π-Cyclopentadienyl and π-Indenyl Compounds of Titanium, Zirconium, and Hafnium Containing σ-Bonded Organic Substituents[1]

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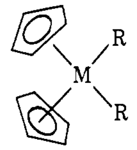
Abstract: Zirconocene and hafnocene dichlorides react with appropriate organolithium reagents to form stable dimethyl and diphenyl derivatives, in the same manner as does titanocene dichloride. The bis(π-indenyl) dihalides of titanium, zirconium, and hafnium likewise lead to dimethyl and diphenyl compounds which in general appear to be more stable than the corresponding π-cyclopentadienyl derivatives. An analysis has been undertaken of trends in the nmr spectra of these new series of organometallic compounds, both with respect to the nature of the metal and to the nature of the π-bonded ligand. The formation and properties of bis(π-indenyl)bis(σ-pentafluorophenyl)titanium and the new titanium metallocycle 5,5-bis(π-indenyl)dibenzotitanole are also described.

It has been known for many years that titanocene dichloride (**1**) undergoes reactions with Grignard and organolithium reagents to yield relatively stable disubstituted σ-alkyl and σ-aryl derivatives. Thus, dimethyltitanocene (**2**)[3,4] and diphenyltitanocene (**3**)[5] were first prepared many years ago, and their chemical and spectral properties have been widely studied. Zirconocene dichloride (**5**) and hafnocene dichloride (**9**), although isoelectronic and most probably isostructural with the titanium homolog **1**, did not seem to form disubstituted σ-alkyl and σ-aryl derivatives as straightforwardly.[6,7] At the inception of our research program in this area, only two such organometallic compounds (**8** and **12**) had been described in the literature.[7,8] Further, the formation of bis(π-idenyl) dichlorides of titanium (**13**) and zirconium (**17**) have been reported earlier,[9] but substitution reactions of these compounds were not investigated.

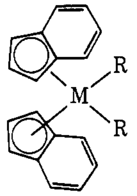
In this paper, we wish to describe the synthesis and spectral properties of σ-bonded dimethyl and diphenyl derivatives of zirconocene and hafnocene. We also report on the formation and properties of various new σ-bonded compounds of bis(π-indenyl)titanium, -zirconium, and -hafnium, as well as a new bis(π-indenyl)-titanium metallocycle.[10]

Results and Discussion

Formation and Properties. Dialkyl and diaryl titanocene compounds were reported in the literature as early as 1955[3-5] and have been found to give many interesting reactions. They are resistant to hydrolysis and can be stored at low temperatures for long periods of time without thermal decomposition. The π-C_5H_5 ring thus has a stabilizing effect on the σ-bonded carbon–titanium linkage. Although it might be predicted that the homologous zirconium and hafnium analogs should be equally stable and isolable, no mention has been made in the literature concerning their existence, and only unsuccessful attempts have been reported concerning the preparation of compounds such as $Cp_2Zr(C_6H_5)_2$.[6,7] σ-Bonded organic derivatives of zirconocene and hafnocene have been isolated only when the metal or the alkyl group bears a highly electronegative substituent. Thus, $Cp_2Zr(C_6F_5)_2$ (**8**)[7] has been isolated and characterized, and the reaction of zirconocene dichloride (**5**) with phenyllithium followed by hydrolysis led to the oxygen-bridged product $[Cp_2Zr(C_6H_5)]_2O$.[11] Likewise, only a few monoalkyl derivatives of zirconocene have been reported thus far.[12-15] As for hafnocene derivatives, Cp_2Hf-



1, M = Ti; R = Cl
2, M = Ti; R = CH_3
3, M = Ti; R = C_6H_5
4, M = Ti; R = C_6F_5
5, M = Zr; R = Cl
6, M = Zr; R = CH_3
7, M = Zr; R = C_6H_5
8, M = Zr; R = C_6F_5
9, M = Hf; R = Cl
10, M = Hf; R = CH_3
11, M = Hf; R = C_6H_5
12, M = Hf; R = C_6F_5



