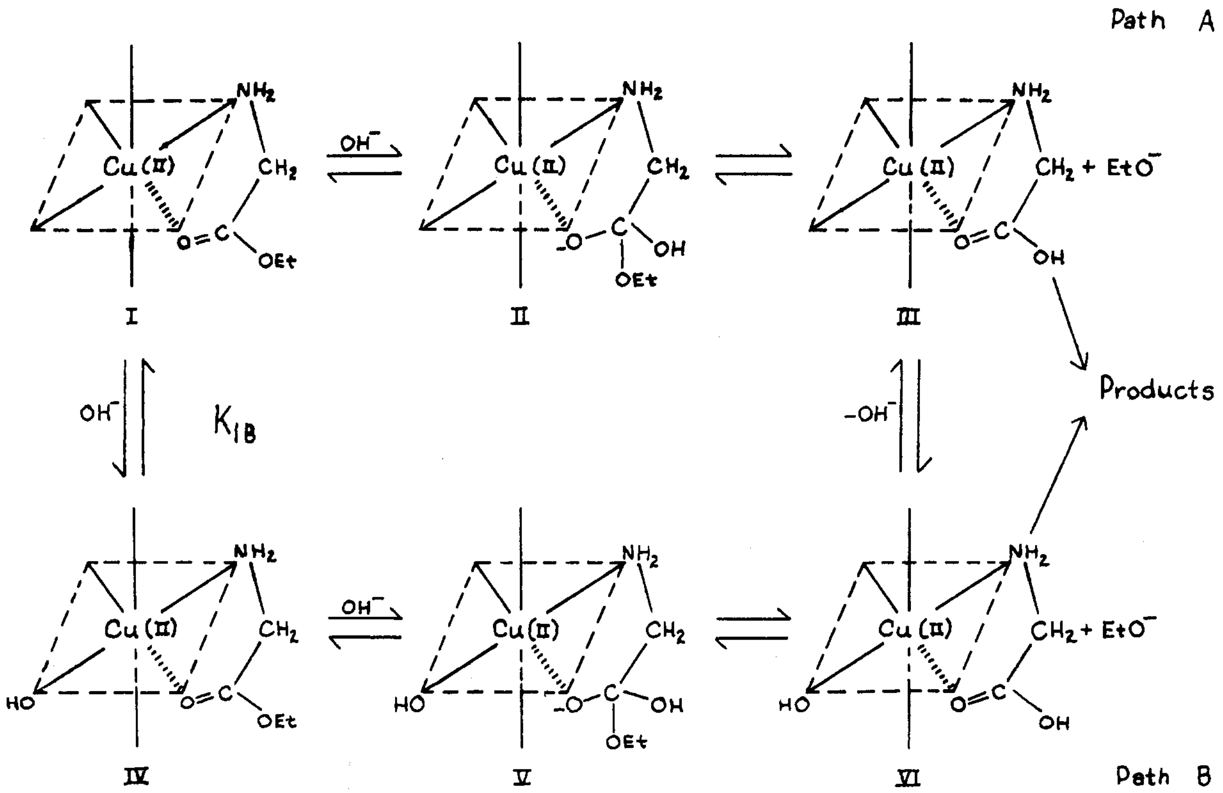

Figure 1.—Mechanism proposed for the copper(II)-catalyzed hydrolysis of ethyl glycinate near pH 5.

of Bender and Turnquest,[5] but involve hydroxide ion as the principal attacking species rather than water. Path A of Figure 1 represents the extremely unimportant portion of the hydrolysis of ethyl glycinate which exhibits a first-order dependence on hydroxide ion concentration.

The preponderance of path B over path A in the hydrolysis may reflect the relative ease of departure of the leaving group, ethoxide ion, from the intermediate structures II and V. Loss of ethoxide ion from II should be much less facile than from V. In II, the complex copper has an effective positive charge of two, whereas in V the charge has been reduced to one by the hydroxide ion ligand. This rationale suggests, but does not demand, that loss of ethoxide ion is the rate-determining step in both paths of hydrolysis.

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Nuclear Magnetic Resonance Spectra of Titanocene Sandwich Compounds[1a]

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Proton chemical shifts of cyclopentadienyl ring protons in a series of substituted bis(cyclopentadienyl)titanium compounds have been correlated with electronegativities of the ligands on titanium. A similar correlation of ring proton shifts with ligand electronegativities was found for a series of methyl-substituted titanocene halides and titanocene dihalides, and a reverse trend was noted when the chemical shift of the methyl protons was considered in the methyl-substituted series. In a series of substituted diaryltitanocenes the average chemical shift of *ortho* and *meta* protons relative to the chemical shift of a reference (bis(cyclopentadienyl)diphenyltitanium) as well as the chemical shifts of the cyclopentadienyl ring protons give a linear correlation with Taft's inductive and resonance parameters and a satisfactory Hammett line.

Introduction

Nuclear magnetic resonance data are of much value in studies of structure elucidation and molecular electronic configurations of metallocene compounds as in many other chemical systems. Since very little n.m.r. data has been published on cyclopentadienyl compounds of titanium, and no references were found concerning the n.m.r. spectra of diaryltitanocene derivatives, n.m.r.

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(1) (a) Supported by a grant from The National Lead Company; (b) taken from the Ph.D. Thesis of S.A.B., June 1965.

studies seemed appropriate at this time. Further, since the metallocene spectral lines are well-resolved and well-separated, the compounds appear to be useful for studies of substituent effects on the ring protons. The relatively simple spectra allow unambiguous assignments of the peaks, whereas in the benzenoid system assignments are more difficult due to the multiplicity of lines resulting from long-range interactions.

The Hammett equation[2]

$$\log k = \rho\sigma + \text{constant}$$

expresses the effect of structure on reactivity in related series of benzene derivatives. The σ factor provides an over-all measure of the polar electronic effect of a *meta* or *para* substituent on the ring relative to the unsubstituted compound and may be regarded as a measure of the alteration of charge density on the ring protons, due to the substituent. The constant ρ for a particular reaction is a measure of the sensitivity of that reaction for the alteration in charge density.

