Metal Complexes of Heteroarenes. 5.[1] Bis(η^6-phosphinine)metal Coordination: Is There Conformational Preference?

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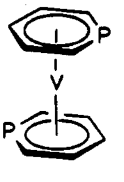
Summary: By means of metal-atom ligand-vapor co-condensation the bis(heteroarene)metal complexes [2,4,6-(t-Bu)$_3$-η^6-phosphinine]$_2$M (M = V, Cr) have been prepared in order to explore the rotamer distribution. Since the tert-butyl groups block rotational interconversion, the original product ratio is conserved over a wide range of temperatures, rendering conformational analysis through magnetic resonance possible. EPR spectra of the vanadium complex and NMR spectra of the chromium analogue both point to a rotamer ratio synclinal:antiperiplanar close to the statistical ratio of 2:1, the deviation from the exact ratio probably stemming from the distorted hexagonal shape of the phosphinine ring. The unequivocal EPR assignment for the individual rotamers of [2,4,6-(t-Bu)$_3$-η^6-C_5H_2P]V suggests that the parent complex [η^6-C_5H_5P]$_2$V in rigid solution (DME, 38 K) assumes the antiperiplanar conformation.

Although the aromaticity of phosphinine C_5H_5P (1) appears to be undisputed,[2] the substitution of a CH fragment by a P atom nevertheless constitutes a severe perturbation of the electronic structure[3] which is caused by the changes in effective electronegativity[4] (C versus P) and bond length[2b] (C–C versus C–P). The effects are, inter alia, loss of π-orbital degeneracies and increased electron affinity of phosphinine,[5] compared to benzene as well as the presence of a dipole moment for the heteroarene.[6] Since the group 15 heteroarenes are capable of forming the sandwich complexes 2,[7] 3,[8] and 4,[9] it is interesting to ask, whether the electronic perturbation in the η^6-heteroarene is of sufficient strength to favor a specific rotamer in the crystal or even to inhibit free rotation of the η^6-ligands in solution. For the closely related heterometallocenes $(C_4H_4E)_2Fe$ (E = P–Bi) no X-ray crystallographic analysis of an unsubstituted complex has yet been disclosed and the conformation adopted by a functional derivative like (3,4-Me$_2$-η^5-C_4H_2P)$_2$Fe (5)[10] may well be governed by interannular interaction of the substituents or by packing forces.[11]



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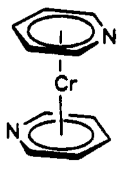

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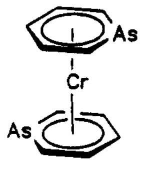

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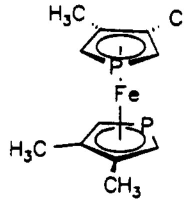

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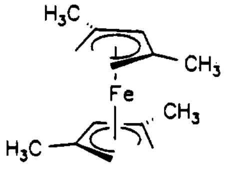

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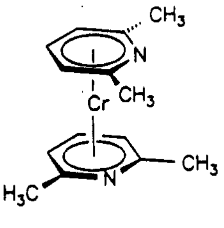

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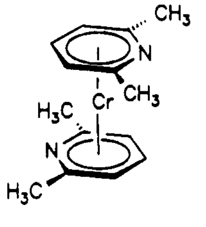

7a

In the case of "open" metallocenes like (2,4-(CH$_3$)$_2$$C_5H_5$)-Fe (6), which, admittedly, contain more profoundly perturbed π-ligands, adoption of the gauche-eclipsed conformation has been established,[12] $\Delta G^{\ddagger}$ for ligand oscillation amounting to 40 kJ mol^{-1}. Concerning the unsubstituted bis(η^6-heteroarene) complexes 2–4, disorder in the crystalline state frustrated attempts to solve the conformational question by means of X-ray diffraction. The tetramethyl derivative bis(η^6-lutidine)chromium (7) could be isolated in two different morphologies which proved to contain the synclinal (7s) and antiperiplanar (7a) rotameres, respectively.[13a] Interestingly, the conformation of the cation 7$^+$ is strictly synperiplanar.[13b] The corresponding complexes of Ti and V were found to crystallize as the anticlinal and synclinal conformers,

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[11] Kostic, N. M.; Fenske, R. F. *Organometallics* **1983,** *2,* 1008.