13, M = Ti; R = Cl
14, M = Ti; R = CH_3
15, M = Ti; R = C_6H_5
16, M = Ti; R = C_6F_5
17, M = Zr; R = Cl
18, M = Zr; R = CH_3
19, M = Zr; R = C_6H_5
20, M = Hf; R = Cl
21, M = Hf; R = CH_3

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(1) Presented by M. D. Rausch at the Fifth International Conference on Organometallic Chemistry, Moscow, U. S. S. R., Aug 16–21, 1971; Abstracts of Plenary and Section Lectures, Vol. III, p 10. M. D. Rausch, *Pure Appl. Chem.*, 30, 523 (1972).

(2) Postdoctoral Research Associate (1970–1971) from the Laboratoire de chimie de coordination, Paris 5°, France.

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(7) M. Chaudari and F. G. A. Stone, *J. Chem. Soc. A*, 838 (1966).

(8) M. D. Rausch, H. B. Gordon, and E. Samuel, *J. Coord. Chem.*, 1, 141 (1971).

(9) E. Samuel and R. Setton, *J. Organometal. Chem.*, **4**, 156 (1965).

(10) Abbreviations: Cp = π-cyclopentadienyl; Ind = π-indenyl.

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(12) J. Surtees, *Chem. Commun.*, 567 (1965).

(13) P. C. Wailes and H. Weigold, *J. Organometal. Chem.*, 24, 405 (1970).

(14) P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometal. Chem.*, 43, C29, C32 (1972).

(15) After our studies in this area had been completed and reported,[1] the synthesis of $Cp_2Zr(CH_3)_2$ (**6**) was independently described: P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometal. Chem.*, **34**, 155 (1972).

$(C_6F_5)_2$ (**12**) and 5,5-bis(π-cyclopentadienyl)octafluorodibenzohafnole are the only σ-bonded compounds described thus far.[8]

In the course of our studies on the formation and properties of σ-bonded organic compounds of the transition metals, we have found that the dimethyl and diphenyl derivatives of zirconocene and hafnocene are products which can be isolated in reasonably good yields, providing that necessary precautions, especially against hydrolysis, are taken.

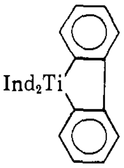
Thus, methyllithium reacts with zirconocene and hafnocene dichlorides (**5** and **9**) to give the dimethyl derivatives **6** and **10**, respectively. Both products are white crystalline solids which sublime readily at relatively low temperatures (70–110°) *in vacuo*. The dimethyl derivatives have melting points much lower than those of the corresponding dihalides and are much more soluble in common organic solvents. They appear to be reasonably stable in solution if oxygen and water are excluded. Both dimethyl derivatives appear to hydrolyze readily, giving new compounds having M–O–M structures as evidenced by the infrared spectra of the products.[16] In general, the zirconium and hafnium compounds (**6** and **10**) appear to be more thermally stable than the titanium homolog **2**. They can be heated to their melting points and also sublimed under vacuum without apparent decomposition, whereas **2** decomposes readily under these same conditions.

The dimethyl compounds of bis(π-indenyl)titanium, -zirconium, and -hafnium (**14**, **18**, **21**) can likewise be prepared in a manner similar to that of their π-cyclopentadienyl analogs. In general, they exhibit properties similar to their metallocene counterparts, except that they seem to exhibit greater thermal and oxidative stabilities. Also, the σ-bonded organic group appears to be less chemically reactive toward cleavage. Thus, $Ind_2Ti(CH_3)_2$ (**14**) does not react with hydrogen under conditions where $Cp_2Ti(CH_3)_2$ (**2**) reacts readily.[16,17] Further, **14** can be stored for considerably longer periods of time than **2** without apparent decomposition.

Phenyllithium also reacts with zirconocene and hafnocene dichlorides (**5** and **9**) to give the corresponding white crystalline diphenyl derivatives **7** and **11**. These products are best purified by recrystallization at low temperature from ethyl ether. They cannot be sublimed, since they decompose on heating above 130° *in vacuo*. The diphenyl derivatives appear to be more stable than the dimethyl analogs toward air and moisture, and the hafnium compound **11** is more stable hydrolytically than the zirconium analog **7**. Once crystallized and dried, $Cp_2Hf(C_6H_5)_2$ (**11**) can be kept for several hours in the air without apparent change.

