Registry No. *cis*-Cr(CO)$_2$(DPM)$_2$, 53092-55-0; *cis*-Mo(CO)$_2$(DPM)$_2$, 53152-36-6; *cis*-W(CO)$_2$(DPM)$_2$, 53092-56-1; *trans*-Cr(CO)$_2$(DPM)$_2^+$, 53152-35-5; *trans*-Mo(CO)$_2$(DPM)$_2^+$, 53154-29-3; *trans*-W(CO)$_2$(DPM)$_2^+$, 53152-41-3.

References and Notes

(1) F. L. Wimmer, M. R. Snow, and A. M. Bond, *Inorg. Chem.*, **13**, 1617 (1974).

(2) R. Colton and J. J. Howard, *Aust. J. Chem.*, **23**, 223 (1970).

(3) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).

(4) G. Hope, private communication, Inorganic Chemistry Department, Melbourne University.

(5) J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Organometal. Chem.*, **29**, 105 (1971).

(6) R. Colton, *Coord. Chem. Rev.*, **6**, 267 (1971).

(7) J. Lewis and R. Whyman, *J. Chem. Soc.*, 5486 (1965).

(8) A. M. Bond, J. A. Bowden, and R. Colton, *Inorg. Chem.*, **13**, 602 (1974).

Contribution from the Department of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada, and the Department of Chemistry, The University of Western Ontario, London, Ontario, N6A 3K7, Canada

Carbon-13 Nuclear Magnetic Resonance Studies of Organometallic Compounds. VI. Phenylthiocarbene Derivatives[1]

CAESAR V. SENOFF[2a] and JOHN E. H. WARD*[2b]

Received June 12, 1974 AIC40373N

^{13}C nuclear magnetic resonance parameters for a series of transition metal carbene complexes of the type p-XC$_6$H$_4$S(CH$_3$)CW(CO)$_5$ are presented. Comparisons of the σ^n and σ^+ substituent constants for X with the carbene carbon shieldings reveal that both σ and π interactions between the aromatic ring and carbene carbon are occurring. This idea is also supported by quantitative evidence derived from the shieldings of the aromatic carbons of the carbene complexes and para-substituted benzenethiols. A direct relationship is revealed by comparisons of the carbene carbon shieldings of a series of complexes of the type R(R')CW(CO)$_5$, where R = p-C$_6$H$_4$X and R' = OCH$_3$, and the central carbon shieldings for carbonium ions of the type (p-XC$_6$H$_4$)$_3$C$^+$.

Introduction

Numerous reports[3-10] of ^{13}C nuclear magnetic resonance parameters derived from the nmr spectra of transition metal carbene derivatives have appeared in the literature. For complexes of the type R(R')CCr(CO)$_5$, where R = CH$_3$ or C$_6$H$_5$ and R' = OCH$_3$, OC$_2$H$_5$, NH(CH$_3$), N(CH$_3$)$_2$, etc., there has been considerable discussion concerning the bonding factors which give rise to alterations in the carbene carbon shieldings when R and/or R' is varied. For example, the upfield shift of the carbene carbon, when R' is varied from an alkoxyl to an amino group, has been attributed to the greater ability of the amino substituent to participate in dative π-bonding with the carbene carbon[3b,6-8] and/or the overall difference in electron release between the alkoxyl and amino groups.[3b,6]

Moreover, when R is a meta- or para-substituted phenyl ring, there is some controversy as to whether[6,8,9] or not[7] distinct π-p-carbene carbon–aryl interactions result in carbene carbon shielding variations as the phenyl substituent is changed. While a qualitative relationship[9] between the increase of the π-donor ability of a p-phenyl substituent and the carbene carbon shielding exists, no *quantitative* attempts have been made to assess this relationship, nor have comparisons been made with analogous systems. In addition, there have been no reports of ^{13}C-nmr studies of carbene derivatives in which the effects of variations of substituents on the *hetero* atom have been extensively examined.

