3$  cm<sup>-1</sup>), 1660 structure factors ( $F_o \geq 3.92\sigma(F_o)$ ) were obtained.

**Solution and Refinement of the Structure.** The positions of the vanadium atoms were located by a Patterson function. Subsequent difference Fourier maps revealed the positions of all carbon atoms and some of the hydrogen atoms. The positions of the remaining hydrogen atoms were calculated according to ideal geometry. Refinement by the full-matrix least-squares method using anisotropic thermal parameters for the metal atoms and some of the carbon atoms converged to  $R_1 = 0.077$  and  $R_2 = 0.074$ . The hydrogen parameters were not refined. The final atomic parameters are given in Table IV.

**Acknowledgment.** We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie which supported our studies in part.

**Registry No.** 5, 79102-48-0; 9, 79121-07-6; 10, 79152-69-5; bromo(ethyltetramethyl- $\eta^5$ -cyclooctadienyl)vanadium, 68185-51-3;  $(\text{C}_5\text{H}_5)_2\text{VCl}$ , 12701-79-0;  $(\text{C}_5\text{H}_4\text{Me})_2\text{VCl}$ , 66446-72-8; 12, 12212-56-5.

**Supplementary Material Available:** A listing of structure factors (10 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,  
University of Minnesota, Minneapolis, Minnesota 55455

## Rhodium Complexes of 1,4-Bis(diphenylphosphino)butane. Crystal and Molecular Structures of $[\text{Rh}(\text{dppb})_2]\text{BF}_4 \cdot \text{C}_4\text{H}_{10}\text{O}$ and $[\text{Rh}(\text{cod})(\text{dppb})]\text{BF}_4$

MICHAEL P. ANDERSON and LOUIS H. PIGNOLET\*

Received June 15, 1981

Bis(diphosphine) complexes of Rh(I) of the type  $[\text{Rh}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_2]\text{BF}_4$  where  $n = 3$  and 4 have been examined by using low-temperature  $^{31}\text{P}$  NMR spectroscopy and found to have complex solution geometries. For  $n = 3$  the solution geometry (solvent = acetone) is trigonal bipyramidal with an equatorial solvent molecule as evidenced by an  $\text{A}_2\text{B}_2\text{X}$   $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at  $-80^\circ\text{C}$ . For  $n = 4$  the solution geometry is more complex and probably involves dppb-bridged solvated species. Single-crystal X-ray structures were determined for the  $n = 4$  complex,  $[\text{Rh}(\text{dppb})_2]\text{BF}_4 \cdot \text{C}_4\text{H}_{10}\text{O}$ , and for  $[\text{Rh}(\text{cod})(\text{dppb})]\text{BF}_4$ , where cod is 1,5-cyclooctadiene. Both complexes crystallize in the monoclinic space group  $C2/c$ . The former has unit cell parameters  $a = 36.60$  (1) Å,  $b = 14.248$  (8) Å,  $c = 26.220$  (4) Å, and  $\beta = 125.18$  (2) $^\circ$ , and for the latter  $a = 30.59$  (1) Å,  $b = 10.326$  (1) Å,  $c = 25.044$  (8) Å, and  $\beta = 123.36$  (2) $^\circ$ .  $[\text{Rh}(\text{dppb})_2]^+$  possesses a coordination core geometry which is significantly distorted toward tetrahedral whereas  $[\text{Rh}(\text{cod})(\text{dppb})]^+$  has an approximately square-planar geometry. The distortion in the former complex results from phosphine-phosphine repulsions. These repulsions also cause a significant lengthening in one of the Rh-P bonds [2.361 (2) Å] compared with the average value for the other three [2.318 (2) Å]. This bond weakening is presumably responsible for the propensity of this complex to form dppb-bridged dimeric species.

### Introduction

Considerable interest has recently been focused on cationic rhodium(I) complexes containing chelating diphosphine ligands, particularly with respect to their use in catalytic hydrogenation<sup>1-4</sup> and decarbonylation<sup>5,6</sup> reactions. Of special importance has been the successful inducement of optical activity by hydrogenation of prochiral olefins using cationic rhodium complexes with chiral diphosphine ligands.<sup>1-4,7</sup>

During the course of our studies on catalytic decarbonylation reactions<sup>5,6,8</sup> using  $[\text{Rh}[(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_2]^+$  complexes, **1**, with  $n = 1-4$ , it became increasingly obvious that the nature of these species in solution was not well understood. For example, the low-temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of  $[\text{Rh}(\text{dppb})_2]\text{BF}_4$  (**1**,  $n = 3$ ) and  $[\text{Rh}(\text{dppb})_2]\text{BF}_4$  (**1**,  $n = 4$ ) showed complex patterns that are inconsistent with simple square-planar coordination (vide infra).<sup>5</sup> In view of the importance of these complexes, we report here the results of a variable-temperature  $^{31}\text{P}$  NMR study on complexes **1**,  $n = 3$  and 4, and of single-crystal X-ray characterizations of  $[\text{Rh}(\text{dppb})_2]\text{BF}_4$  (**1**,  $n = 4$ ) and  $[\text{Rh}(\text{cod})(\text{dppb})]\text{BF}_4$  (**2**), where cod = 1,5-cyclooctadiene. With the exception of a brief abstract,<sup>9</sup> this is only the second<sup>10</sup>

(1) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 5952.

(2) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262.

(3) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. *Adv. Chem. Ser.* **1974**, *No. 132*, 274.

(4) James, B. R.; Mahajan, D. *Can. J. Chem.* **1979**, *57*, 180.

(5) Doughty, D. H.; Anderson, M. P.; Casalnuovo, A. L.; McGuiggan, M. F.; Tso, C. C.; Wang, H. H.; Pignolet, L. H. *Adv. Chem. Ser.*, in press.

(6) Doughty, D. H.; Pignolet, L. H. *J. Am. Chem. Soc.* **1978**, *100*, 7083.

(7) Brown, J. M.; Chaloner, P. A. *J. Chem. Soc., Chem. Commun.* **1980**, 344.

(8) Doughty, D. H.; McGuiggan, M. F.; Wang, H. H.; Pignolet, L. H. In "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, p 909.

(9) Knowles, W. S. "Abstracts of Papers"; American Crystallographic Association: 1978; Vol. 6, No. PA1.