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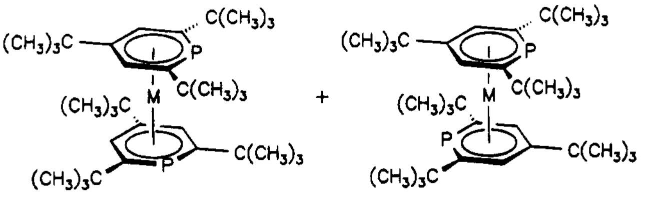
respectively.[13b] In solution, however, these complexes as well as the parent compound **3** feature ring rotation which is fast on the ^{1}H NMR time scale.[8,13b] Therefore, in order to employ NMR to gauge conformational preference induced by a ring heteroatom, bulky groups must be introduced which bar rotamer interconversions, thereby conserving the rotamer ratio formed during the course of synthesis. If symmetrical 2,4,6-trisubstitution is applied, repulsive forces between the bulky groups should not affect the ratio synclinal/antiperiplanar and the relative proportions of these rotameres, present in solution, should be governed by the electronic effect exerted by the heteroatoms. For diamagnetic bis(η^6-heteroarene)metal complexes this ratio should be inferrable from the NMR spectra, while in the case of paramagnetic species, information concerning the presence of more than one rotamer is expected from EPR spectroscopy since different rotamers should give rise to differing **g** tensors.[14] We therefore set out to prepare the complexes bis(2,4,6-tri-*tert*-butyl-η^6-phosphinine)vanadium (**9**) and -chromium (**10**).

Results and Discussion

Bis(2,4,6-tri-*tert*-butyl-η^6-phosphinine)vanadium (**9**) (greenish-brown) and -chromium (**10**) (dark red) are accessible in small yields by means of metal-atom ligand-vapor cocondensation (cc). Both complexes are exceedingly soluble in organic solvents such that controlled crystallization could not be effected; they differ in their thermal stability, **9** being sublimable at 130 °C (10^{-2} mbar) whereas **10** experiences metal–ligand cleavage under these conditions. This gradation probably results from the decrease in the atomic radii of the central metals and the concomitant increase in interligand repulsion caused by the bulky *t*-Bu groups.

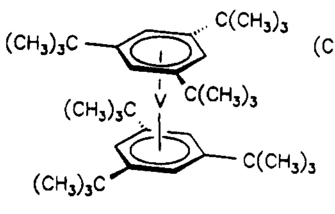
$$2\ 2,4,6\text{-}(t\text{-Bu})_3\text{-}C_5H_2P\ (g) + M\ (g) \xrightarrow{cc}$$



9s, 10s **9a, 10a**

No	M
9	V
10	Cr

Interannular repulsion should be even more pronounced for the smaller diameter ligand 1,3,5-tri-*tert*-butylbenzene. Bis(1,3,5-tri-*tert*-butyl-η^6-benzene)vanadium (**11**) and -chromium (**12**),[15] readily formed through metal–ligand cocondensation, in our hands proved to be too labile for isolation in pure form. Whereas spectral characterization of **11** and **12** was straightforward, the samples were always contaminated by free ligand, in particular if a complex–ligand separation was attempted by means of fractional sublimation.[15] This contrasts with the corresponding phosphinine complexes **9** and **10** which are much more stable with regard to metal–ligand cleavage.



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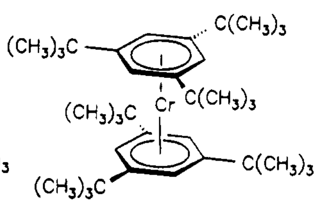

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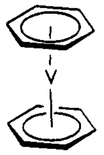

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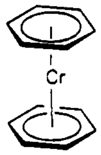

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Since, due to rotational disorder, unequivocal X-ray crystal structure analyses for **9** or **10** are unavailable, the problem of conformational preference must be tackled by means of magnetic resonance. **9** displays well resolved EPR spectra in fluid as well as in rigid solution (Figure 1, spectroscopic parameters in Table I). The isotropic hyperfine coupling constant $a(^{51}V, 9) = 7.59$ mT is the largest ever reported for a bis(arene)vanadium complex. It markedly surpasses the values for the bis(arene)vanadium complexes of benzene [$a(^{51}V, 13) = 6.35$ mT], 1,3,5-tri-*tert*-butylbenzene [$a(^{51}V, 11) = 6.75$ mT], and unsubstituted phosphinine [$a(^{51}V, 2) = 7.03$ mT[7]]. Obviously, both bulky peripheral substitution and introduction of P for CH effect a decrease in vanadium–arene spin transfer as a result of diminished metal–ligand orbital overlap: sterically demanding groups will bring about an increase in metal–ring distance and the incorporation of P into the ring strengthens its π-acceptor character. The latter effect enhances the polarity $V(\delta^+)$arene(δ^-) causing a contraction of the singly occupied HOMO $V(3d_{z^2})$ and therefore a decrease in spin delocalization. The individual $m_I(^{51}V)$ components in the isotropic spectrum of **9** lack additional splitting by ^{1}H or ^{31}P; inspection of the line widths suggests that $a(^{31}P, 9) \leq 0.5$ mT. The absence of discernable ^{31}P hyperfine splitting results from the nature of the SOMO $(V(3d_{z^2}))$, the ring atoms taking up positions in its nodal plane. Whereas the isotropic EPR spectrum of **9** does not provide hints to the presence of different rotamers, analysis of the rigid solution spectrum requires the presence of *two rotamers*, each possessing individual orthorhombic **g** and ^{51}V hyperfine tensors. This is obvious from the fact that each nuclear spin quantum number