A new, facile route to a series of phenylthiocarbene complexes of the type p-XC$_6$H$_4$S(CH$_3$)CW(CO)$_5$ has been recently reported,[3a] and we now wish to present the complete set of ^{13}C-nmr parameters derived from six of these derivatives. We will compare these data with the ^{13}C-nmr parameters obtained from the parent thiophenols and two series[9] of transition metal carbene complexes which have para-substituted phenyl groups directly attached to the carbene carbon. Finally, the ^{13}C-nmr data for the last series of complexes will be carefully reexamined; a striking relationship between the carbene carbon shieldings and the shieldings of the central carbon atoms of a series of related carbonium ions of the type (p-XC$_6$H$_4$)$_3$C$^+$ [11] is noted.

Experimental Section

Samples of the carbene complexes and para-substituted thiophenols and the ^{13}C-nmr parameters of these compounds were obtained as described previously.[3a,12]

Results

The ^{13}C-nmr shieldings obtained from the phenylthio(methyl)carbene complexes **1–6** and the parent thiophenols are provided in Table I.

The assignments of the carbon resonances of the carbene methyl carbons, *cis*- and *trans*-carbonyl carbons, and carbene carbons were carried out by comparisons with related derivatives.[9] However, the assignments of all the aromatic carbons were not as straightforward. The signals arising from the *quaternary* carbons C$_1$ and from the para carbons C$_4$ could be distinguished from the ortho and meta carbons on the basis of their relative intensities. In theory, the ortho and meta carbons of **5** can be differentiated by the proton-coupled method described by Scott.[13] However, the appropriate proton-coupled experiments carried out on both **5** and **11** yielded only broad, unresolved signals for the ortho and meta carbons. Since it is well known that meta-carbon shieldings are relatively insensitive to the presence of a substituent in monosubstituted benzenes,[14] the meta carbons of **5** and **11** were arbitrarily assigned to those signals closest to 128.7 ppm, the shielding of the carbons in benzene.[14b] Once the complete assignments were made for **5** and **11**, the signals of the aromatic carbons of the remaining compounds **1–4**, **6–10**, and **12** were assigned by assuming additivity of the individual substituent effects[14c] on the aryl carbon shieldings. The average deviation between the observed and predicted shieldings of all the aromatic carbons is 0.9 ppm.

Discussion

(a) Qualitative Shielding Trends. The shieldings of the *cis*- and *trans*-carbonyl carbons of **1–6** are almost invariant, fluctuating randomly in the ranges 196.8–197.4 and 207.4–207.8 ppm, respectively. The shieldings of the carbene-methyl carbons also undergo slight variations (0.5 ppm). The carbene carbons are apparently more sensitive to alterations in the para-aryl substituent and they vary from 331.1 to 333.3 ppm, over a range of *ca.* 2 ppm. Finally, the

Table I. Observed (and Predicted) ^{13}C Shieldings[a,b] for the Carbene Complexes p-$XC_6H_4(CH_3)SCW(CO)_5$ (1-6)[c] and the Parent Thiols p-XC_6H_4SH (7-12)[c]