The diphenyl derivatives of bis(π-indenyl)titanium and -zirconium (**15** and **19**) were likewise prepared readily from phenyllithium and the corresponding dichlorides **13** and **17**. They are both stable in air in the solid state, and the zirconium analog can be recrystallized in air and filtered without substantial hydrolysis taking place, provided the operation is done rapidly. In view of the difficulty in preparing Ind_2HfCl_2 (**20**), we have not yet been able to obtain the corresponding diphenyl derivative.

Ind_2TiCl_2 (**13**) also reacts with 2,2′-dilithiobiphenyl to give a dark red product which presumably has the metallocyclic structure **22**. This titanocycle appears to be indefinitely stable in the air, in contrast to the diphenyl analog **15**. A similar metallocycle and relative stability findings have previously been reported in the π-cyclopentadienyl series.[18] Pentafluorophenyllithium also reacts readily with Ind_2TiCl_2 (**13**) to give $Ind_2Ti(C_6F_5)_2$ (**16**). The product is remarkably stable, even more so than the dichloride **13**, since it does not decompose in organic solvents as does the latter. The corresponding zirconium and hafnium derivatives will be investigated at a later date.



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Nmr Spectra. One of the most interesting aspects of this new series of organometallic compounds is that they represent the first example of isostructural organometallic compounds covering a complete transition metal subgroup having both methyl and phenyl substituents σ bonded to the metal. Further, they involve two distinct types of organometallic π complexes, one series containing an unsubstituted π-C_5H_5 ring and the other the C_5 ring of a π-indenyl group. Thus, the effect of changing the geometry and electron density of the π-bonded ring can be expected to influence the chemical shifts of the σ-bonded organic moiety, and also the effects of changing the central metal atom in each series can be compared. Table I shows the values of the proton chemical shifts for the series of compounds studied.

CH_3 Chemical Shifts. A striking characteristic of the methyl resonance in all the compounds studied is the fact that it lies upfield from tetramethylsilane. The methyl singlet shifts to lower field, as expected, when one of the two methyl groups is replaced by a halogen atom. Thus, $Cp_2ZrCl(CH_3)$ exhibits a singlet at τ 9.58,[12] whereas the singlet in $Cp_2Zr(CH_3)_2$ (**6**) lies at τ 10.39. The following additional observations can also be drawn from the nmr measurements.

(i) The methyl resonance exhibits appreciable shifts to higher field when proceeding from lighter to heavier metals in the subgroup (Figure 1). The largest shift occurs between titanium and zirconium (*e.g.*, 0.22 ppm in the $Cp_2M(CH_3)_2$ series), which is twice the difference of the values between the zirconium and hafnium analogs. These changes are likely owing both to electronegativity and electron polarizability differences associated with the respective metals. A similar trend is seen in comparing the values of the methyl proton resonances in the $Ind_2M(CH_3)_2$ series, and in this series the chemical shift differences as a function of the metal are even more greatly pronounced (*vide infra*).

(ii) For the same metal, the chemical shift of the methyl proton resonance increases significantly in the

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[16] E. Samuel and M. D. Rausch, unpublished studies.

[17] H. Brintzinger and J. Bercaw, *J. Amer. Chem. Soc.*, 92, 6182 (1970).