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[14] Note, that the radical cation $6^{\bullet+}$ was shown to possess an orthorhombic **g** tensor, $g_x \neq g_y \neq g_z$: Elschenbroich, Ch.; Bilger, E.; Ernst, R. D.; Wilson, D. R.; Kralik, M. S. *Organometallics* **1985**, *4*, 2068.

[15] See however: Cloke, F. G. N.; Courtney, K. A. E.; Sameh, A. A.; Swain, A. C. *Polyhedron* **1989**, *8*, 1641. Typically, bis(arene)metal complexes of tri-*tert*-butylbenzene have as yet only been described for the fairly large early transition metal atoms, Y, Ti, Zr, Hf, Nb, Cr, W, and a few lanthanoid atoms: Anderson, D. M.; Cloke, F. G. N.; Cox, P. A.; Edelstein, N.; Green, J. C.; Pang, T.; Sameh, A. A.; Shalimoff, G. *J. Chem. Soc., Chem. Commun.* **1989**, 53. Even in the case of $[1,3,5\text{-}(t\text{-Bu})_3\text{-}\eta^6\text{-}C_6H_3]_2$Gd, despite the large interarene distance of 444 pm [compare: $(C_6H_6)_2$Cr, 322 pm], the *tert*-butyl groups are bent out of the planes of the arene rings by 6–10°; Cloke, F. G. N.; Lappert, M. F.; Lawless, G.-A.; Swain, A. C. *J. Chem. Soc., Chem. Commun.* **1987**, 1667.

[16] Hägele, G.; Harris, R. K.; Nichols, J. M. *J. Chem. Soc., Dalton Trans.* **1973**, 79. Goodfellow, R. J.; Hardy, M. J.; Taylor, B. F. *Ibid.* **1973**, 2450. Verkade, J. G. *Coord. Chem. Rev.* **1972/73**, *9*, 86.

[17] Compare: (η^5-cyclopentadienyl)(2,4,6-triphenyl-η^6-phosphinine)manganese, $\delta(^{31}P) = -50$ ppm. Nief, F.; Charrier, C.; Mathey, F.; Simalty, M. *J. Organomet. Chem.* **1980**, *187*, 277. Fischer, J.; De Cian, A.; Nief, F. *Acta Crystallogr.* **1981**, *B37*, 1067. (η^1-Phosphinine)$_4$Ni: $\delta(^{31}P) = 213.3$ ppm.[7]

