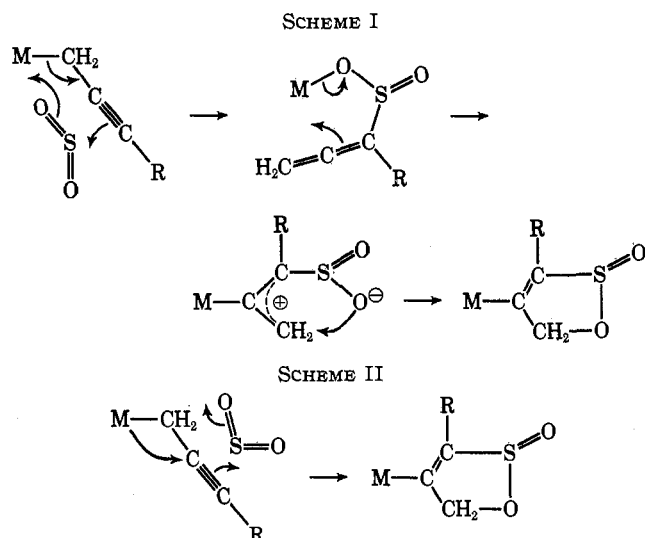


convincingly to an electrophilic interaction of SO_2 with organometallic compounds. In its reactions with transition metal-carbon systems, SO_2 may be best regarded as attacking at the M—C bond site in the alkyls and aryls and either at the M—C or at the C=C linkage in the σ -allyls. Accordingly, with the latter compounds, rearrangement of the allylic moiety often accompanies the insertion.³

It appears most reasonable that in the reactions under consideration the site of attack by the electrophilic SO_2 is the electron-rich C≡C bond. Following such an initial interaction, either of the two general pathways given below (Schemes I and II) will lead to the formation of the sultine derivative.



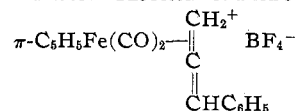
Path I receives support from the reaction of $(\text{C}_6\text{H}_5)_3\text{SnCH}_2\text{C}\equiv\text{CH}$ with SO_2 which gives the stable $(\text{C}_6\text{H}_5)_3\text{Sn}[\text{OS}(\text{O})\text{CH}=\text{C}=\text{CH}_2]$.³⁰ This compound is strictly analogous to the allenyl-*O*-sulfinate intermediate proposed in pathway I. However, unlike its transition

metal counterpart, the tin *O*-sulfinate should be very stable toward subsequent rearrangement because of an expected greater strength of its M—O linkage. Path II²² represents a one-step reaction with rearrangement. It is certainly as plausible as path I, especially in view of the fact that the suggested *O*-sulfinate intermediate has yet to be detected.

Any attempt at differentiation among the two foregoing and other reasonable pathways³² must be deferred until additional data become available. One may conclude, however, that the formation of the metal sultines from the corresponding 2-alkynyls and SO_2 is a kinetic rather than a thermodynamic effect. This follows from our successful isolation of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{SO}_2\text{CH}_2\text{C}\equiv\text{CCH}_3)$ and demonstration that it does not rearrange to the isomeric sultine. Also worth noting is that allenyl-*S*-sulfonates, $\text{MS}(\text{O})_2\text{C}(\text{R})=\text{C}=\text{CH}_2$, do not form in the reactions under consideration as might be expected by analogy with the behavior of the σ -allyls.³ This may be best attributed to the linearity of the 2-alkynyl moiety which prevents simultaneous interaction of the sulfur with the metal and the C≡C bond (see Scheme I).

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(32) NOTE ADDED IN PROOF.—The recent isolation of



from the reaction of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}\equiv\text{CC}_6\text{H}_5$ with HBF_4 , as well as the demonstration that $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}=\text{CR}$ and tetracyanoethylene yield

the cyclic $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}=\text{C}(\text{R})\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{CH}_2$, suggests that reactions of transition metal-2-alkynyl complexes with various electrophiles may proceed via the intermediacy of the corresponding π -allenyls: D. W. Lichtenberg and A. Wojcicki, unpublished results, and S. R. Su and A. Wojcicki, *J. Organometal. Chem.*, in press, respectively.

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The Synthesis and Stereochemistry of Some β -Diketone Derivatives of Titanocene and Zirconocene Dichlorides

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By the interaction of $(\text{C}_5\text{H}_5)_2\text{MCl}_2$ ($\text{M} = \text{Ti}, \text{Zr}$) (1 mol) and a β -diketone (keH) (2 mol), in the presence of triethylamine (1 mol), in acetonitrile solution at 20° , the compounds $\text{C}_5\text{H}_5\text{MCl}(\text{ke})_2$ were prepared. A similar reaction with tropolone (TH) gave $\text{C}_5\text{H}_5\text{ZrT}_3$. The monomeric nonelectrolytes $\text{C}_5\text{H}_5\text{MCl}(\text{ke})_2$ were investigated by infrared and variable-temperature ^1H nmr spectroscopy, which indicated that these compounds all exist as the *cis* isomer in solution with the exception of $\text{C}_5\text{H}_5\text{TiCl}(\text{acac})_2$ for which two isomers are observed.