There have been a few attempts to correlate n.m.r. shielding values or chemical shifts (δ) with Hammett σ constants, with varying degrees of success.[3] A modified interpretation of the relationship between δ values and σ constants has been proposed by Taft[3d,4] which is based on inductive and resonance contributions to Hammett's σ values and leads to a closer correlation of the two parameters than that obtained by the previous workers (ref. 3). Taft assumes that reactivities of *meta*- and *para*-substituted benzene derivatives can be treated as a combination of inductive and resonance effects, thus quantitatively separating the Hammett σ values into two independent contributions

$$\sigma = \sigma_I + \sigma_R$$

The inductive contribution, σ_I, is regarded as an electronic perturbation by the substituent occurring across space or through the σ bonds of the benzene ring. The resonance contribution, σ_R, results from the ability of the substituent to repel or attract electrons through resonance interaction with the benzene π orbitals. The σ_I values have been obtained from aliphatic series reactivities in which resonance contributions are insignificant, while σ_R values are the difference between Hammett σ_p and σ_I. The correlation of nuclear magnetic shielding parameters thus follows an equation of the general form

$$\delta = \alpha\sigma_I + \beta\sigma_R + \gamma$$

and the empirical constants α and β are regarded as the susceptibilities of the nuclear magnetic shielding to the inductive and resonance contributions of the substituent.

Experimental

All reactions were run in glassware that had been baked at 120° and were blanketed with dry nitrogen. Yields of the Grignard or lithium reagent were determined by a simple acid titration with 0.100 *N* HCl of a 0.5–1.0-ml. aliquot removed from the reaction mixture and hydrolyzed. The progress of the reaction of organolithium reagents with bis(cyclopentadienyl)-titanium dichloride was determined and followed by Gilman's Color Test 1.[5]

For the series of disubstituted phenyltitanocene compounds the aryllithium reagent must be used since the aryl Grignard results in a monosubstituted product with only minor amounts of the disubstituted compound.

A small amount of impurity was found in most of these reactions. Isolation of a small quantity of this material revealed a melting point (with decomposition) of *ca.* 230° and an infrared spectrum identical with that of a compound identified as 1,1,3,3-tetrakis(cyclopentadienyl)-1,3-dichlorodititoxane, $(Cp_2TiCl)_2O$.[6]

Most of the organotitanium compounds appeared to be unaffected by exposure to air or moisture but were thermally and photosensitive; therefore precautions were taken to avoid strong light and the compounds were stored in a cold chest.

Bis(cyclopentadienyl)titanium Dichloride was obtained from Arapahoe Chemicals, Inc., and recrystallized from toluene, m.p. *ca.* 275° dec.

Anal. Calcd. for $C_{10}H_{10}TiCl_2$: C, 48.23; H, 4.04; Ti, 19.2; Cl, 28.5. Found: C, 48.18; H, 4.09; Ti, 19.1; Cl, 28.4.

Bis(cyclopentadienyl)dimethyltitanium was prepared by the method of Piper and Wilkinson,[7] m.p. *ca.* 97° dec.

Bis(cyclopentadienyl)methyltitanium chloride was prepared by a modification of Long's method.[8] A solution of 60 mmoles of methyl Grignard prepared from excess methyl chloride and 1.36 g. (0.056 g.-atoms) of magnesium in 45 ml. of ethyl ether was added to 14.93 g. (0.060 mole) of Cp_2TiCl_2 in 100 ml. of methylene chloride. After 3 hr. of stirring the solvents were evaporated and the solids extracted into carbon tetrachloride. Recrystallization from methylene chloride–petroleum ether afforded orange crystals in 51% yield, m.p. 169–172° dec. (lit. 168–170°).

Anal. Calcd. for $C_{10}H_{13}TiCl$: Ti, 20.9; Cl, 15.5. Found: Ti, 20.6; Cl, 15.2.

Bis(cyclopentadienyl)titanium bis(trifluoroacetate) was prepared by the method of Drozdov from silver trifluoroacetate and Cp_2TiCl_2.[9] The orange product (96% yield) was recrystallized from toluene, m.p. 178–180° (lit. 177–178.5°).

Anal. Calcd. for $C_{14}H_{10}O_4TiF_6$: C, 41.61; H, 2.49. Found: C, 41.95; H, 2.61.

Bis(cyclopentadienyl)diphenyltitanium.—This compound and the *p*-dimethylamino-, *p*-tolyl-, and *m*-tolyl- derivatives were prepared according to procedures described by Summers, *et al.*[10] *para*-Substituted bromobenzenes reacted with finely cut lithium metal in ether and the resulting lithium reagents were slowly added to a slurry of Cp_2TiCl_2 in ether. Crude products were recrystallized from methylene chloride–petroleum ether solution.

Anal. Calcd. for $C_{22}H_{20}Ti$: C, 79.53; H, 6.03; Ti, 14.5. Found: C, 76.86; H, 6.13; Ti, 14.6; m.p. 146–148° (lit. 146–148°).

Anal. Calcd. for bis(cyclopentadienyl)bis(*p*-dimethylaminophenyl)titanium ($C_{26}H_{30}TiN_2$): Ti, 11.5. Found: Ti, 11.3; m.p. 137–139° dec. (no literature value).

Anal. Calcd. for bis(cyclopentadienyl)bis(*p*-tolyl)titanium ($C_{24}H_{24}Ti$): C, 79.99; H, 6.71; Ti, 13.3. Found: C, 79.12; H, 6.88; Ti, 13.1; m.p. 133–134° dec. (no literature value).

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(3) (a) H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952); (b) P. L. Corio and B. P. Dailey, *ibid.*, **78**, 3043 (1956); (c) A. A. Bothner-By and R. E. Glick, *ibid.*, **78**, 1071 (1956); (d) R. W. Taft, *ibid.*, **79**, 1045 (1957); (e) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); (f) H. C. Beachell and D. W. Beistel, *Inorg. Chem.*, **3**, 1028 (1964).

(4) (a) R. W. Taft, *J. Am. Chem. Soc.*, **80**, 2436 (1958); (b) R. W. Taft in M. S. Newman, Ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13; (c) R. R. Frazer, *Can. J. Chem.*, **38**, 2226 (1960).

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(6) J. S. Skelcy, Ph.D. Thesis, Michigan State University, 1961.

(7) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(8) W. P. Long, *J. Am. Chem. Soc.*, **81**, 5312 (1959).

(9) G. V. Drozdov, *Zh. Obsch. Khim.*, **32**, 2390 (1962).

(10) L. Summers, R. H. Uloth, and A. Holmes, *J. Am. Chem. Soc.*, **77**, 3604 (1955).