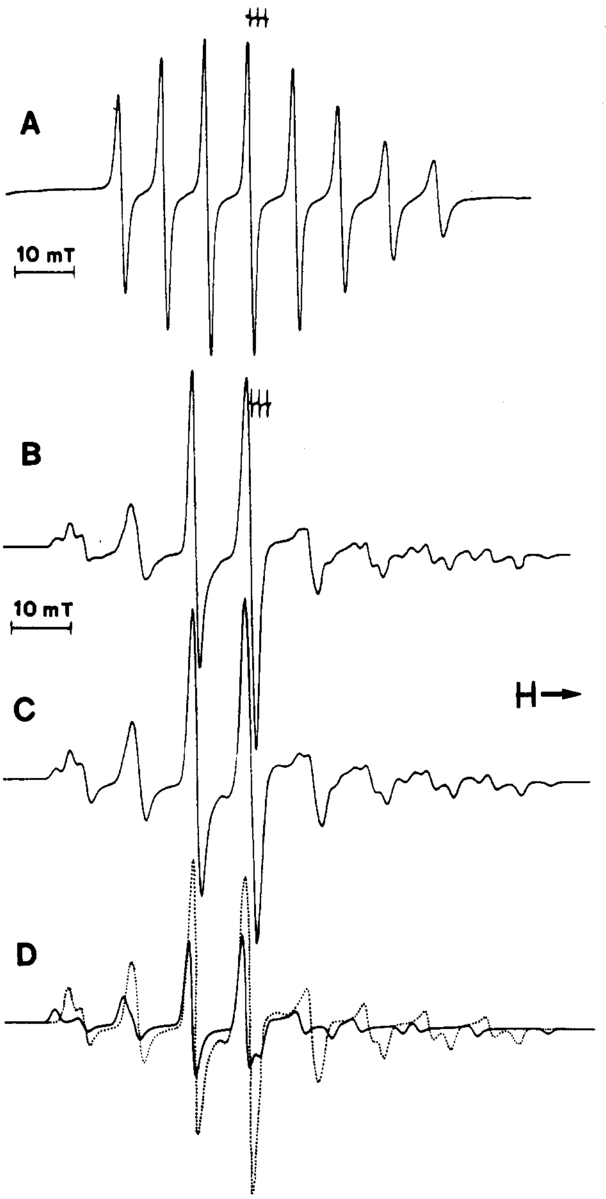

Figure 1. EPR spectra of [2,4,6-(t-Bu)$_3$C$_5$H$_2$P]$_2$V (**9**) in fluid (300 K, A) and rigid (130 K, B) solution in DME. Trace C depicts the simulated spectrum of a 2:1 mixture of **9s** and **9a**, (D) shows the spectra of the individual components (**9s** ···, **9a** —).

m_I(^{51}V) is associated with *four* lines in the "perpendicular" pattern of the spectrum. These lines are clearly resolved only for $m_I = \pm^7/_2, \pm^5/_2$, though. The relative intensities within the $m_I = \pm^7/_2$ sets suggest that the two rotameres **9s** and **9a** are present in a ≈2:1 ratio. This conclusion rests on the assignment of the component spectrum displaying the larger anisotropy to the antiperiplanar rotamer **9a**. In support of this assignment it is worth mentioning that in the antiperiplanar conformation **9a** the perturbation by the two P atoms will raise the degeneracies of the e$_2$(x^2–y^2, xy) and e$_1$(xz, yz) levels more extensively than in the synclinal form **9s**. Therefore, the deviations between $\mathbf{g}_x$, $\mathbf{g}_y$, and A_x(^{51}V) and A_y(^{51}V) are expected to be larger in **9a** compared to **9s**. The 2:1 ratio of **9s** and **9a**, inferred from the EPR spectrum in rigid solution, is the one anticipated for statistic reasons. Interestingly, the rigid solution EPR spectrum of the parent complex (η^6-C$_5$H$_5$P)$_2$V (**2**) in the perpendicular subspectrum showed two lines only for each value of m_I(^{51}V).[7] Since the spectrum of **9** has demonstrated that the differences in the anisotropies of **g** and A(^{51}V) for the **s** and **a** forms are resolved, it must be inferred that in a rigid solution of **2** only one rotamer is present. Comparison with the constituent spectra of the **9a** + **9s** mixture leads to the conclusion that **2** in rigid solution adopts the antiperiplanar conformation. This preference had already been surmised from an X-ray crystal structure analysis of rotationally disordered **2**.[7] Conceivably, the initial product of the cocondensation of phosphinine with vanadium atoms will also be a 2:1 mixture of the synclinal and antiperiplanar rotamers. But, in contrast to the sterically congested ligand 2,4,6-tri-*tert*-butyl phosphinine, which conserves this product ratio due to hindered rotation, in the case of the parent ligand the most stable conformation of the complex can be reached easily.

For the diamagnetic complex **10**, information concerning the conformational question may be deduced from nuclear magnetic resonance; ^{1}H, ^{13}C, and ^{31}P NMR data are collected in Table II. In the η^6-arene region of the ^{1}H NMR spectrum of **10**, two "filled in" doublets[16] centered at δ 5.34 (H$_{3',5'}$, **10s**) and δ 5.13 (H$_{3',5}$, **10s**) and one doublet at δ 4.89 (H$_{3,3',5,5'}$, **10a**) attest to the presence of both the synclincal and the antiperiplanar rotamers in solution. According to the integrated signal intensities the ratio **10s**:**10a** amounts to 3:1. The analysis of the conformational distribution is confirmed by the resonances in the *tert*-butyl proton region where **10s** (δ 1.31, 1.42, 1.57) and **10a** (δ 1.40, 1.37) also absorb in a 3:1 intensity ratio. Furthermore, two ^{31}P NMR signals are observed at δ −53.17 (relative intensity 3, **10s**) and δ −53.78 (relative intensity 1, **10a**). The sign and the magnitude of these ^{31}P coordination shifts concur with the η^6 bonding mode in **10**,[17] and the relative intensities support the rotamer distribution inferred from ^{1}H NMR. Additional corroborative evidence is provided by the ^{13}C NMR spectrum which also points at the rotamer ratio **10s**:**10a** = 3:1. This value is more precise than the ratio derived from EPR of **9**, and therefore, the departure from the 2:1 statistical ratio must be regarded as real. By way of rationalization it may be argued that due to the deviation of the phosphorin ring from hexagonal symmetry, the cofacial approach of two (t-Bu)$_3$–phosphinine ligands in an orientation leading to the synclinal rotamer **10s** is a path of lower energy (slightly reduced interannular *tert*-butyl repulsion) than the alternative approach which yields the antiperiplanar rotamer **10a** (Figure 2). Because of the severe steric hindrance to ring rotation this initial rotamer ratio is conserved at ambient temperature for extended periods of time.[18]