Introduction

As a continuation of our work on the reactions of the group IVa metallocene dihalides with chelating ligands containing a replaceable hydrogen atom,¹ the reactions

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(1) J. Charalambous, M. J. Frazer, and W. E. Newton, *J. Chem. Soc. A*, in press.

of $(\text{C}_5\text{H}_5)_2\text{MCl}_2$ ($\text{M} = \text{Ti}, \text{Zr}$) with some β -diketones (keH) [keH = pentane-2,4-dione (acacH), 1-phenylbutane-1,3-dione (bzacH), 1,3-diphenylpropane-1,3-dione (bzbzH)] and tropolone (TH) have been studied, resulting in the preparation of the compounds $\text{C}_5\text{H}_5\text{MCl}(\text{ke})_2$, the first preparation of compounds of this type with $\text{M} = \text{Ti}$. Two reports on related titanium

TABLE I
ANALYTICAL DATA

Compound	Color	Analyses, %								Conductivity ^b		
		C		H		M		Cl		Λ_m	$10^3 \times$ concn	Mol wt ^{a,c}
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found			
$C_5H_5TiCl(acac)_2$	Orange	52.0	52.6	5.5	5.4	13.8	14.2	10.2	10.0	0.168	1.46	...
$C_5H_5TiCl(bzac)_2$	Orange	63.8	63.3	4.9	5.0	10.2	10.6	7.5	7.9	0.238	0.70	...
$C_5H_5ZrCl(acac)_2$	Colorless	46.2	45.9	4.9	4.8	23.4	23.3	9.1	9.6	0.087	1.15	...
$C_5H_5ZrCl(bzac)_2$	Colorless	58.4	58.9	4.5	4.6	17.7	18.2	6.9	7.1	0.075	0.64	512 (512)
$C_5H_5ZrCl(bzbz)_2$	Yellow	65.9	65.9	4.3	3.7	14.3	14.3	5.6	5.6	0.039	0.39	636 (636)
$C_5H_5ZrT_3$	Yellow	60.1	59.5	3.9	3.8	17.6	17.7	0.025	0.31	...

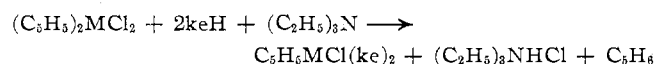
^a Required values in parentheses. ^b Nitrobenzene solutions at 26°; specific conductance of solvent was 1.4×10^{-8} mho cm^{-1} ; Λ_m in mho $cm^2 mol^{-1}$ and concentrations are molar. ^c By mass spectrometry; all of these compounds, and the related 8-quinolinolato compounds,¹ gave unusual mass spectra which will form the basis of a future publication.

chemistry have appeared recently. One was concerned with the reactions of $(C_5H_5)_2Ti(ClO_4)_2$ with β -diketones and tropolone (chelH), in aqueous solution, when the compounds $[(C_5H_5)_2Ti(chel)]^+ClO_4^-$ were prepared,² and the other,³ with the preparation of the compounds $(C_5H_5)_2TiClY$ ($Y = bzbz, acetoacetanilidate$). Several publications⁴⁻¹³ have appeared concerning the preparation of chelated cyclopentadienylzirconium(IV) compounds of the types $C_5H_5ZrX(ke)_2$ ($X = Cl; ke = acac, bzac, bzbz$; and $X = Br, acetoxy; ke = acac$) and $C_5H_5Zr(ke)_3$ ($ke = acac, bzac, bzbz$) by reactions usually under reduced pressure and at temperatures between 60 and 110°. The compounds $C_5H_5ZrCl(ke)_2$ ($ke = acac, bzac, bzbz$) were prepared again in this present work by a more convenient method and in better yields.

Results and Discussion

Syntheses and Properties.—We had found previously¹ that $(C_5H_5)_2MX_2$ ($M = Ti, Zr, Hf; X = Cl, Br, I$) reacted with 8-quinolinol (oxH), in dry acetonitrile under nitrogen at 20°, to produce the compounds $C_5H_5MX(ox)_2$. It thus seemed logical to attempt to extend this reaction to other related ligands and so determine the generality of its application. When a reaction, under similar conditions, was attempted with $(C_5H_5)_2TiCl_2$ and pentane-2,4-dione (acacH), the reactants were recovered in 92% yield after 7 days' stirring. However, in the presence of a hydrogen halide acceptor, such as triethylamine, the reaction proceeded very quickly to give the anticipated product $C_5H_5TiCl(acac)_2$. It was found that the reactions between these metallocene dichlorides (1 mol) and β -diketones (2 mol), in the presence of triethylamine (1 mol), in acetonitrile solution, resulted in the formation of dark orange ($M = Ti$) or colorless ($M = Zr$) solutions. On removal of the

solvent and extraction of the resultant solids with benzene, a colorless residue of triethylammonium chloride (1 mol) was obtained. From the benzene extracts, the orange ($M = Ti$) or colorless ($M = Zr$) compounds $C_5H_5MCl(ke)_2$ ($M = Ti, Zr; ke = acac, bzac$) were obtained (see Table I for analytical data).



A similar reaction of $(C_5H_5)_2ZrCl_2$ with 1,3-diphenylpropane-1,3-dione (bzbzH) gave a yellow precipitate of $C_5H_5ZrCl(bzbz)_2$. Tropolone (TH) (2 mol) and $(C_5H_5)_2ZrCl_2$ (1 mol) reacted together, not to give the expected product but, with further substitution, to produce cyclopentadienyltris(tropolonato)zirconium(IV) ($C_5H_5ZrT_3$). Unreacted $(C_5H_5)_2ZrCl_2$ (30% recovery) was isolated from the filtrate. (See Table I for analyses.) This reaction with tropolone further illustrates the tendency of this ligand to form complexes with high coordination numbers¹⁴⁻¹⁸ due to the relatively small "bite" of the ligand, e.g., $2.50 \pm 0.1 \text{ \AA}$ in $C_5H_5ZrT_3$ ¹⁹ as compared with, say, $2.74 \pm 0.05 \text{ \AA}$ for acac in $C_5H_5ZrCl(acac)_2$,²⁰ due to the planarity and rigidity of the donor oxygen atoms. However, the related compounds $C_5H_5Zr(chel)_3$ ($chel = hexafluoroacetylacetonate$ and trifluoroacetylacetonate), with the ligand "bite" of $2.69 \pm 0.01 \text{ \AA}$ for the former,^{21a} have been readily prepared by the direct interaction of $(C_5H_5)_2ZrCl_2$ and the appropriate ligand under anhydrous conditions.^{21b}