Anal. Calcd. for bis(cyclopentadienyl)bis(*m*-tolyl)titanium ($C_{24}H_{24}Ti$): Ti, 13.3. Found: Ti, 13.1; m.p. 137–139° dec. (lit. *ca.* 135 or 140°).

All other *para* or *meta*-substituted phenyltitanocene derivatives were synthesized *via* the organolithium reagent derived from butyllithium and the corresponding *para*- or *meta*-substituted bromobenzene. A typical synthesis follows.

Bis(cyclopentadienyl)bis(*p*-trifluoromethylphenyl)titanium.—*p*-Bromobenzotrifluoride (6.94 g., 0.031 mole) was slowly added to an equivalent amount of butyllithium solution in 17 ml. of pentane and 40 ml. of ethyl ether at 0°. After stirring 2 hr. the clear organolithium solution was added to a slurry of 3.46 g. (0.014 mole) of Cp_2TiCl_2 in 40 ml. of ether. After an additional 0.5 hr. at room temperature, the mixture was filtered and the solids washed with ether. The filtrate and washings were poured into an equal volume of ice–water and the layers separated. The water layer was extracted with ether and the total ether extract dried over sodium sulfate. Evaporation of the solvent left an oily product which was washed with petroleum ether until a light, fluffy solid remained. Recrystallization from petroleum ether gave orange crystals, m.p. 142–143° dec.

Anal. Calcd. for $C_{24}H_{18}TiF_6$: Ti, 11.7. Found: Ti, 11.7.

Bis(cyclopentadienyl)bis(*m*-trifluoromethylphenyl)titanium.—Recrystallization from petroleum ether gave orange-yellow crystals, m.p. 145–146° dec.

Anal. Calcd. for $C_{24}H_{18}TiF_6$: Ti, 11.7. Found: Ti, 11.8.

The orange *p*-fluorophenyltitanocene crystals melted with decomposition at *ca.* 120° while the orange *p*-chloro- and *p*-bromophenyltitanocenes decomposed at *ca.* 130°.

Anal. Calcd. for $C_{22}H_{18}TiCl_2$: Ti, 11.9. Found: Ti, 11.8.

Nuclear Magnetic Resonance Measurements.—N.m.r. spectra were determined on a Varian Model A-60 spectrometer on approximately 8% solutions in carbon tetrachloride. No dilution effects were found in sample concentrations between 5 and 10%. Tetramethylsilane was used as an internal standard. The n.m.r. spectra of the titanocene compounds are summarized in Tables I and II.

TABLE I

H^1 N.M.R. CHEMICAL SHIFTS OF TITANOCENE COMPOUNDS (P.P.M.)

Titanocene	C_5H_5 ring protons	Other protons
Cp_2TlCl_2	−6.60	
Cp_2TiBr_2	−6.67	
Cp_2TiI_2	−6.76	
$Cp_2Ti(OOCCF_3)_2$	−6.80	
$Cp_2Ti(CH_3)_2$	−5.90	−0.06 methyl
$CpTiCl_3$	−7.00[a]	
C_5H_6 (cyclopentadiene)	−6.34	−2.85 methylene
$Cp_2Ti(CH_3)Cl$	−6.19	−0.68 methyl
$Cp_2Ti(CH_3)Br$	−6.28	−0.41 methyl
$Cp_2Ti(CH_3)I$	−6.36	+0.20 methyl
$Cp_2Ti(C_6H_4R)_2$[b]		
R = *p*-$(CH_3)_2N$	−6.08	−2.81 methyl
p-CH_3O	−6.07	−3.65 methoxy
p-CH_3	−6.09	−2.18 methyl
m-CH_3	−6.10	−2.16 methyl
H	−6.11	−6.79 phenyl
p-F	−6.12	
p-Cl	−6.13	
p-Br	−6.16	
p-CF_3	−6.19	
m-CF_3	−6.18	

[a] From C. A. Sloan and W. A. Barber, *J. Am. Chem. Soc.*, **81**, 1364 (1959). [b] Table II lists phenyl proton shifts for this series.

TABLE II

H^1 CHEMICAL SHIFTS FOR $Cp_2Ti(C_6H_4R)_2$ SERIES[a]

R	$\delta_{C_5H_5}$, c.p.s.	$\delta_{C_5H_5}$ rel., p.p.m.	$\delta_{C_6H_4}$, c.p.s.	$\delta_{C_6H_4}$ rel., p.p.m.	J_{AB}, c.p.s.
p-$(CH_3)_2N$	−363.9	+0.032	−384.6	+0.378	8.7
p-CH_3O	−363.8	+0.033	−391.7	+0.259	8.4
p-CH_3	−364.3	+0.025	−398.6	+0.144	. . .
m-CH_3	−365.5	+0.005	. . .	. . .	. . .
H	−365.8	0.000	−407.2	0.000	. . .
p-F	−367.0	−0.020	−397.1	+0.169	. . .
p-Cl	−367.3	−0.025	−409.7	−0.042	8.5
p-Br	−368.8	−0.050	−408.8	−0.027	8.4
m-CF_3	−369.3	−0.075	−419.5	−0.206	. . .
p-CF_3	−370.9	−0.085	−420.9	−0.229	8.2

[a] See discussion below for explanation of symbols.

In Table II cyclopentadienyl (C_5H_5) ring proton shifts are given in c.p.s. from tetramethylsilane and in p.p.m. relative to the chemical shift of the cyclopentadienyl ring protons of bis(cyclopentadienyl)diphenyltitanium (BDT) which occurs as a single sharp line. Also tabulated are phenyl (C_6H_4) ring proton shifts (average shift of *ortho* and *meta* protons) in c.p.s. from the center of the symmetrical A_2B_2 band system and in p.p.m. relative to the single-line phenyl proton resonance of bis(cyclopentadienyl)diphenyltitanium. The latter compound was chosen as primary reference in the Hammett-type correlations, thereby correcting for the effect of $(C_5H_5)_2Ti$ as a group, eliminating the need to correct for diamagnetic susceptibilities, and adjusting the magnitude of all chemical shifts relative to the *para* hydrogen substituent which is assigned a zero chemical shift, *i.e.*

$$\delta_{\text{rel}} = \delta - \delta_{\text{BDT}}$$

The phenyl ring–proton resonance spectra of all *para*-substituted phenyltitanocene compounds were essentially the characteristic symmetrical four-line spectrum containing two doublets, an inner strong pair and a weaker outer pair, except for the *p*-methyl compound where the aryl protons consisted of a single line as in the case of the unsubstituted diphenyl compound. The aryl proton signal of the *m*-methyl compound was poorly resolved and no attempt was made to define a chemical shift, whereas the *m*-trifluoromethyl derivative protons appeared as a single peak somewhat broadened with very weak fine structure on either side of the main line, the center of which was defined as the shift for the aryl protons. The spectrum of the *p*-fluorophenyl compound was somewhat complicated due to coupling of fluorine with the phenyl ring hydrogens, and the splitting pattern was altered from two doublets into a pattern approximating two triplets. The centers of the multiplets were used as before for the average *ortho* and *meta* proton phenyl shift.