Although cyclic voltammetry is not expected to resolve possible differences in the redox potentials of the conformers **9s**, **9a** and **10s**, **10a**, respectively, it is nevertheless instructive to compare the potentials for the η^6-phosphinine complexes with those of their carbocyclic analogues. Cyclovoltammetric traces are depicted in Figure 3, and the relevant data are collected in Table III. Reversible waves are observed for electron transfer to and from the HOMO a$_{1g}$ (mainly metal 3d$_{z^2}$) only, i.e. for one-electron oxidation and reduction of the bis(arene)vanadium and oxidation of the bis(arene)chromium species, all other

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(18) The activation energy for the interconversion of two rotamers of bis(1-methyl-4-*tert*-butylbenzene)chromium amounts to 35.6 kJ mol^{-1}. Here the eclipsed transition state features the interannular repulsion between a methyl- and a *tert*-butyl group. In the case of three pairs of *tert*-butyl groups as in **9** or **10**, such a torsional process may safely be excluded: Zenneck, U.; Elschenbroich, Ch.; Möckel, R. *J. Organomet. Chem.* 1981, *219*, 177.

Table I. EPR Data for the Complexes $(\eta^6\text{-}C_5H_5P)_2V$ (2), $[2,4,6\text{-}(t\text{-}Bu)_3\text{-}\eta^6\text{-}C_5H_2P]_2V$ (9), $(\eta^6\text{-}C_6H_6)_2V$ (13), and $[1,3,5\text{-}(t\text{-}Bu)_3\text{-}\eta^6\text{-}C_6H_3]_2V$ (11)[a]

	2^b						9							
	$2a^c$		2^d		$2a^c$		$9a^c$		$9s^c$		13		11	
g_{iso}^{300}			1.9874				1.9830				1.9869		1.9860	
g_{aniso}	g_1^{38}	2.0020	g_1^{300}	2.0020	g_1^{120}	2.0020	g_1	2.0020	g_1	2.0020	$g_\parallel^{130}$	2.0020	$g_\parallel^{100}$	2.0030
	g_2^{38}	1.9844	g_2^{300}	1.9801	g_2^{120}	1.9840	g_2	1.9838	g_2	1.9761	$g_\perp^{130}$	1.9795	$g_\perp^{100}$	1.9775
	g_3^{38}	1.9764	g_3^{300}	1.9801	g_3^{120}	1.9745	g_3	1.9632	g_3	1.9710				
$a_{iso}^{300}(^{51}V)$			7.03				7.58				6.29		6.75	
$A(^{51}V)$	A_1^{38}	1.76	A_1^{300}	2.30	A_1^{120}	1.66	A_1^{130}	1.96	A_1^{130}	2.73	$A_\parallel^{130}$	0.78	$A_\parallel^{100}$	1.25
	A_2^{38}	8.78	A_2^{300}	9.39	A_2^{120}	8.77	A_2^{130}	9.25	A_2^{130}	9.49	$A_\perp$	9.01	$A_\perp^{100}$	9.50
	A_3^{38}	10.55	A_3^{300}	9.39	A_3^{120}	10.66	A_3^{130}	11.55	A_3^{130}	10.57				

[a] Fluid and rigid solutions in DME. **a** and **s** designate the antiperiplanar and synclinal conformers, respectively. The coupling constants are given in mT, and the temperatures (K) of measurement are stated as exponents. The anisotropic spectra of **2** at 38 and 300 K were obtained from mixed crystal powders, [2.2]paracyclophane serving as a matrix, those at 100, 120, and 130 K from rigid solutions in DME. [b] Reference 7. [c] Slow ring rotation on the EPR time scale. [d] Fast ring rotation on the EPR time scale.