The compounds $C_5H_5MCl(ke)_2$ are all fairly susceptible to atmospheric moisture in the solid state and are readily hydrolyzed in solution. They are soluble in benzene, chloroform, and tetrahydrofuran but insoluble in petroleum ethers and diethyl ether. Molar conductance measurements on these compounds in nitrobenzene solution showed them to be nonelectrolytes, while mass spectrometric molecular weight determinations on $C_5H_5ZrCl(ke)_2$ ($ke = bzac, bzbz$) indicated monomeric structures. Previous molecular weight determinations^{7,22} on $C_5H_5ZrCl(acac)_2$ also indicated a monomeric structure and this has been confirmed by a single-crystal X-ray study.²⁰ The related 8-quinolinolato

- (2) G. Doyle and R. S. Tobias, *Inorg. Chem.*, **6**, 1111 (1967).
- (3) D. N. Sen and U. N. Kantak, *J. Indian Chem. Soc.*, **46**, 358 (1969).
- (4) E. M. Brainina, R. Kh. Freidlina, M. Kh. Minacheva, and L. A. Petrashkevich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1396 (1966).
- (5) E. M. Brainina, R. Kh. Freidlina, E. I. Mortikova, and L. A. Petrashkevich, *Dokl. Akad. Nauk SSSR*, **169**, 335 (1966).
- (6) E. M. Brainina, R. Kh. Freidlina, and A. N. Nesmayanov, *ibid.*, **138**, 1369 (1961).
- (7) E. M. Brainina and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1421 (1964).
- (8) E. M. Brainina, R. Kh. Freidlina, M. Kh. Minacheva, and A. N. Nesmayanov, *ibid.*, 1417 (1964).
- (9) E. M. Brainina, R. Kh. Freidlina, and A. N. Nesmayanov, *Dokl. Akad. Nauk SSSR*, **164**, 1113 (1964).
- (10) E. M. Brainina, G. G. Dvoryantseva, and R. Kh. Freidlina, *ibid.*, **156**, 1375 (1964).
- (11) E. M. Brainina and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 835 (1963).
- (12) E. M. Brainina, R. Kh. Freidlina, and M. Kh. Minacheva, *ibid.*, 1710 (1961).
- (13) E. M. Brainina, M. Kh. Minacheva, and R. Kh. Freidlina, *Dokl. Akad. Nauk SSSR*, **173**, 581 (1967).

- (14) E. L. Muettterties and C. M. Wright, *J. Amer. Chem. Soc.*, **86**, 5132 (1964).
- (15) E. L. Muettterties and C. M. Wright, *ibid.*, **87**, 21 (1965).
- (16) E. L. Muettterties and C. M. Wright, *ibid.*, **87**, 4706 (1965).
- (17) E. L. Muettterties, *ibid.*, **88**, 305 (1966).
- (18) E. L. Muettterties, H. Roesky, and C. M. Wright, *ibid.*, **88**, 4856 (1966).
- (19) J. D. Matthews and E. M. McPartlin, private communication.
- (20) J. J. Stezowski and H. A. Eick, *J. Amer. Chem. Soc.*, **91**, 2890 (1969).
- (21) (a) M. Elder, J. G. Evans, and W. A. G. Graham, *ibid.*, **91**, 1245 (1969); (b) J. J. Howe and T. J. Pinnavaia, *ibid.*, **92**, 7342 (1970).
- (22) (a) T. J. Pinnavaia, J. J. Howe, and E. D. Butler, *ibid.*, **90**, 5288 (1968); (b) M. Kh. Minacheva, E. M. Brainina, and L. A. Federov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1104 (1969).

compounds were also found to be monomeric nonelectrolytes.^{1,23} The infrared (4000–80 cm⁻¹) and proton nmr spectra of the compounds indicated the presence of both chelated β -diketonato groups and π -cyclopentadienyl. The spectra of the analogous titanium and zirconium chelates were very similar.

The tropolonato compound C₅H₅ZrT₃ was found to be sparingly soluble in benzene, slightly soluble in chloroform and dichloromethane, but insoluble in the other usual organic solvents. Its infrared and proton nmr spectra were consistent with the presence of π -cyclopentadienyl and bidentate tropolonato groups.¹⁶ It was also a nonconductor in nitrobenzene solution and single-crystal X-ray analysis showed it to be monomeric with a distorted pentagonal-bipyramidal configuration.¹⁹

These compounds were subjected to an infrared spectroscopic examination, initially with the object of gaining some insight into their stereochemistry, particularly by studying the metal–oxygen vibrations, but unfortunately these compounds have such low symmetry (*vide infra*) that no definite structural information was forthcoming. Therefore, the assignment of metal–halogen (ν (MCl)), metal–cyclopentadienyl ring (ν (M–ring)), and metal–ligand (ν (MO)) modes became the main objectives. The assignments are based on the criteria established previously²⁴ and are listed in Table II, with some assignments made previously in related