A positive sign preceding the chemical shift indicates resonance at higher field strength (increased shielding) compared to the reference (BDT), while a negative shift represents resonance downfield from the reference (deshielding).

Results and Discussion

All ten protons of the two C_5H_5 rings of the titanocene compounds studied are chemically equivalent, the signal consisting of one sharp peak with a relative area of ten units. When the substituents on titanium furnish electrons compared to the reference and the effect is transmitted to the C_5H_5 rings, the ring protons are more shielded, resulting in a positive chemical shift. Conversely, when the substituents withdraw electron density, the deshielded ring protons show a negative chemical shift as resonance is found on the low-field side of the reference. Figure 1 graphically depicts these facts. Ring proton shifts are plotted as a function of the electronegativity of the first atom of the group attached to titanium; only the first atom is considered to give a simply qualitative picture. The ring proton shift is seen to be related to this electronega-

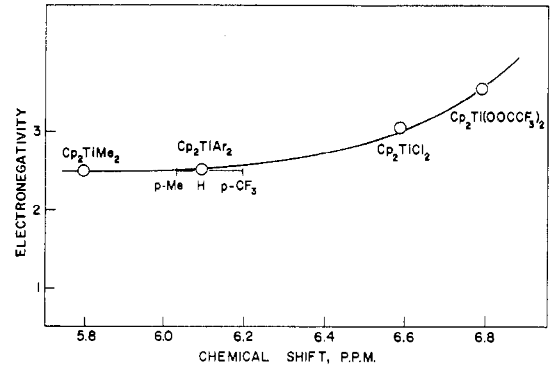

Figure 1.—The variation of the ring proton chemical shifts with the electronegativity of the first atom in titanocene compounds.

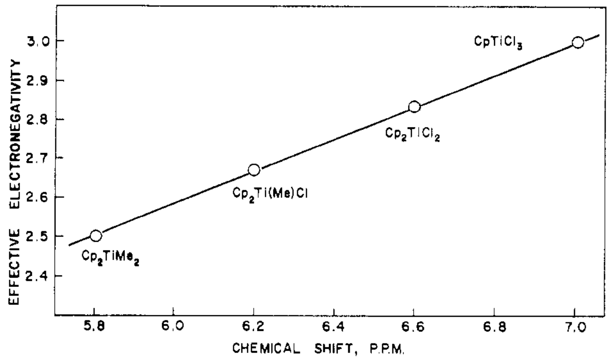

Figure 2.—The variation of the ring proton chemical shift with the effective electronegativity (X_e) of the first atoms of the other ligands attached to titanium.

tivity as shown by the smooth curve. The area within the brackets (between 6.0 and 6.2 p.p.m.) was chosen for a more quantitative study of the transmission of substituent effects through the titanocene bonding system. This region represents the ring proton shifts of a series of ten substituted phenyltitanocene derivatives, and the shifts will be correlated with a more quantitative value representing the polar effect of the substituent, the Hammett σ constant.

Methyltitanocene Halides.—Figure 2 correlates ring proton chemical shifts with the composite electronegativity (of the first atoms) of the other ligands attached to titanium. These compounds are of the general class $(C_5H_5)TiC_nCl_{3-n}$, where C_n is the number of organic ligands attached to titanium *via* a carbon atom. The electronegativity of a methyl or cyclopentadienyl group is assumed to be that of carbon, 2.5, while that of chlorine is 3.0. The four points represent the following titanocene compounds

	n	$3-n$
$(C_5H_5)_2Ti(CH_3)_2$	3	0
$(C_5H_5)_2Ti(CH_3)Cl$	2	1
$(C_5H_5)_2TiCl_2$	1	2
$(C_5H_5)TiCl_3$	0	3

The effective electronegativity, X_e, is derived from

$$X_e = {}^1/_3[2.5n + 3.0(3 - n)]$$

and correlates linearly with the ring proton shift.

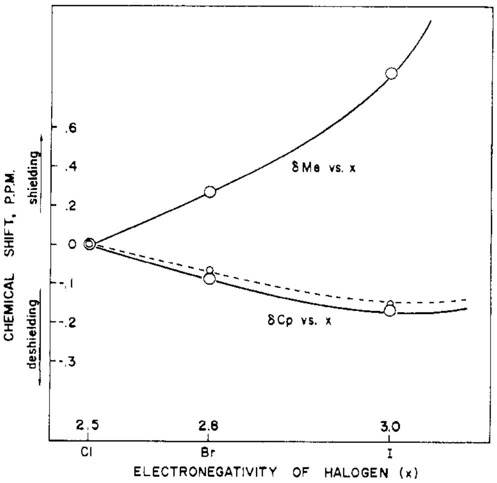

Figure 3.—The variation of the ring and methyl proton chemical shift with the electronegativity of halogen for methyl-substituted titanocene halides: solid line, monohalides; dotted line, dihalides.

This relationship implies that a methyl, cyclopentadienyl, or chlorine ligand contributes an equal electronic effect (relative to the electronegativity of a carbon or chlorine atom as a first approximation), and this effect is reflected in the chemical shift of the remaining cyclopentadienyl ring.