Table II. ^{13}C, ^1H, and ^{31}P NMR Data (δ, Hz) for Complex 10 and the Free Ligand 8[a]

^{13}C NMR

		2,6′	3,5′	4,4′	3′,5	2′,6	7,10′	8,9′	8′,9	7′,10	11,11′	12,12′
$\delta(^{13}C)$	**10s**	120.8	79.1	99.4	76.1	112.9	38.1	34.7	33.2	37.5	30.6	35.9
	10a	114.4				114.4		33.8	33.8		31.6	
	8	182.9	126.8	151.8	126.8	182.9	39.2	33.3	33.3	39.2	31.9	36.4
$^1J(^{13}C\text{-}^1H)$	**10s**		154.43		160.66			118.63	124.37		126.76	
	10a		156.32		156.32							
	8		158.24		158.24			122.81	122.81		125.83	
$^1J(^{31}P\text{-}^{13}C)$	**10s**	64.13			60.36							
	10a	67.73			67.73							
	8	56.52			56.52							
$^2J(^{31}P\text{-}^{13}C)$	**10s**		5.77	6.41	14.22[b]	20.40			19.99			
	10a		6.41	6.41								
	8		12.30	12.30		21.88			21.88			
$^3J(^{31}P\text{-}^{13}C)$	**10s**					9.68[b]	10.81					
	10a						11.44					
	8						12.53					
$^4J(^{31}P\text{-}^{13}C)$	**10s**						7.54[b]					

^1H NMR

		3,5′	3′,5	8,9′	8′,9	11,11′
$\delta(^1H)$	**10s**	5.34	5.13	1.31	1.42	1.57
	10a	4.89	4.89	1.40	1.40	1.37
	8	7.89	7.89	1.45	1.45	1.26
$^3J(^{31}P\text{-}^1H)$	**10s**	2.50	2.90			
	10a					
	8	6.34	6.34			
$^4J(^{31}P\text{-}^1H)$	**10s**			3.57	3.39	
	10a					
	8			1.14	1.14	

^{31}P NMR

$\delta(^{31}P)$	**10s**	−53.17
	10a	−53.78
	8	181.24

[a] All spectra were recorded in toluene-d_8 at 25 °C. **10s** and **10a** designate the synclinal and antiperiplanar rotamers. According to the integrated signal intensities, they are present in a 3:1 ratio. [b] Interannular coupling.

processes being irreversible. The incorporation of a P atom into the π-bonded arene results in anodic shifts of 530 mV (**13**, **2**) and 260 mV (**12**, **10**) which attest to the *increased π-accepting nature of phosphinine as compared to benzene*. The central metal atom thus acquires a somewhat larger positive partial charge in the phosphinine complexes, and its ionization potential increases. Whereas substitution of H by CH_3 causes additive cathodic shifts of 21 mV/CH_3, peripheral substitution of H atoms by *t*-Bu groups exerts only a minute influence on the redox potentials $E_{1/2}(+/0)$.[19] Apparently, the hyperconjugative and inductive effects of the *tert*-butyl groups, which should cause cathodic shifts of the redox potential $E_{1/2}(+/0)$, are counterbalanced by the steric effects of these encumbering substituents, which results in an increase of metal–ligand distance with a concomitant decrease of ligand → metal charge transfer. The increased metal–ligand distance, caused by the incorporation of six *tert*-butyl groups, may also explain the attenuated anodic shift for the pair **12**, **10** compared to **13**, **2**, since the acceptor character of the η^6-arene operates via an e_{2g} interaction of δ symmetry which is very sensitive to overlap modification.

Conclusion

Ring rotation in unsubstituted bis(η^6-phosphinine)metal complexes is virtually uninhibited since in the liquid range of common solvents NMR spectroscopy failed to exhibit

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(19) Bilger, E. Dissertation, Marburg, 1984.

(20) Elschenbroich, Ch.; Bilger, E.; Metz, B. *Organometallics* **1991**, *10*, 2823.

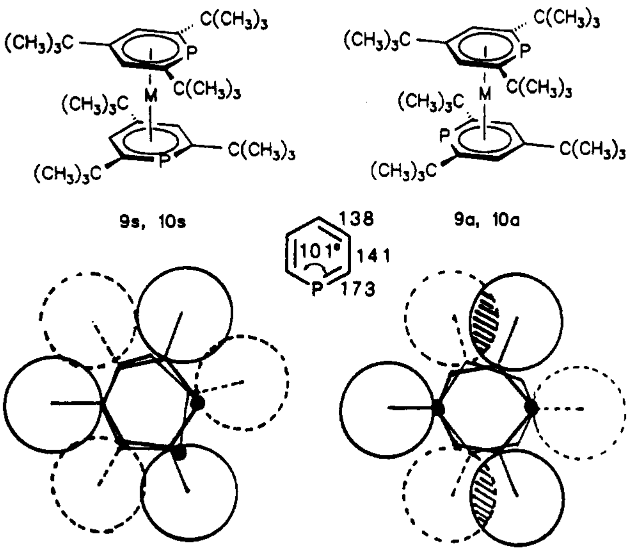

Figure 2. Projection of the structures of synclinal and antiperiplanar bis(2,4,6-tri-*tert*-butylphosphorin)metal complexes emphasizing the different extents of interligand *t*-Bu interaction.