TABLE II
ASSIGNMENTS MADE IN THE INFRARED
SPECTRA OF C₅H₅MCl(ke)₂ (CM⁻¹)^a

Compound	ν (MCl)	ν (M–ring)	ν (MO)	Ref
C ₅ H ₅ TiCl(acac) ₂	362	350	463 sh, 453	...
C ₅ H ₅ TiCl(bzac) ₂	367	352	445 sh, 420	...
TiCl ₂ (acac) ₂	366	...	480 sh, 470	24, 25a
C ₅ H ₅ TiCl(ox) ₂	380	356	...	1
C ₅ H ₅ ZrCl(acac) ₂	312	331	445, 431	...
C ₅ H ₅ ZrCl(bzac) ₂	308	320–340	443 sh, 416	...
C ₅ H ₅ ZrCl(bzbz) ₂	310–330	310–330	458	...
ZrCl ₂ (acac) ₂	337	...	460 sh, 450	25b
ZrCl(acac) ₃	314	...	449 sh, 432	25b
C ₅ H ₅ ZrCl(ox) ₂	321	333	...	1
C ₅ H ₅ ZrT ₃	...	315 (?)	417 (?)	...

^a sh = shoulder.

compounds.^{1,24,25} The frequencies of the bands assigned to ν (TiCl) are in the region expected for compounds with hexacoordination,^{24,26} while those for ν (TiO) in C₅H₅TiCl(acac)₂ are 17 cm⁻¹ lower than those observed previously in TiCl₂(acac)₂.^{25a} A similar comparison for the zirconium acac compounds indicated that the assignments made in this present work for ν (ZrCl) and ν (ZrO) are very close to those made previously^{25b} for ZrCl(acac)₃.²⁷ These data indicate that

(23) J. D. Matthews, N. Singer, and A. G. Swallow, *J. Chem. Soc. A*, 2545 (1970).

(24) I. Douek, M. J. Frazer, Z. Goffer, M. Goldstein, B. Rimmer, and H. A. Willis, *Spectrochim. Acta, Part A*, **23**, 373 (1967).

(25) (a) R. C. Fay and R. N. Lowry, *Inorg. Nucl. Chem. Lett.*, **3**, 117 (1967); (b) R. C. Fay and T. J. Pinnavaia, *Inorg. Chem.*, **7**, 508 (1968).

(26) R. J. H. Clark, M. L. Greenfield, and R. S. Nyholm, *J. Chem. Soc. A*, 1254 (1966).

(27) (a) We thank a referee for this observation. It was also suggested that if the assignments for ν (TiCl) and ν (Ti–ring) in the infrared spectrum of C₅H₅TiCl(acac)₂ were reversed, ν (TiCl) at 350 cm⁻¹ would be 16 cm⁻¹ lower than that observed in TiCl₂(acac)₂ (*i.e.*, a lowering similar to that observed for ν (TiO)) and thus be in line with the observed lowering in the analogous zirconium compounds. However, we prefer the assignments given in Table II on the basis of comparison with the spectra of the related compounds.^{1,27b} C₅H₅TiX(ox)₂ (X = Cl, Br, I, OC₂H₅; ox = 8-quinolinolate) and TiX(OC₂H₅)(ox)₂ (X = Cl, Br), where ν (TiCl) is found consistently at a higher frequency than ν (Ti–ring). (b) M. J. Frazer and W. E. Newton, unpublished observations.

the coordination number in these C₅H₅MCl(ke)₂ compounds may be somewhat greater than 6. It has been suggested previously from single-crystal X-ray analyses of C₅H₅TiCl(ox)₂²³ and C₅H₅ZrCl(acac)₂²⁰ that the angular distribution of bonds about the metal, the displacement of the metal toward the C₅H₅ ring, and the metal–chlorine bond distances all indicate a coordination number rather higher than 6 for these complexes, possibly 8.

The assignments made for ν (MO) are all in the region expected for these vibrations.²³ It has been suggested²³ that the substitution of phenyl for methyl in the β -diketonato ligand should lead to a strengthening of the metal–oxygen bond and so result in a shift of ν (MO) to higher frequency in the order acac < bzac < bzbz. This is the order generally observed, but the assignments listed in Table II indicate that the metal–oxygen bond is weaker in C₅H₅MCl(acac)₂ than in MCl₂(acac)₂ and that, in contrast to the above, this bond in the acac compounds is stronger than in the bzac compounds, while it is strongest of all in the bzbz compound. A parallel effect is observed in the nmr spectra (*vide infra*), when the C₅H₅ resonance shifts downfield in the order bzac > acac > bzbz, supporting an increase in donor strength for the β -diketonato ligands in this order.

Stereochemistry.—It is most likely that all the compounds C₅H₅MCl(ke)₂ exist as discrete monomolecular species, with an “approximate” coordination number of 6 (considering the cyclopentadienyl ring as occupying one coordination position only and undergoing rapid rotation). Two geometrical isomers, based on an octahedron (see Figure 1), are therefore

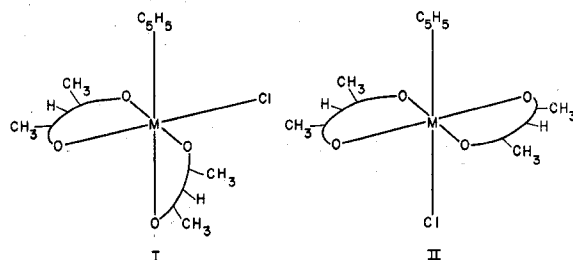


Figure 1.—The geometrical isomers of “octahedral” C₅H₅MCl(ke)₂.

possible for ke = acac and bzbz. The cis isomer (I) has no elements of symmetry (point group C₁), which leads to nonequivalent environments both for the γ protons and for all four organic (methyl or phenyl) groups on the two chelated ligands, while the trans isomer (II) has C_{2v} symmetry which results in just one environment for the γ protons and one for the methyl (or phenyl) protons. For ke = bzac, there are six possible geometric isomers, two trans and four cis.