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Table I. Proton Nmr Data for Titanium-Group Metallocene Dialkyls and Diaryls[a,b]

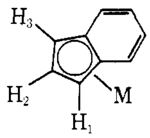
Metallocene	No.	Cp (τ)	R (τ)	Metallocene	No.	Ind		R (τ)
						C_5 Ring (τ)	C_6 Ring (τ)	
Cp_2TiCl_2	**1**	3.43 (s)		$Ind_2Ti(CH_3)_2$	**14**	4.32 (t)[c] 3.92 (d)	2.5–3.0 (m)	10.83 (s)
Cp_2ZrCl_2	**5**	3.53 (s)		$Ind_2Zr(CH_3)_2$	**18**	3.8–4.2 (m)	2.5–3.0 (m)	11.13 (s)
Cp_2HfCl_2	**9**	3.63 (s)		$Ind_2Hf(CH_3)_2$	**21**	3.9–4.2 (m)	2.6–3.0 (m)	11.30 (s)
$Cp_2Ti(C_6F_5)_2$	**4**	3.50 (t)[d]		$Ind_2Ti(C_6H_5)_2$	**15**	4.28 (s)	3.0–3.6 (m)	3.0–3.6 (m)
$Cp_2Zr(C_6F_5)_2$	**8**	3.56 (s)		$Ind_2Zr(C_6H_5)_2$	**19**	3.8–4.1 (m)	2.6–3.2 (m)	2.6–3.2 (m)
$Cp_2Hf(C_6F_5)_2$	**12**	3.63 (s)						
$Cp_2Ti(CH_3)_2$	**2**	3.95 (s)	10.17 (s)					
$Cp_2Zr(CH_3)_2$	**6**	3.89 (s)	10.39 (s)					
$Cp_2Hf(CH_3)_2$	**10**	4.00 (s)	10.50 (s)					
$Cp_2Ti(C_6H_5)_2$	**3**	3.80 (s)	3.0 (br s)					
$Cp_2Zr(C_6H_5)_2$	**7**	3.90 (s)[e]	2.7–3.2 (m)[e]					
$Cp_2Hf(C_6H_5)_2$	**11**	3.84 (s)	2.6–3.0 (m)					

[a] Recorded in $CDCl_3$ solution unless otherwise indicated. [b] Key: s = singlet, d = doublet, t = triplet, m = multiplet. [c] $J = 3$ Hz. [d] $J_{H-F} = 0.4$ Hz: M. D. Rausch, *Inorg. Chem.*, 3, 300 (1964). [e] Measured in CS_2 solution; compound appears to react with $CDCl_3$.

π-indenyl compounds relative to their π-C_5H_5 counterparts. This increased shielding of the methyl protons in the π-indenyl series may be related to enhanced screening, owing to the magnetic field resulting from the aromatic ring current effects of the two π-indenyl ligands. In view of the supposedly pseudotetrahedral structure of the molecule, the two benzo substituents on the C_5 rings should for steric reasons lie in positions on the same side of the two methyl groups and thereby effect increased shielding. Single-crystal X-ray diffraction studies are presently underway to confirm these structural postulations and to ascertain any trends in various carbon–metal bond distances in these new organometallic compounds.

C_5-Ring Protons. (i) Cyclopentadienyl Compounds. In all of the dimethyl and diphenyl derivatives of the type $Cp_2M(CH_3)_2$ examined (Table I), the π-cyclopentadienyl ring protons exhibit a sharp singlet which is shifted by *ca.* 0.4–0.5 ppm to higher fields than the corresponding dichlorides. This result is consistent with the electron-attracting character of a halogen *vis-à-vis* a σ-bonded alkyl or aryl substituent.[6] No distinct trends of the π-C_5H_5 protons as a function of the metal were observed in these two series, in contrast to Cp_2MR_2 series where R represents an electronegative substituent such as –Cl or –C_6F_5. In the latter two series, the effect of changing the metal from titanium to zirconium to hafnium in each case results in a progressive upfield shift of the π-cyclopentadienyl resonance.