decoalescence, and even in the solid state, bis(η^6-phosphinine)vanadium, present in a [2.2]paracyclophane matrix, displays ring rotation which is rapid on the EPR time scale at $T > 170$ K. In order to probe whether there exists a preference for a specific ring conformation, we have synthesized the vanadium and chromium sandwich complexes of 2,4,6-tri-*tert*-butylphosphinine. In these complexes the original distribution of conformers is conserved due to severe hindrance of rotation caused by the bulky substituents. However, the results of the present study gathered from EPR (M = V) as well as NMR spectroscopy (M = Cr) revealed that, measured against statistical expectation, there is only a slight excess of the synclinal form present in the mixture of rotamers. Considering that a certain preference for the synclinal form will be caused by steric effects of the *tert*-butyl groups since the phosphinine ring deviates from hexagonal symmetry, the electronic preference for a certain rotamer in bis(η^6-phosphinine)metal complexes must be regarded as very small indeed. As we have observed previously, however, the parent complex **2** at very low temperature (38 K) features an orthorhombic **g** tensor, attesting to quenching of ring rotation. Comparison of the **g** tensor components of **2** with those obtained for **9a** suggests that, at low temperature, **2** prefers the antiperiplanar conformation.

Experimental Section

All manipulations were carried out under an atmosphere of dry prepurified nitrogen. The hydrocarbon solvents were dried by refluxing over CaH_2 and then K. They were freshly distilled prior to use. Instrumental analysis: ^1H and ^{13}C NMR, Bruker AC 300 (300.1 and 75.5 MHz, respectively) and Bruker AM-400 (400.1 and 100.6 MHz, respectively) (NMR measurements, were performed on solutions in sealed tubes); MS, Varian MAT, CH7A (EI, 70 eV); EPR, Varian E12 (X-band); cyclic voltammetry, AMEL 552 potentiostat, 566 function generator, and 563 multipurpose unit, Nicolet 2090-1 digital storage oscilloscope, Kipp and Zonen BD 90 X/Y recorder, glassy carbon working electrode, Pt wire counter electrode, saturated aqueous calomel reference electrode coupled to the sample solution via a nonaqueous salt bridge. Cyclic voltammetry was performed under argon protection.

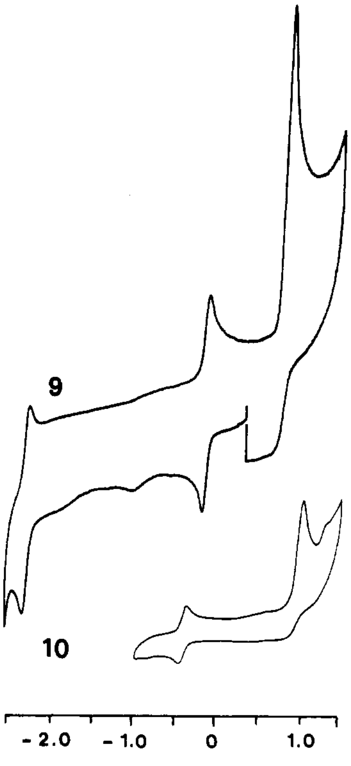

Figure 3. Cyclic voltammograms of **9** (upper trace, −50 °C) and **10** (lower trace, +25 °C) in DME/0.1 M Bu_4NClO_4, ν = 0.1 V/s.

1,3,5-Tri-*tert*-butylbenzene (Aldrich), chromium (Zinsser), and vanadium (Koch Chemicals Ltd.) were from commercial sources. 2,4,6-Tri-*tert*-butylphosphinine was prepared as described in the literature.[21]