It is interesting to note that most of the complexes of the type MX₂(ke)₂ (M = group IV metal; X = halogen (not I), alkoxy group; ke = bidentate, anionic ligand) of known stereochemistry^{25,29–37} have the atoms

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(30) M. J. Frazer and Z. Goffer, *ibid.*, **A**, 544 (1966).

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(32) J. A. S. Smith and E. J. Wilkins, *Chem. Commun.*, 381 (1965).

(33) J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc. A*, 1749 (1966).

(34) A. Davison and J. W. Faller, *Inorg. Chem.*, **6**, 182 (1967).

(35) R. C. Fay and R. N. Lowry, *ibid.*, **6**, 1512 (1967).

(36) R. C. Fay and N. Serpone, *ibid.*, **6**, 1835 (1967).

(37) D. C. Bradley and C. E. Holloway, *Chem. Commun.*, 284 (1965).

X mutually cis, those with X = carbanion may have either cis³⁸ or trans³⁹⁻⁴² configurations, and the compounds $R\text{SnCl}(\text{acac})_2$ ($R = \text{CH}_3, \text{C}_6\text{H}_5$) have the organic group and chlorine cis.^{33,43,44} $\text{TiI}_2(\text{acac})_2$ and $\text{GeCl}_2(\text{acac})_2$ are unusual in that they exhibit cis-trans isomerism in solution.^{45,46}

Proton nmr spectroscopy is a well-established technique for the investigation of β -diketonato complexes, particularly those of the type $\text{MX}_2(\text{acac})_2$, when information regarding stereochemistry may be obtained from both the number of signals and possibly their chemical shift for any particular proton or group of protons.³²⁻⁴⁷ This technique was applied to the compounds $\text{C}_5\text{H}_5\text{MCl}(\text{ke})_2$ prepared in this work.

The spectra of the acac compounds, in deuteriochloroform solution, exhibited three resonances (or groups of resonances) at (i) *ca.* τ 3.5, (ii) *ca.* τ 4.3, and (iii) *ca.* τ 8.0. Integration and comparison with the spectra of related compounds^{25a,35-37} allowed the assignment of these resonances to the cyclopentadienyl group, the γ proton, and the methyl protons of the ligands, respectively. For the bzac compounds, an additional resonance at *ca.* τ 2.5, due to the phenyl protons of the ligand was observed, while for the bzbz compound, the resonance at *ca.* τ 8.0 was absent. The observed chemical shifts for these resonances are listed in Table III. Also included are the values for the

The number of cyclopentadienyl and methyl resonances observed in the spectra obtained at $+33.5^\circ$ in this present work confirmed these stereochemical assignments. The nonequivalent γ protons of both $\text{C}_5\text{H}_5\text{ZrCl}(\text{acac})_2$ and $\text{C}_5\text{H}_5\text{ZrCl}(\text{bzac})_2$, which gave rise to coincident (or nearly so) signals at $+33.5^\circ$ in CDCl_3 , could be resolved by cooling, thus demonstrating the different temperature dependences of their chemical shifts. Only three of the expected eight γ proton signals for the four cis isomers of $\text{C}_5\text{H}_5\text{ZrCl}(\text{bzac})_2$ could be resolved in this way (see Figure 2).

TABLE III
NMR DATA FOR THE COMPOUNDS $\text{C}_5\text{H}_5\text{MCl}(\text{ke})_2$,
 $\text{C}_5\text{H}_5\text{ZrT}_3$, AND SOME RELATED COMPOUNDS^{a,b}

Compound	C_5H_5	γ	CH_3	C_6H_5	Ref
$\text{C}_5\text{H}_5\text{TiCl}(\text{acac})_2$	3.40	4.33	7.95
$\text{C}_5\text{H}_5\text{TiCl}(\text{bzac})_2$	3.44	3.64	7.67	<i>Ca.</i> 2.5 m	...
$\text{TiCl}_2(\text{acac})_2$...	3.99	7.86	...	<i>c, e</i>
$\text{TiCl}_2(\text{bzac})_2$...	3.31	7.71	...	<i>c, f</i>
$\text{C}_5\text{H}_5\text{ZrCl}(\text{acac})_2$	3.45	4.47	7.97 m
$\text{C}_5\text{H}_5\text{ZrCl}(\text{bzac})_2$	3.46	3.76 m	7.89 m	<i>Ca.</i> 2.5 m	...
$\text{C}_5\text{H}_5\text{ZrCl}(\text{bzbz})_2$	3.34	3.08	...	<i>Ca.</i> 2.5 m	...
$\text{ZrCl}_2(\text{acac})_2$...	4.01	7.87	...	<i>c, g</i>
$\text{C}_5\text{H}_5\text{ZrT}_3$	3.70	2.3-3.0 ^d	...

^a In deuteriochloroform solution at $+33.5^\circ$, with TMS as an internal standard. ^b m is multiplet; all other signals are singlets. ^c In dichloromethane solution. ^d For the tropolonato groups. ^e Reference 35. ^f Reference 36. ^g R. C. Fay and T. J. Pinnavaia, *Inorg. Chem.*, **7**, 502 (1968).

$\text{C}_5\text{H}_5\text{ZrT}_3$ spectrum, when a strong singlet (intensity 1) and a complex signal (intensity 3) are observed due to cyclopentadienyl and tropolonato groups, respectively. This latter multiplet is very similar to that reported previously¹⁶ for the compound $(\text{T}_4\text{Ta})^+\text{Cl}^-$.