The diverging curves in Figure 3 correlate the electronegativity of the halogen atom with the proton chemical shift of both the cyclopentadienyl ring protons and the methyl protons in a series of methyl-substituted titanocene halides of the type $(C_5H_5)_2Ti(CH_3)X$, where X is the halogen atom.[11] The smooth curve of δ_{CH_3} *vs.* X indicates that increasing the electronegativity of the halogen in the order I, Br, Cl results in a deshielding of the methyl protons. The reverse trend is noted in the curve of δ_{Cp} *vs.* X where the ring proton shift is plotted against the electronegativity of the halogen. The "apparent electron-withdrawing power" is in the order I > Br > Cl as the effect of halogen–titanium double bonding or the resonance effect comes into play and the chloro compound ring protons are most shielded while the ring protons in the iodo compound are now least shielded. This same trend is also noted in the series of titanocene dihalides, Cp_2TiX_2, shown also in Figure 3 by the dotted line. A somewhat related reverse trend (opposite to that expected from a consideration of only electronegativity) in δ values was noted by Dailey and Shoolery[12] and Bothner-By and Naar-Colin[13] for the methyl protons in compounds of the ethyl

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(11) It was observed in the preparation of $Cp_2Ti(CH_3)Cl$ that an exchange of halogens occurred between the Grignard halogen and the chlorine on Cp_2TiCl_2. When the Grignard is formed from methyl bromide a mixture of products results

$$Cp_2TiCl_2 + CH_3MgBr \rightarrow Cp_2Ti(CH_3)Br + Cp_2Ti(CH_3)Cl$$

Similarly, the methyl iodide Grignard results in some $Cp_2Ti(CH_3)I$ together with the chloride compound. To prepare pure bis(cyclopentadienyl)-methyltitanium iodide or bis(cyclopentadienyl)methyltitanium bromide the corresponding titanocene diiodide or titanocene dibromide should be treated with the appropriate Grignard, methylmagnesium iodide or methylmagnesium bromide, respectively.

(12) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

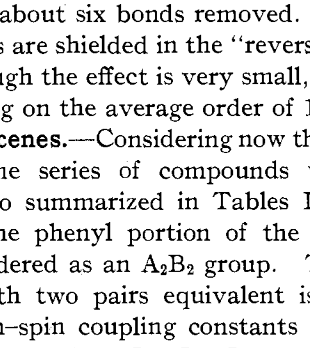
(13) A. A. Bothner-By and C. Naar-Colin, *ibid.*, **80**, 1728 (1958).

halide series. The CH_2 proton shifts were deshielded with increasing electronegativity as expected, indicating that an inductive electron-withdrawal mechanism is operative. This is the situation found for the methyl group in the methyl-substituted titanocene halides. However, the CH_3 shifts in the ethyl compounds were shifted to more shielded positions with increasing halogen electronegativity. This reversal in trend for ethyl CH_3 protons has been explained by Bothner-By and Naar-Colin on the basis of certain contributing resonance structures.[13]

A possible explanation of the trend reversal for C_5H_5 *vs.* CH_3 protons in the methyltitanocene halides follows a different line of reasoning. It must first be assumed that some degree of double-bond character exists in the halogen–titanium bond due to electron-release resonance of the halide increasing in the order I, Br, Cl. It is emphasized that whereas the CH_3 group is bonded to titanium *via* a σ bond through which the resonance effect is unlikely to be transmitted, the C_5H_5 ligands have a much greater degree of π bonding to titanium. The resonant effect of the halogen on titanium is transmitted onto the C_5H_5 protons, resulting in an increased shielding in the order Cl > Br > I, whereas the σ-bonded CH_3 protons only experience the inductive electronegative effect which decreases in the order Cl, Br, I.

It will be seen in a later section that the order of phenyl proton shifts in halogen-substituted phenyltitanocenes is also opposite to the predicted order based on inductive electronegative effects. Since the aromatic phenyl ring can accept resonance electron release from the halogen increasing in the order I, Br, Cl, this effect may be expected to dominate the phenyl ring chemical shift values. Since the phenyl ring has a greater degree of π bonding to titanium than the methyl group, the resonance effect of the *para* halogen is transmitted through titanium to the cyclopentadienyl protons about six bonds removed. In this case also the protons are shielded in the "reverse" order F > Cl > Br, although the effect is very small, the shielding differences being on the average order of 1 c.p.s.

Phenyltitanocenes.—Considering now the substituted phenyltitanocene series of compounds whose n.m.r. spectra are also summarized in Tables I and II, the lines due to the phenyl portion of the molecule are generally considered as an A_2B_2 group. The four-proton system with two pairs equivalent is represented below, the spin–spin coupling constants between protons being designated as J_A, J_B, J_{AB}, and J'_{AB}.



The complete matrix for this system has been evaluated and the analysis of A_2B_2 proton spectra has appeared in the literature.[14,15] Coupling across the phenyl ring is very small in the phenyltitanocenes and $J'_{AB} \approx 0$ c.p.s. Further, $J_A = J_B \approx 1$ c.p.s. The coupling constant between protons in adjacent positions of the phenyl ring, J_{AB}, is tabulated in Table II and appears very little affected by the nature of the substituents on the phenyl ring. The mean value of J_{AB} is 8.4 c.p.s. and agrees with other values previously recorded.[15–17]

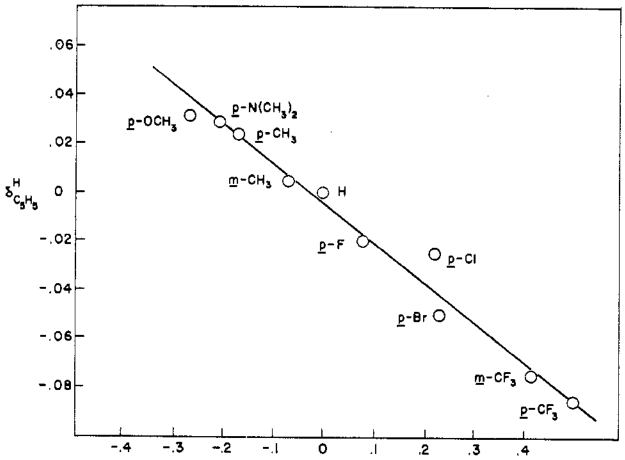


Figure 4.—The correlation of the relative cyclopentadienyl (C_5H_5) proton chemical shifts with the Hammett σ constant.

Chemical Shift and σ-Correlations.—To determine the effect of varying the *para* and *meta* substituents of phenyl-substituted titanocenes on the shielding of the ring protons, the relative chemical shifts were analyzed as a function of the Hammett σ values of the substituents. These values together with Taft's inductive and resonance parameters are given in Table III.