(ii) Indenyl Compounds. In these compounds, the three protons H_1, H_2, and H_3 of the C_5 ring might be expected to exhibit an A_2B pattern, consistent with a symmetrical bonding of the ring to the metal. Although this result is clearly observed in the spectrum of $Ind_2Ti(CH_3)_2$ (**14**), which exhibits a doublet (J = 3 Hz) for H_1 and H_3 and a triplet for H_2, all the other π-indenyl compounds examined give spectra which correspond to different values of $J_{1,2}$, $J_{1,3}$, or $J_{2,3}$ and also for δ $H_{1,3}$ and H_2. For these derivatives, the resonance representing the C_5-ring protons occurs as an unresolved multiplet. Perhaps the most interesting spectrum in this entire series of new organometallic compounds is that of $Ind_2Ti(C_6H_5)_2$ (**15**), in which the resonance representing protons H_1, H_2, and H_3 appears as an apparent *singlet.* Such a unique result may possibly be the result of a number of factors, and additional studies to elucidate this point are in progress. It appears, therefore, that the charge density of the three carbon atoms of the C_5-indenyl ring is very sensitive to the nature of the metal as well as to the nature of the σ-bonded substituent.



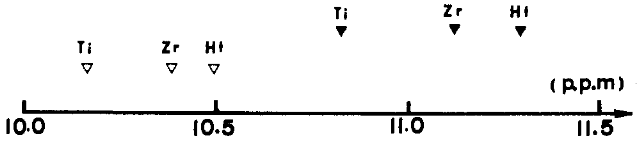


Figure 1. Proton chemical shifts (in τ ppm) of the methyl groups in: ▽, $Cp_2M(CH_3)_2$; ▼, $Ind_2M(CH_3)_2$.

Experimental Section

All reactions were carried out under a nitrogen atmosphere unless otherwise specified. Ethyl ether was dried over calcium chloride and then freshly distilled from sodium-benzophenone. Titanocene dichloride (**1**) and zirconocene dichloride (**5**) were purchased from Arapahoe Chemicals Co., while hafnocene dichloride (**9**) was prepared by a literature procedure.[8] Methyllithium and phenyllithium were obtained from Alfa Inorganics, Inc. Bis(π-indenyl)titanium dichloride (**13**) and bis(π-indenyl)zirconium dichloride (**17**) were synthesized by a method previously described.[9] Nmr spectra were recorded on a Varian A-60 spectrometer; all solutions were introduced into the sample tube under nitrogen. Melting points were measured in sealed capillary tubes under nitrogen and are uncorrected. Microanalyses were performed by the Microanalysis Laboratory, Office of Research Services, University of Massachusetts. The elemental analysis data for all the compounds described below are summarized in Table II.

Dimethylzirconocene (6). A suspension of 1.5 g (5 mmol) of zirconocene dichloride in 20 ml of ethyl ether was cooled to −20° in the reaction flask. Under magnetic stirring, 6.0 ml of 1.66 *M* methyllithium in ethyl ether was added dropwise *via* a syringe over a period of 45 min. The temperature was then allowed to rise to 0° and was maintained at this temperature for an additional 30 min, during which time a crystalline solid was observed to form in the flask. The solvent was then evaporated and the solid residue was transferred to a sublimation apparatus. Sublimation at 60–80° and at 2×10^{-4} mm for 2 hr produced 1.0 g (79%) of $Cp_2Zr(CH_3)_2$ (**6**) as a white crystalline solid.

Dimethylhafnocene (10). A suspension of hafnocene dichloride (1.0 g, 2.6 mmol) in ethyl ether was treated with 3.0 ml of 1.66 *M* methyllithium following the procedure described above. Sublimation of the reaction residue at 90° *in vacuo* gave 0.5 g (60%) of $Cp_2Hf(CH_3)_2$ (**10**) as white crystals.

Diphenylzirconocene (7). This reaction was conducted under an atmosphere of argon. A suspension of 1.0 g (3.4 mmol) of zir-

Table II. Elemental Analysis Data for Titanium-Group Metallocene Dialkyls and Diaryls