The spectra of the compounds $\text{C}_5\text{H}_5\text{ZrCl}(\text{ke})_2$ ($\text{ke} = \text{acac}, \text{bzac}$), at 36° in benzene solution, have been reported previously.²² These spectra demonstrated a cis stereochemistry for these compounds in solution, as found in the solid state by X-ray crystallography.²⁰

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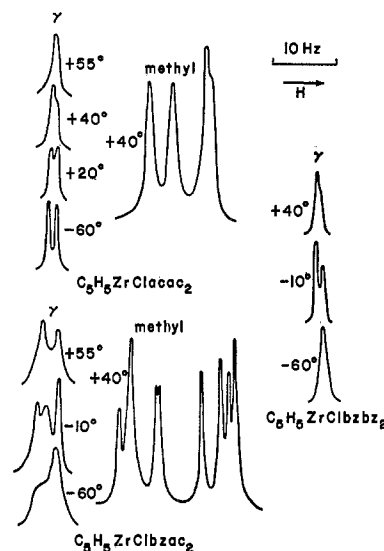


Figure 2.—Variable-temperature ^1H nmr spectra of $\text{C}_5\text{H}_5\text{ZrCl}(\text{ke})_2$.

For the compound $\text{C}_5\text{H}_5\text{ZrCl}(\text{bzbz})_2$, the spectrum consisted of a phenyl resonance at *ca.* τ 2.5, which was too complex to be used as a probe for signal splitting, and a singlet for both the cyclopentadienyl and the γ proton resonances. The γ proton resonance in this spectrum is the only one suitable for use as a probe for stereochemistry. No change was observed in the C_5H_5 singlet, but on cooling to -10° , the γ -proton resonance split into a doublet, indicating a cis configuration for this compound also. However, as the temperature was lowered still further to -60° , this doublet coalesced into a singlet again. The reason for this is not understood, although viscosity broadening may be a contributing factor. Similarly, both the three γ -proton signals and the eight methyl signals observed at -10° for $\text{C}_5\text{H}_5\text{ZrCl}(\text{bzac})_2$ showed some merging when the temperature was lowered to -60° (see Figure 2).

It was not possible to determine the preferred stereochemistry for the titanium compounds from their spectra at $+33.5^\circ$. The spectra of both the acac and bzac compounds showed some asymmetry of the methyl singlet but no definite indications of stereochemistry were forthcoming. The ligand γ -proton resonances for both compounds, at this temperature and in this solvent, were also singlets (see Table III and Figure 3).

The spectrum of $\text{C}_5\text{H}_5\text{TiCl}(\text{bzac})_2$ showed no change in the C_5H_5 resonance with decreasing temperature, but the γ -proton resonance split into two, and the methyl signal, into a distorted quintet at -10° . At -60° , the γ -proton signal became a distorted triplet, and the methyl signal, a distorted sextet, indicating that all

four cis isomers are probably present in solution together (see Figure 3).

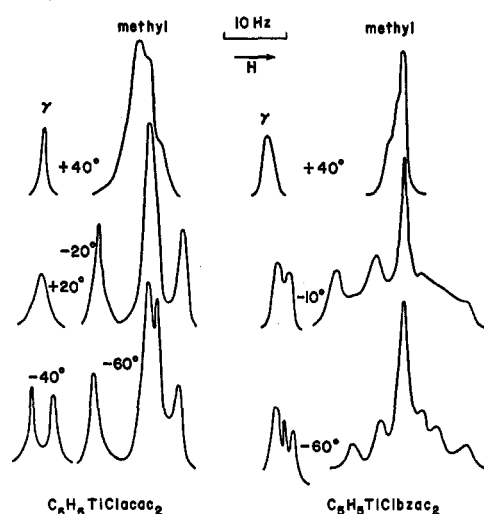


Figure 3.—Variable-temperature ^1H nmr spectra of $\text{C}_5\text{H}_5\text{TiCl}(\text{ke})_2$.

For $\text{C}_5\text{H}_5\text{TiCl}(\text{acac})_2$, not only did the methyl signal split into four and the γ -proton signal into two as the temperature was lowered (see Figure 3), but the C_5H_5 resonance also split. This is the only case of a split in the C_5H_5 resonance recorded in this work or in the work on the related 8-quinolinolate compounds.¹ This indicated that two isomers (at least) were present in solution. Two possible explanations for this phenomenon are discussed below.

(i) The C_5H_5 group is σ bonded and fluxional above $\sim -20^\circ$; *i.e.*, a *monohaptocyclopentadienyl* group⁴⁸ ($h^1\text{-C}_5\text{H}_5$) is present; below this temperature the different types of proton environment in this group become observable. However a comparison with the published nmr spectra of known ($h^1\text{-C}_5\text{H}_5$) compounds⁴⁹⁻⁵⁵ indicated that this is not the case for $\text{C}_5\text{H}_5\text{TiCl}(\text{acac})_2$. The infrared spectrum of this compound also does not support this explanation. It showed, like all the other $\text{C}_5\text{H}_5\text{MCl}(\text{ke})_2$ ($\text{ke} = \beta$ -diketonate) compounds prepared in this work (but interestingly not the analogous 8-quinolinolate chelates¹), a sharp single band of medium intensity at *ca.* 3100 cm^{-1} (CH stretching) and another at *ca.* 1020 cm^{-1} (CH in-plane wagging) (neither of which are present^{24,25} in the spectrum of $\text{TiCl}_2(\text{acac})_2$), which are consistent only with a π -bonded C_5H_5 group, *i.e.*, a *pentahaptocyclopentadienyl* ($h^5\text{-C}_5\text{H}_5$) group.^{56,57}