TABLE III

HAMMETT AND TAFT σ VALUES

Substituent	σ^a	$\sigma_I{}^b$	$\sigma_R{}^b$
p-$(CH_3)_2N$	−0.205	+0.10	−0.54
p-OCH_3	−0.268	+0.23	−0.50
p-CH_3	−0.170	−0.05	−0.13
m-CH_3	−0.069	−0.05	−0.02
H	0.000	0.00	0.00
p-F	+0.080	+0.50	−0.44
p-Cl	+0.227	+0.47	−0.24
p-Br	+0.232	+0.45	−0.22
m-CF_3	+0.420	+0.41	+0.00
p-CF_3	+0.500	+0.41	+0.14

[a] From D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958), and R. W. Taft, Jr., *Ann. Rev. Phys. Chem.*, **9**, 287 (1958). [b] From R. W. Taft, Jr., *J. Am. Chem. Soc.*, **81**, 5356 (1959).

Figure 4 shows the linear dependence of chemical shifts on Hammett σ constants. A linear regression analysis[18] of these data (Tables II and III) results in the equation

$$\delta^{H}_{C_5H_5} = -0.004 - 0.160\sigma \qquad (1)$$

with a linear correlation coefficient, r, of 0.988. Replacing Hammett's σ values by Taft's separate induc-

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(14) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *Can. J. Chem.*, **35**, 1060 (1957).

(15) J. Martin and B. P. Dailey, *J. Chem. Phys.*, **37**, 2594 (1962).

(16) R. E. Richards and T. P. Schaeffer, *Trans. Faraday Soc.*, **54**, 1280 (1958).

(17) H. S. Gutowsky, *et al.*, *J. Am. Chem. Soc.*, **79**, 4596 (1957).

(18) M. Ezekiel and K. A. Fox, "Methods of Correlation and Regression Analysis," John Wiley and Sons, New York, N. Y., 1959.

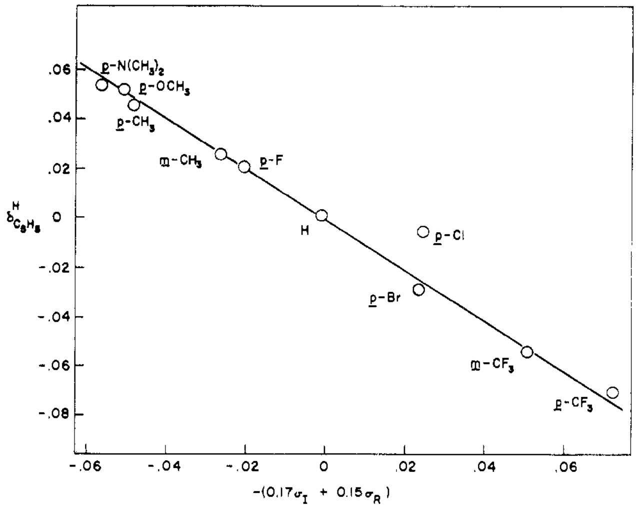

Figure 5.—The correlation of the relative cyclopentadienyl (C_5H_5) proton chemical shifts with Taft's inductive (σ_I) and resonance (σ_R) parameters.

tive and resonance constants, σ_I and σ_R, analysis of the data by a multiple regression analysis[16] of $\delta^{H}{}_{C_5H_5}$ on σ_I and σ_R gives the closer relationship

$$\delta^{H}{}_{C_5H_5} = -0.001 - 0.17\sigma_I - 0.15\sigma_R \qquad (2)$$

and a multiple correlation coefficient, R, equal to 0.998. Figure 5 is a plot of this excellent linear correlation. Equation 2 is of the form

$$\delta = \alpha\sigma_I + \beta\sigma_R + \gamma \qquad (3)$$

and the empirically-determined constants, α and β, are regarded as the susceptibilities of the nuclear magnetic shielding to the inductive and resonance contributions of the substituent. In eq. 2 the different α and β values account for the scatter of points about the least-squares line in the Hammett σ *vs.* ring proton shift correlation. Since by definition

$$\sigma_p = 1.00\sigma_I + 1.00\sigma_R \qquad (4)$$

the chemical shift *vs.* σ correlation expressed by eq. 2 implies that ring proton shifts are 1.13 times more susceptible to the inductive effect than to the resonance effect, or the influence of the resonance contribution is only 0.88 times that of the inductive contribution.

Since a definite linear dependence was observed in correlating σ values with proton shifts many bonds removed from the substituent, the effect of these substituents on the phenyl ring proton shifts was examined. From Table II it is seen that as the *para* substituent of the phenyl becomes more electron-releasing, the centers of the A_2B_2 multiplet system are shifted to more shielded positions.

Richards and Schaeffer in examining n.m.r. spectra of *para*-substituted benzenes noted a qualitative correlation between the chemical shifts of the A_2B_2 band system and the inductive power of the *para* substituents.[16] Beachell and Beistel noted that the attempt in this type of study to assign the chemical shift of the multiplet center from a standard reference such as benzene neglected the effect of the second substituent.[3f] A quantitative correlation could be made in comparing relative proton shifts with σ constants when the same reference substituent was present in each member of the series. A quantitative study of proton chemical shifts in monosubstituted benzenes was made by Spiesecke and Schneider, who tabulated shifts of *ortho*, *meta*, and *para* protons relative to benzene.[3e] Whereas earlier workers (*e.g.*, Corio and Dailey[3b]) made assignments to benzene protons, resolution was not high and the assignments were not unambiguous. Spiesecke and Schneider made assignments by comparison with the spectra of appropriately deuterated species. A plot of the *para* proton chemical shift *vs.* Hammett σ_p value for the substituent gave a fairly good linear correlation, but no correlation existed for the *meta* proton shifts with either Hammett's σ_m or Taft's σ_I parameter.

An inspection of the latter author's data showed that a fair correlation existed between the average shift of the *ortho* and *meta* protons[19] and the Hammett σ_p constant for the substituent, although no relationship was found for the average shift of the *meta* and *para* protons. The slope of the line formed in the plot of the average *ortho* and *meta* proton shift *vs.* σ_p was noted to be approximately -0.77. This type of correlation was also noted in an examination of the data of Martin and Dailey and Schaefer and Schneider which listed proton shifts in *para*-substituted toluenes.[15,20] The resonably linear regression line had a slope approximately equal to -0.70 unit. It should be noted that the data from which these correlations are drawn use as a reference benzene or chloroform.

The present work points out the correlation between the average *ortho* and *meta* proton shifts *vs.* σ_p for the titanocene series of compounds, but uses as a reference for the shifts a compound within the series, *viz.*, bis(cyclopentadienyl)diphenyltitanium. The slope of the least-squares line in this case is -0.75 unit.