Compound	No.	Formula	Mp, °C	Analysis found (calcd), %			
				C	H	Metal	Halogen
$Cp_2Zr(CH_3)_2$	**6**	$C_{12}H_{16}Zr$		57.20	6.30	36.00	
				(57.31)	(6.41)	(36.27)	
$Cp_2Hf(CH_3)_2$	**10**	$C_{12}H_{16}Hf$		42.71	4.52	52.50	
				(42.55)	(4.76)	(52.69)	
$Cp_2Zr(C_6H_5)_2$	**7**	$C_{22}H_{20}Zr$	140 dec	70.40	5.40	24.10	
				(70.35)	(5.37)	(24.28)	
$Cp_2Hf(C_6H_5)_2$	**11**	$C_{22}H_{20}Hf$	145 dec	56.72	4.48	38.60	
				(57.08)	(4.36)	(38.65)	
Ind_2HfCl_2	**20**	$C_{18}H_{14}Cl_2Hf$		45.20	3.07		
				(45.07)	(2.94)		
$Ind_2Ti(CH_3)_2$	**14**	$C_{20}H_{20}Ti$	105 dec	77.34	6.35	15.90	
				(77.92)	(6.54)	(15.54)	
$Ind_2Zr(CH_3)_2$	**18**	$C_{20}H_{20}Zr$	107 dec	68.07	5.60	25.80	
				(68.32)	(5.73)	(25.95)	
$Ind_2Hf(CH_3)_2$	**21**	$C_{20}H_{20}Hf$	120 dec	*a*	*a*	40.60	
						(40.67)	
$Ind_2Ti(C_6H_5)_2$	**15**	$C_{30}H_{24}Ti$	105 dec	83.22	5.43		
				(83.33)	(5.59)		
$Ind_2Zr(C_6H_5)_2$	**19**	$C_{30}H_{24}Zr$	100 dec	75.58	5.10		
				(75.74)	(5.09)		
$Ind_2Ti(C_6H_5)_2$	**16**	$C_{30}H_{14}F_{10}Ti$	215	59.01	2.30	7.80	30.98
				(58.84)	(2.30)	(7.82)	(31.03)
$Ind_2TiC_{12}H_8$	**22**	$C_{30}H_{22}Ti$	130 dec	83.70	4.98	11.03	
				(83.72)	(5.15)	(11.13)	

[a] A reproducible carbon–hydrogen analysis could not be obtained.

conocene dichloride in 20 ml of ethyl ether was cooled to −40°. Phenyllithium (3.0 ml, 2.3 *M*) was subsequently added dropwise *via* a syringe over a 45-min period with magnetic stirring, during which time a white crystalline solid separated from solution. Stirring was continued at −40° for 1 hr and the temperature was slowly allowed to rise to 0°. The solvent was then evaporated under reduced pressure and the solid residue was washed with pentane and decanted. The remaining residue was extracted with ethyl ether and the extracts were filtered under nitrogen. Concentration of the filtrate yielded 1.0 g (80%) of white, crystalline $Cp_2Zr(C_6H_5)_2$ (**7**). The compound gives a well-resolved ir spectrum in Nujol with major peaks at 1405 (m), 1240 (w), 1050 (m, doublet), 1005 (m), 980 (m), 827 (w), and 820 (s) and characteristic phenyl bands at 775 (s) and 698 (s) cm^{-1}.

Diphenylhafnocene (11). A suspension of 1.0 g (2.6 mmol) of hafnocene dichloride was treated with 2.5 ml of 2.3 *M* phenyllithium following the above procedure. Concentration produced 0.9 g (75%) of $Cp_2Hf(C_6H_5)_2$ (**11**) as white crystals. The ir spectrum was virtually identical with that of the zirconium analog.

Bis(π-indenyl)dimethyltitanium (14). A suspension of 1.0 g (2.9 mmol) of bis(π-indenyl)titanium dichloride in 50 ml of ethyl ether was cooled to −20° and 5 ml of 1.66 *M* methyllithium in ethyl ether was added dropwise over a 30-min period with stirring. The color gradually changed to orange, then yellow. The temperature was allowed to warm to 0° and was maintained at this temperature for an additional 1 hr. The ether suspension was then hydrolyzed and the organic layer was dried over sodium sulfate and concentrated to give 0.5 g (56%) of $Ind_2Ti(CH_3)_2$ (**14**) as orange-yellow crystals. An analytical sample was crystallized from ethyl ether–pentane solution.