(ii) The C_5H_5 group is π bonded (see material above for the infrared support of this), with the compound undergoing rapid cis-trans isomerism above $\sim -20^\circ$ as well as rapid exchange of ligand groups between the non-equivalent environments of the cis isomer. Below this temperature, the different C_5H_5 environments are observed. This would appear to be the more likely ex-

planation. Some support for this comes from a planimetric integration of the methyl proton signals in the spectrum obtained at -60° (see Figure 3). Although overlapping of the signals made a precise integration somewhat difficult to achieve, it was found that each of the two outer, weaker signals accounts for $\sim 17\text{--}20\%$ of the total area of this complex resonance. Assuming that they both are part of the spectrum of the cis isomer and correspond to three protons each, *i.e.*, to one particular methyl group environment each, then the other signals account for $\sim 60\text{--}66\%$ of the area or $\sim 9\text{--}12$ protons. Only six of these protons can be assigned to the cis isomer; the others, therefore, are likely to be due to the presence of the trans isomer at approximately one-fourth to one-half the concentration of the cis isomer. No unambiguous assignment of the inner methyl resonances to either isomer can be made, nor can this be done for the two γ -proton resonances observed although the broader, higher field resonance showed indications of splitting further at -60° and possibly consists of the signal from the trans isomer superimposed upon half of the cis doublet (see Figure 3). Planimetric integration of the γ -proton signals indicated a $\sim 2:3$ area ratio, which supports the above conclusion.

It has been suggested, from X-ray studies,^{20,23} that the stereochemistry of the compounds $\text{C}_5\text{H}_5\text{MCl}(\text{ke})_2$ may possibly be better described by a dodecahedron, rather than an octahedron. If this is so, then 12 isomers are possible for the acac compounds.²²

In support of this dodecahedral model, two cis isomers have been observed in solution for the related compound²¹ $\text{C}_5\text{H}_5\text{TiCl}(\text{hfac})_2$. Although no example of a nonfluorinated β -diketonate compound of this type exhibiting such behavior was known, this raised the possibility that the signal splitting observed in the spectrum of $\text{C}_5\text{H}_5\text{TiCl}(\text{acac})_2$ may be due to the presence of two or more interconverting "dodecahedral" isomers. However, the assignments made in the far-infrared spectrum of $\text{C}_5\text{H}_5\text{TiCl}(\text{acac})_2$ (*vide supra*) suggested that it may be possible to treat the overall geometry of this compound as "octahedral" and to interpret the results obtained from these physical measurements on this basis. In this case, an adequate description of the nmr spectral changes is that of an "octahedral" cis-trans isomerization. An alternative description could be isomerization between two "dodecahedral" isomers, possibly between one with Cl cis to C_5H_5 and the other with Cl and C_5H_5 trans, with the acac methyl groups in nearly equivalent environments,²⁷ or perhaps between two cis isomers.

Finally, it is of interest to note that these titanium compounds are less stereochemically rigid than their zirconium analogs, which is the reverse of that found^{35,36,58} in $\text{MX}_2(\text{acac})_2$ ($\text{M} = \text{Ti}, \text{Zr}$; $\text{X} = \text{F}, \text{Cl}, \text{Br}$). The coalescence temperatures for the titanium compounds are both $\sim +40^\circ$, while the signals from the zirconium complexes only coalesce at much higher temperatures.

Experimental Section

All manipulations were carried out in an anhydrous nitrogen atmosphere. $(\text{C}_5\text{H}_5)_2\text{MCl}_2$ ($\text{M} = \text{Ti}, \text{Zr}$) was obtained from Alfa Inorganics, Inc., and was sublimed *in vacuo* before use. Pentane-2,4-dione was Hopkin and Williams Ltd. GPR grade and was fractionally distilled before use; the fraction of bp $138\text{--}139^\circ$

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TABLE IV

M	$(C_5H_5)_2MCl_2$ soln		keH soln		Amt of $(C_5H_5)_3N$, g	Amt of CH_3CN , ml	Amt of products				Remarks
	Amt of solute, g	Amt of CH_3CN , ml	Type ^a	Amt, g			$(C_5H_5)_3NHC1$	$C_5H_5MCl(ke)_2$	g	mol	
Ti	4.34	350	acacH	3.50	1.76	50	2.00	0.84	3.90	65	a-c
Ti	5.10	300	bzacH	6.60	2.10	75	2.25	0.81	6.05	63	a, b, d
Zr	2.22	100	acacH	1.62	0.74	50	0.90	0.90	2.80	98	a, b
Zr	1.98	150	bzacH	2.21	0.68	70	0.90	0.96	3.40	97	a, b

^a Analytical results for $C_5H_5MCl(ke)_2$ are given in Table I. ^b $(C_5H_5)_3NHC1$ was confirmed by chlorine analysis and infrared spectrum. ^c In this reaction, a tarry product (1.3 g) was formed. ^d In this reaction, a tarry product (2.5 g) was formed. ^e acacH = pentane-2,4-dione; bzacH = 1-phenylbutane-1,3-dione.

was collected. 1-Phenylbutane-1,3-dione was Hopkin and Williams Ltd. Fine Chemicals grade and was used as received. 1,3-Diphenylpropane-1,3-dione was obtained from BDH Ltd. and dried at 120° (0.3 mm) before use. Tropolone was obtained from Aldrich Chemical Co., Inc., and sublimed at 40° (0.3 mm) before use. Triethylamine was stored over barium oxide and fractionally distilled before use; the fraction of bp 89–90° was collected. All solvents were dried by conventional techniques before use.