Figure 6 illustrates the correlation of the relative phenyl proton shift as a function of the Hammett σ constant of the substituent. A linear regression analysis of the least-squares line gives the equation

$$\delta^{H}{}_{C_6H_4} = 0.117 - 0.748\sigma \qquad (5)$$

with a linear correlation coefficient of 0.760. When σ_I and σ_R are used instead of σ, a multiple regression analysis of the same proton shifts gives the least-squares line plotted in Figure 7 and the closer relationship expressed by eq. 6 is obtained, with a multiple correlation coefficient of 0.893. From eq. 6 it is seen that phenyl

$$\delta^{H}{}_{C_6H_4} = 0.004 - 0.35\sigma_I - 0.76\sigma_R \qquad (6)$$

proton shifts are 2.17 times more susceptible to the resonance effect than to the inductive effect.

Comparing ρ values in eq. 1 and 5, relative phenyl proton shift values are seen to be 4.7 times more susceptible to the polar electronic effect of the substituent than

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[19] This chemical shift is defined as the midpoint between the *ortho* and *meta* proton shifts relative to the benzene reference as given in the author's data.

[20] T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1218 (1960).

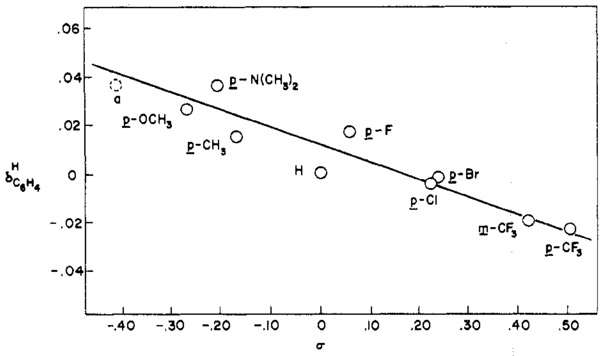

Figure 6.—The correlation of the relative phenyl proton chemical shifts with the Hammett σ constants; a, value from H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, **73**, 3404 (1951).

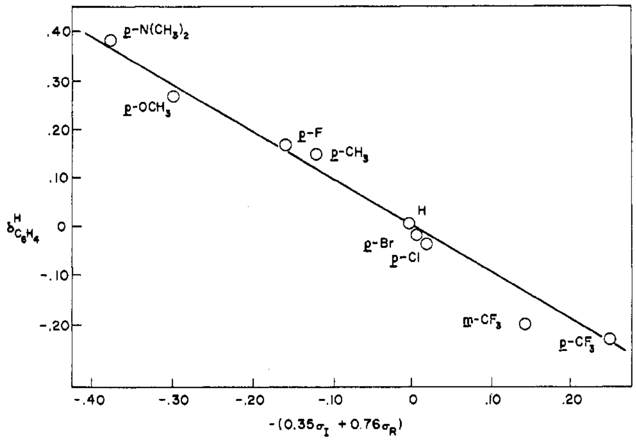

Figure 7.—The correlation of the relative phenyl proton chemical shifts with Taft's inductive (σ_I) and resonance (σ_R) parameters.

are the cyclopentadienyl ring proton chemical shift values. This extent of attenuation of the substituent effect is in accord with the classical theory that the polar effect rapidly diminishes in passing through more bonds. Restated, only about one-quarter of the polar effect, due to the substituent, experienced by the phenyl rings is transmitted across titanium to the cyclopentadienyl rings. Comparison of ρ values or α and β values in eq. 2 shows that inductive withdrawal or donation of electronic charge is slightly more significant than the resonance contribution when the "active center" (the cyclopentadienyl ring protons) is many bonds removed from the substituent. This may be due to a strong field effect contribution[21] to the substituent effect or an effective transmission of the inductive effect through the π-bonding orbitals of the phenyltitanocene system. It should be emphasized that the inductive effect is that due to polarization of the bonds connecting the substituent with the reactive center on which the measurement is made and these bonds may be either σ or π bonds. When the substituent is directly attached to and conjugated with the "active center" it is expected that the resonance effect predominates over the inductive effect and eq. 6 bears this out. Again, comparing ρ or α and β values implies that the nuclear magnetic shielding is more than twice as susceptible to resonance contribution as to inductive contribution. A future paper will deal further with these implications and the transmission of electron effects in metallocene systems.

To examine why the A_2B_2 phenyl proton shift may be correlatable with σ_p when the protons are *ortho* and *meta* to the substituent it is instructive to consider the magnitude of the chemical shift in monosubstituted benzenes together with *ortho* and *meta* proton shifts in the phenyltitanocene compounds. It has been observed that the substituent effect on *meta* and *para* protons in a substituted benzene is almost an order of magnitude larger than the corresponding γ and δ proton shift in aliphatic compounds.[22,23] It seems reasonable then that this enhanced substituent effect must be related to the delocalized π electron system found in the benzene ring. It has been noted that *para* proton shieldings correlate with Hammett σ constants, suggesting that π-electron density on the *para* proton is a dominant factor in transmitting the substituent effect. The *meta* proton shieldings cover about one-half the range of the *para* proton shifts and these it was noted did not correlate with Hammett's σ or Taft's σ_I, although *meta* fluorine shifts do correlate with Taft's inductive σ_I parameter.[3d] It has been suggested that *meta* proton shifts may be consistent with those expected from a π electron density contribution plus nearest neighbor contributions resulting from π electron charge at *ortho* and *para* positions.[24] The largest shielding values are found for *ortho* protons, and noting that theories of molecular structure predict that π electron charge densities at *ortho* and *para* positions should be similar, two groups of workers have found that *ortho* proton shifts correlate with *para* proton shifts and reactivity parameters.[25,26]

Thus, although many factors may be present, shielding data have supported the conclusion that the major factor in determining *ortho* and *para* proton shifts, and probably *meta* shifts also, is π electron charge density resulting from the substituent perturbation. In some instances the n.m.r. spectra in this study have suggested that the effect of π electron density is felt equally at *ortho* and *meta* protons as in bis(cyclopentadienyl)bis(*m*-trifluoromethylphenyl)titanium, where one line is noted for the phenyl protons. From the n.m.r. spectrum of 4-ethylfluorobenzene it is also inferred that ring protons are equivalent and all couple equally to fluorine.[27] Thus the effect of π bond resonance at times may be undiminished around the benzene ring. The assumption then made in the present study is that reactivity parameters as Hammett's σ_p relate to an effect not solely localized on the *para* group, but reflect the π electron density surrounding all

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[21] M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3539, 3548 (1962).