Bis(π-indenyl)dimethylzirconium (18). Bis(π-indenyl)zirconium dichloride (1.0 g, 2.5 mmol) was introduced into a reaction flask with 20 ml of ethyl ether. The resulting suspension was cooled to −20° and 3 ml of 1.66 *M* methyllithium in ethyl ether was added dropwise *via* a syringe with stirring over a period of 30 min. The temperature was then allowed to rise gradually, and the yellow suspension changed color to cream white at 0°. Stirring was continued for several minutes at this temperature and the solvent was then removed at reduced pressure. The solid residue was purified by vacuum sublimation (the cold finger is maintained below the level of the oil bath) to produce 0.5 g (57%) of $Ind_2Zr(CH_3)_2$ (**18**) as a straw-colored solid.

Bis(π-indenyl)hafnium Dichloride (20). Ind_2HfCl_2 (**20**) was prepared in 38% yield by an extension of an earlier method,[9] utilizing indenylsodium and freshly sublimed hafnium tetrachloride (purity >99% on a metal–metal basis) in tetrahydrofuran solution.

Bis(π-indenyl)dimethylhafnium (21). $Ind_2Hf(CH_3)$ (**21**) was prepared from bis(π-indenyl)hafnium dichloride and methyllithium in ethyl ether solution by a procedure completely analogous to that described for the zirconium analog. The product was purified by vacuum sublimation at *ca.* 120°. It was isolated in 36% yield as a straw-colored solid.

Bis(πin-denyl)diphenyltitanium (15). The reaction was run under argon. A suspension of 1.0 g (2.9 mmol) of bis (π-indenyl)titanium dichloride and 50 ml of ethyl ether was cooled to −20°. Phenyllithium (2.5 ml, 2.3 *M*) was added dropwise during a period of 30 min with stirring.[19] The dark brown suspension gradually changed to orange. When the addition was complete, the temperature was allowed to rise to 20° and the solvent was removed under reduced pressure. Following the addition of 70 ml of 70/30 ethyl ether–pentane, the crude product was extracted with stirring and filtered. The orange filtrate was cooled to −10° to yield 0.3 g (25%) of $Ind_2Ti(C_6H_5)_2$ (**15**) as orange-red crystals.

Bis(π-indenyl)diphenylzirconium (19). The same procedure as above was followed to prepare $Ind_2Zr(C_6H_5)_2$ (**19**) from 1.0 g (2.5 mmol) of bis(π-indenyl)zirconium dichloride and 4 ml of 1.66 *M* phenyllithium. The product is yellow-white and was isolated in 60% yield.

Bis(π-indenyl)bis(pentafluorophenyl)titanium (16). Pentafluorophenyllithium was prepared by adding dropwise 2.8 ml of 2.38 *M* *n*-butyllithium in hexane over a 30-min period to 1.5 g (6.0 mmol) of bromopentafluorobenzene in 25 ml of ethyl ether cooled to −78°. To this solution at −78° was added 1.0 g (3.0 mmol) of bis(π-indenyl)titanium dichloride with vigorous stirring. The temperature was then allowed to warm to −20° during which time the color changed to wine red. Stirring was continued for 1 hr at this temperature and the solvent was then evaporated at room temperature. The residue was washed successively with water, ethanol, and ethyl ether and then dried. Chromatography of the product on alumina using hexane as eluent produced 1.2 g (66%) of dark burgundy crystals of $Ind_2Ti(C_6F_5)_2$ (**16**).

5,5-Bis(π-indenyl)dibenzotitanole (22). 2,2′-Dilithiobiphenyl was prepared from 2.5 g (8.0 mmol) of 2,2′-dibromobiphenyl and 7 ml of 2.38 *M* *n*-butyllithium in hexane at 0°.[20,21] To this solution was added 2.0 g (5.7 mmol) of bis(π-indenyl)titanium dichloride over a 30-min period. Stirring was continued for 1 hr, during which time the color of the reaction mixture became dark red. The solvent

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(19) The quantity of phenyllithium should be rigorously stoichiometric, since an excess of the lithium reagent seems to react with the product.

(20) H. Gilman and R. D. Gorsich, *J. Amer. Chem. Soc.*, 77, 6380 (1955).