1. Reactions with β -Diketones. (a) $(C_5H_5)_2TiCl_2$ (1 mol) with acacH (2 mol).—A solution of pentane-2,4-dione (2.84 ml, 2.76 g, 2 mol) in acetonitrile (50 ml) was added dropwise with stirring to a solution of dichlorobis(cyclopentadienyl)titanium(IV) (3.43 g, 1 mol) in acetonitrile (350 ml). The mixture was stirred for 7 days and then concentrated to 50 ml, when red crystals of dichlorobis(cyclopentadienyl)titanium(IV) separated (confirmed by ir spectrum) (2.75 g, 80% recovery). *Anal.* Calcd for $C_{10}H_{10}Cl_2Ti$: Cl, 28.5. Found: Cl, 28.4. Diethyl ether (300 ml) was added to the filtrate to give more dichlorobis(cyclopentadienyl)titanium(IV) (0.4 g, 12% recovery; identified by infrared spectrum).

(b) Chlorocyclopentadienylbis(β -diketonato)metal(IV) $(C_5H_5MCl(ke)_2)$; M = Ti, Zr; ke = acac, bzac.—The general procedure used was to add a solution of the β -diketone (keH, pentane-2,4-dione (acacH), or 1-phenylbutane-1,3-dione (bzacH)) (2 mol) and triethylamine (1 mol) in acetonitrile (ca. 50 ml) to a solution of dichlorobis(cyclopentadienyl)metal(IV) $([C_5H_5]_2MCl_2)$; M = Ti, Zr (1 mol) also in acetonitrile (ca. 250 ml). The mixture was stirred at ambient temperature for several hours; the solvent was then removed and the resultant solid dried under reduced pressure. Benzene (ca. 250 ml) was added and the mixture was stirred and filtered. The residue of triethylammonium chloride was washed with benzene and dried at reduced pressure. The yield was recorded and a sample was analyzed. The filtrate was reduced to ca. 30 ml and the *product* precipitated with petroleum ether (bp 100–120°). After recrystallization from benzene–petroleum ether, the yield of the product was recorded and a sample was analyzed. For the reactions involving $(C_5H_5)_2TiCl_2$, a dark tarlike product was initially precipitated with petroleum ether. This was removed by decantation and the desired product was obtained by addition of more petroleum ether. Experimental details are given in Table IV, and analytical data, in Table I.

(c) Chlorocyclopentadienylbis(1,3-diphenylpropane-1,3-dionato)zirconium(IV).—On mixing acetonitrile solutions of 1,3-diphenylpropane-1,3-dione (3.18 g, 2 mol), triethylamine (0.71 ml, 0.98 g, 1 mol), and dichlorobis(cyclopentadienyl)zirconium-

(IV) (2.07 g, 1 mol), a yellow precipitate of the *product* (71%) was obtained, which was washed with acetonitrile (two 30-ml portions) and dried under reduced pressure (see Table I for analysis). The filtrate was evaporated to dryness and then extracted with benzene (75 ml) to leave a colorless residue of triethylammonium chloride (0.90 g, 0.92 mol; confirmed by infrared spectrum). *Anal.* Calcd for $C_8H_{16}ClN$: Cl, 25.8. Found: Cl, 25.8. The benzene filtrate was then evaporated to dryness to give more *product* (24%).

2. Reaction with Tropolone. Cyclopentadienyltris(tropolonato)zirconium(IV).—(a) On mixing acetonitrile solutions of tropolone (1.72 g, 2 mol), triethylamine (0.97 ml, 0.71 g, 1 mol), and dichlorobis(cyclopentadienyl)zirconium(IV) (2.04 g, 1 mol) in the manner described above, much fuming occurred, and the pale yellow *product* (76%) which precipitated was washed and dried (see Table I for analysis). The filtrate was evaporated to dryness and the resultant solid was extracted with benzene (25 ml). After removal of the solvent from this extract and on subsequent heating to 280° (0.05 mm) a colorless sublimate of dichlorobis(cyclopentadienyl)zirconium(IV) (0.6 g, 30% recovery; identified by infrared spectrum) was obtained. The residue remaining after the initial benzene extraction was further extracted with benzene (five 100-ml portions) and from this extract more *product* (13%) was obtained. The remaining solid residue was then heated at 200° (0.2 mm) to give a colorless sublimate of triethylammonium chloride (1.0 g, 1 mol; confirmed by infrared spectrum). *Anal.* Calcd for $C_8H_{16}ClN$: Cl, 25.8. Found: Cl, 25.7.

(b) A similar reaction was then carried out with tropolone (3 mol), triethylamine (2 mol), and dichlorobis(cyclopentadienyl)zirconium(IV) (1 mol) when the same *product* (84%) precipitated. The filtrate was evaporated to dryness and the resultant solid was heated at 140° (0.1 mm) to give a colorless sublimate of triethylammonium chloride (1.91 mol).

Infrared Spectroscopy.—Spectra from 4000 to 400 cm^{-1} were obtained as Nujol and hexachlorobutadiene mulls on Perkin-Elmer 237 and 137 spectrophotometers and from 450 to 80 cm^{-1} as pressed polyethylene disks on an RIIC FS-520 Michaelson Interferometer with computations made on an NCR Elliot 4100 computer.

Nmr Spectroscopy.—Spectra were obtained on a Perkin-Elmer R10 instrument operating at 60 MHz, using ~15% solutions in deuteriochloroform with TMS as an internal standard, at temperatures from +55 to –60°.

Mass Spectroscopy.—An AEI MS9 spectrometer was used. Samples were introduced with a direct-insertion probe and an excitation potential of 70 eV was used.