Bis(2,4,6-tri-*tert*-butyl-η^6-phosphinine)vanadium (9). The synthesis was performed in a metal-atom reactor of the bell-jar type which was equipped with a positive hearth electron gun furnace for metal vaporization[22] and a heatable inlet system to introduce the ligand vapor. After the reactor wall was cooled with liquid nitrogen, the surface was covered with a layer (≈60 mL) of methylcyclohexane. Then, during a period of about 1 h, vanadium (0.39 g, 7.57 mmol) was condensed (electron-beam current input 350 mA, accelerating voltage 3.3 kV) with 2,4,6-tri-*tert*-butylphosphinine (4 g, 15.15 mmol) at the reactor surface. The reactor was flooded with nitrogen and allowed to reach ambient temperature, and the blackish brown suspension was filtered over a G 4 frit which was covered with a layer of silylated silica gel. After the solvent was removed in vacuo, the residue was freed from excess ligand by means of sublimation at 70 °C (10^{-2} mbar). When the temperature was raised to 130 °C, **9** was obtained as a dark red microcrystalline sublimate. Yield: 45 mg (≈1% based on evaporated vanadium); mp 203 °C dec. Anal. Calcd for $C_{34}H_{58}P_2V$: C, 70.43; H, 10.08. Found: C, 70.66; H, 10.48.

Bis(2,4,6-tri-*tert*-butyl-η^6-phosphinine)chromium (10). Chromium (0.4 g, 7.69 mmol) was vaporized from a resistively heated tungsten spiral (12 V, 40 A) and cocondensed with 2,4,6-tri-*tert*-butylphosphinine (5 g, 18.9 mmol) on the cooled reactor surface (77 K). After flooding with nitrogen and warmup to room temperature, the reaction product was taken up in cyclohexane and the solution filtered over silylated silica gel. The filtrate

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[21] Dimroth, K.; Mach, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 460.

[22] Cloke, F. G. N.; Green, M. L. H.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1978**, 72. Green, M. L. H. *J. Organomet. Chem.* **1980**, *200*, 119.

Table III. Cyclic Voltammetry Data[a] for the Redox Processes of the η^6-Phosphinine Complexes 2, 9, and 10, the Carbocyclic Counterparts 12–14, and the Free Ligands 8 and 15

		$E_{1/2}(0/-)/\mathrm{V}$	$\Delta E_p/\mathrm{mV}$	r	$E_{1/2}(+/0)/\mathrm{V}$	$\Delta E_p/\mathrm{mV}$	r	E_{pa}/V[b]
$(C_6H_6)_2V$	**13**[c]	−2.71 r	74	0.93	−0.35 r	66	1.00	0.24
$(C_5H_5P_2)V$	**2**[d]	−1.99 q	80	1.10	0.18 r	44	1.00	1.02
$[(t\text{-Bu})_3(C_5H_2P]_2V$	**9**	−2.25 r	61	1.50	−0.10 r	56	1.30	0.86
$(C_6H_6)_2Cr$	**14**[c]	<−3.1			−0.69 r	87	0.95	0.97
$[(t\text{-Bu})_3C_6H_3]_2Cr$	**12**	<−3.1			−0.69 r			0.71
$[(t\text{-Bu})_3C_5H_2P]_2Cr$	**10**				−0.43 r	76	1.07	0.98
C_5H_5P	**15**	−2.27[e]	100	0.56	−1.05[f,g]			−0.14[f,g]
$(t\text{-Bu})_3C_5H_2P$	**8**	−2.57 −2.75[h]	56	0.70				

[a] In DME/$(n\text{-Bu})_4NClO_4$ (0.1 M) at glassy carbon vs SCE, $T = -50$ °C (V complexes), 25 °C (Cr complexes). [b] Peak potential of an irreversible wave. [c] Reference 20. [d] Reference 7. [e] 25 °C, partially reversible. [f] Irreversible, see ref 7. [g] E_{pa}(ECE). [h] $T = 25$ °C, irreversible.

still contained some colloidal chromium. After the solvent was stripped off and excessive ligand was removed by sublimation (60 °C, 10^{-3} mbar), the residue was dissolved in petroleum ether 40/60 and the filtration was repeated twice, using a 0.2-μm Teflon filter. Evaporation to dryness yielded analytically pure **10** as a greenish-brown amorphous material. Due to the extremely high solubility, attempts to grow crystals for an X-ray diffraction study were abortive. Yield: 40 mg ($\approx$1% based on evaporated chromium); 150 °C dec before reaching mp. Anal. Calcd for $C_{34}H_{58}P_2Cr$: C, 70.31; H, 10.06. Found: C, 69.61; H, 10.93.

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Additions and Corrections

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Santiago Ciruelos, Tomás Cuenca, Juan Carlos Flores, Rafael Gómez, Pilar Gómez-Sal, and Pascual Royo*: Monocyclopentadienyl-Type Titanium Complexes with the $[\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]^{2-}$ Ligand. X-ray Crystal Structure of $[(TiCl)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2\text{-}SiMe_2\}]_2(\mu_2\text{-}O)_2$. The First Example of a Nonplanar "Ti_4O_4" Core.

Page 945. In the first line in column 1, *bridging* instead of chelating should be written.