[22] J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

[23] H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 722 (1961).

[24] Although these π electron charges cannot yet be accurately calculated; see ref. 25.

[25] J. H. Martin and B. P. Dailey, *J. Chem. Phys.*, **39**, 1722 (1963).

[26] P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961).

[27] E. B. Baker, *J. Chem. Phys.*, **23**, 984 (1955).

the protons of the benzene ring. It therefore seemed reasonable to correlate σ_p with *ortho* and *meta* proton shieldings in substituted benzene systems.

It should also be noted that the second *para* group, the $(C_5H_5)_2Ti$ group, is also perturbing and interacting with the delocalized phenyl π electron system. It is interesting to consider the influence of this group relative to the other *para* substituent. The fact that all phenyl proton shifts in this study appear at higher field strength compared to benzene suggests that the $(C_5H_5)_2Ti$ system is releasing electron density to the benzene ring. The following comparisons are of value[28]: (a) The phenyl shift in the xylenes is -7.0 to -7.1 p.p.m., whereas in $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$ it is -6.6 p.p.m.; the methyl resonance in the xylenes is at -2.25 to -2.3 p.p.m., while in the titanocene compound the methyl group is found at -2.18 p.p.m. (b) In $Cp_2Ti(C_6H_5)_2$, $Cp_2Ti(p\text{-}ClC_6H_4)_2$, and $Cp_2Ti(p\text{-}BrC_6H_4)_2$ the phenyl shift is approximately -6.8 p.p.m., whereas in C_6H_6, C_6H_5Cl, and C_6H_5Br it is about -7.2 to -7.3 p.p.m. (c) In $Cp_2Ti(p\text{-}CH_3OC_6H_4)_2$ the phenyl shift is -6.53 p.p.m. and the CH_3O -3.65 p.p.m. In $C_6H_5OCH_3$ and $CH_3C_6H_4OCH_3$ the phenyl proton shift is -6.9 p.p.m. and the methoxy group appears at -3.75 to -3.78 p.p.m. (d) Finally, in $p\text{-}(CH_3)_2NC_6H_4Br$ the *ortho* and *meta* protons (to $(CH_3)_2N$) are shifted to -6.43 and -7.18 p.p.m., respectively, and the CH_3 shift is found at -2.88 p.p.m. In the related $Cp_2Ti(p\text{-}(CH_3)_2NC_6H_4)_2$ compound the corresponding proton shifts are at -6.32 and -6.62 p.p.m., and the methyl shift at -2.82 p.p.m.

The conclusion drawn from these facts is that $(C_5H_5)_2Ti$ as a *para* substituent on the benzene ring is more electron-releasing than the second *para* substituent and may be considered approximately as electron-donating as a dimethylamino substituent.

[28] Chemical shifts of benzene compounds taken from "Varian NMR Spectra Catalog," Varian Associates, 1962.

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The Crystal Structure of Ditechnetium Decacarbonyl[1]

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A three-dimensional single crystal X-ray analysis of $Tc_2(CO)_{10}$ has made possible a detailed comparison of the molecular features of $Tc_2(CO)_{10}$ and $Mn_2(CO)_{10}$. These two compounds and $Re_2(CO)_{10}$ are isomorphous and consist of dimeric molecules of approximately D_{4d} symmetry in which each metal atom is octahedrally coordinated to five carbonyl groups and the other metal atom such that the equatorial carbons are arranged in a staggered configuration. Crystals of $Tc_2(CO)_{10}$ contain four dimeric molecules in a monoclinic unit cell of symmetry I2/a and of dimensions $a = 14.65 \pm 0.03$ Å., $b = 7.18 \pm 0.02$ Å., $c = 14.93 \pm 0.03$ Å., and $\beta = 105.6 \pm 0.1°$. Anisotropic refinement of all atoms has resulted in final discrepancy factors of $R_1 = 6.9\%$ and $R_2 = 7.4\%$ for 1296 observed reflections. The observed Tc–Tc bond distance is 3.036 ± 0.006 Å. compared to a Mn–Mn distance of 2.923 ± 0.003 Å. in $Mn_2(CO)_{10}$ and a Re–Re distance of 3.02 ± 0.01 Å. in $Re_2(CO)_{10}$. All of the carbonyl groups are less strongly bonded to the metal in $Tc_2(CO)_{10}$ than in $Mn_2(CO)_{10}$, as evidenced by longer Tc–C bond distances (Tc–C 1.98 Å. (av.) *vs.* Mn–C 1.83 Å. (av.)). The average Tc–C bond distance of the four equatorial carbonyls is significantly greater (by 0.10 Å.) than the Tc–C_1 bond distance of the apical carbonyl; however, the average equatorial C–O bond distance of 1.12 Å. is significantly less than the apical C_1–O_1 distance of 1.21 Å., so that all nonbonding Tc · · · O distances are equal within the estimated error. The four equatorial carbonyl groups attached to each technetium are bent away from the apical carbonyl toward the other half of the dimer.

Introduction

Two-dimensional X-ray analyses of the isomorphous compounds $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ first established the molecular configuration of these two metal carbonyls.[4] A subsequent three-dimensional X-ray analysis of $Mn_2(CO)_{10}$,[5] which included anisotropic least-squares refinement, gave additional information concerning the crystallographic and molecular features of this compound. A three-dimensional investigation of $Re_2(CO)_{10}$ was not carried out, however, due to the large scattering power and high linear absorption of the rhenium atoms which would result in relatively inaccurate carbon and oxygen positional parameters. The later synthesis of $Tc_2(CO)_{10}$[6] provided an excellent opportunity for a detailed comparison of its molecular parameters with those of $Mn_2(CO)_{10}$, since the congener element, technetium, provides a relatively small percentage of the scattering power in $Tc_2(CO)_{10}$ and since absorption is much lower in $Tc_2(CO)_{10}$ than in $Re_2(CO)_{10}$. A preliminary X-ray study of $Tc_2(CO)_{10}$[7] indicated that

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[1] Based in part on a dissertation submitted by M. F. Bailey to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] National Science Foundation Predoctoral Fellow, 1962–1964.

[3] Alfred P. Sloan Fellow, 1963–1965.

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[5] L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

[6] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 2953 (1961).

[7] D. Wallach, *Acta Cryst.*, **15**, 1058 (1962).