(21) S. A. Gardner, H. B. Gordon, and M. D. Rausch, *J. Organometal. Chem.*, in press.

was then evaporated and the residue was washed with pentane and filtered. The solid was dissolved in ethyl ether and the solution was filtered. Concentration of the filtrate followed by cooling gave 1.2 g (49 %) of dark red crystals of the metallocycle **22**.

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Kekulé Index for Valence Bond Structures of Conjugated Polycyclic Systems[1a]

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Abstract: Individual formal valence structures of conjugated hydrocarbon systems have been characterized by an index K, called the Kekulé index, which relates a given set of molecular orbitals to orbitals localized on pairs of adjacent carbons. The localized orbitals can be associated with valence bond structures in a simple and unique way. It is then shown that for systems built from condensed benzene rings the valence structure with the largest values of the Kedulé index corresponds to Kekulé-type valence structures with the largest number of formal benzene Kekulé-type formulas, *i.e.*, to structures for which the empirical Fries rule predicts the greatest stability. The Kekulé index orders different valence structures in a series which should qualitatively indicate relative importance of the individual structures. The approach can be extended also to excited formal structures as discussed for naphthalene. Application of such analyses to a number of alternate polycyclic conjugated systems confirms an intuitive extension of the Fries rule to systems constructed from rings of various sizes.

Despite considerable computational difficulties which make the application of complete VB calculations to large conjugated systems impractical, the method nevertheless has its attractive features and has proved useful for qualitative discussions of organic systems. The results of VB calculations would be of considerable interest as they would indicate the relative weights of different Kekulé-type structures. The valence bond method which forms another basis for description of molecules and bonding has been conceptually closer to chemical ideas and has been found useful even at the very crude qualitative level avoiding actual computations and limited to operating with a few well-selected valence bond structures. It seems desirable to be able to use the language of the valence bond model at a somewhat quantitative level whenever that can be achieved without going into tedious and impractical VB computations. In this paper we consider this problem and describe an approach to arrive at some indication of the relative weights of different Kekulé-type structures although this is accomplished in a somewhat indirect and intuitive way. We associate with individual valence structures an index derived by projecting the given molecular orbitals (HMO or SCF) on a space spanned by functions which characterize individual CC double bonds, selected corresponding to individual formal valence structures of the conjugated system considered. We interpret the results as a measure of overlap between the HMO or SCF wave function and one characterizing the valence structure under the examination. The index thus constructed does not represent a true overlap between an MO description and a VB wave function of the considered conjugated hydrocarbon. The evaluation of the genuine index of overlap between MO and VB wave functions is much more involved and cumbersome. It has been considered, but it appeared that the calculation seemed not sufficiently practical and did not appear to be of compensating value.[2] Although the present approach is not directly connected with VB wave functions, it may nevertheless be associated with individual valence structures, and perhaps represents the simplest intuitive measure of the relative weights of individual VB structures. In fact, we do not deal with any one Kekulé structure directly at all: we take the double bonds in a chosen Kekulé structure *one by one*, and find their overlap with each of the occupied MO's. The point about any Kekulé structure is that it represents a form of pairing of *all* the electrons at the same time. Instead we have been finding something like the sum of bond orders (or double bond characters) of the "double bonds" of a Kekulé structure, when using an MO wave function. This gives something like the importance of a Kekulé wave function within the MO wave function. The argument for the importance of this new index is therefore rather empirical, and as will be demonstrated, it gives sensible results. One may interpret the results to indicate the relative importance of various Kekulé-type formal valence structures: the larger the index the more important the contribution of that particular structure in the total wave function. Such an interpretation is supported by the result that the valence structures with the largest number of benzene Kekulé structures are those with greatest Kekulé index, in complete agreement with the empirical Fries rule.[3]

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[2] C. A. Coulson, University of Oxford, England, unpublished results, private communication, 1972.

[3] K. Fries, *Justus Liebigs Ann. Chem.*, **454**, 121 (1927); K. Fries, R. Walter, and K. Schilling, *ibid.*, **516**, 248 (1935).

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