Complex	X	δ_C(carbene)	δ_{C_1}	$\delta_{C_{2,6}}$	$\delta_{C_{3,5}}$	δ_{C_4}	$[\delta_{C_4}-\delta_{C_{3,5}}]$	δ_{CH_3}	δ_{CO}(trans)	δ_{CO}(cis)	Other
1	OH	333.3	129.1 (130.0)	133.0 (132.5)	116.5 (117.8)	157.1 (156.6)	40.6	49.0	207.7	197.1	
2	OCH_3	333.3	128.7 (129.6)	132.6 (132.1)	115.1 (116.1)	161.1 (161.1)	46.0	49.0	207.5	197.1	$\delta_{CH_3O} = 55.3$
3	CH_3	332.8	134.4 (134.4)	130.8 (131.0)	131.3 (132.2)	141.3 (138.6)	10.0	49.1	207.8	197.4[l]	$\delta_{CH_3} = 21.4$
4	F	332.4	133.6[d] (132.8)	133.4[e] (132.5)	117.1[f] (117.6)	163.8[g] (164.5)	46.7	49.1	207.7	197.1	
5	H	332.0	137.3	131.1	130.5	129.7	−0.8	49.3	207.5	197.1	
6	Br	331.1	136.3 (135.7)	132.7 (132.8)	132.7 (133.9)	125.3 (124.2)	−7.4	49.5	207.4	196.8	
7	OH		119.8 (123.2)	132.0 (130.5)	116.0 (116.0)	153.3 (152.1)	37.3				
8	OCH_3		119.4 (122.8)	131.7 (130.1)	114.2 (114.3)	157.8 (156.6)	43.6				$\delta_{CH_3O} = 54.0$
9	CH_3		126.3 (127.6)	129.6 (129.0)	129.6 (129.4)	135.2 (134.1)	5.6				$\delta_{CH_3} = 20.6$
10	F		124.8[h] (126.0)	131.5[i] (130.5)	115.8[j] (115.8)	161.1[k] (160.0)	45.3				
11	H		130.5	129.1	128.7	125.2	−3.5				
12	Br		129.6 (128.9)	130.6 (130.8)	131.7 (132.1)	119.1 (119.7)	−12.6				

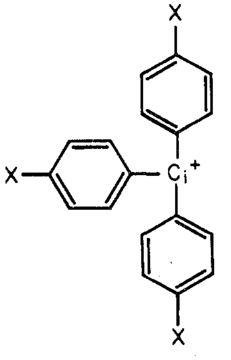
[a] All ppm (±0.1) (downfield positive) from TMS. [b] All spectra were obtained in chloroform-*d* solutions and were calibrated using the solvent resonances as secondary standards.[12] [c] Numbering of the substituted phenyl rings starts at the sulfur substituted carbon. [d] $^4J_{CF}$ not observed. [e] $^3J_{CF}$ not observed. [f] $^2J_{CF} = 20 \pm 3$ Hz. [g] $^1J_{CF} = 254 \pm 3$ Hz. [h] $^4J_{CF} = 4 \pm 2$ Hz. [i] $^3J_{CF} = 8 \pm 2$ Hz. [j] $^2J_{CF} = 22 \pm 2$ Hz. [k] $^1J_{CF} = 246 \pm 2$ Hz. [l] $^1J_{WC} = 130 \pm 2$ Hz. This way the only ^{13}C–^{183}W coupling constant observed.

shieldings of the aromatic carbons of **1–12** are extremely sensitive to variations in X, as would be anticipated.[14]

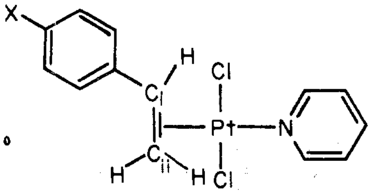
(b) Carbene Carbon Shieldings. If the effects of varying the para-substituent X on the carbene carbon shieldings are mainly transmitted *via* a σ-inductive mechanism, quantitative relationships between the $\sigma^n{}_{meta}$[15a] or Taft σ_I[15b] parameters for X and the carbene carbon shieldings would be expected. Both plots reveal only scattered arrays of points. Thus, we conclude that such relationships do not exist or that they are masked by variations in some other parameters.

On the other hand, if the effects of varying the para substituent are mainly transmitted by a π-inductive mechanism, a quantitative relationship between the Taft $\sigma_R{}^0$ parameters[15c] for X and the carbene carbon shieldings might be anticipated. A plot of these parameters also reveals a scattered array of points.

However, if σ *and* π effects are important in the p-$XC_6H_4S(CH_3)CW$ bonding system, we might anticipate a quantitative relationship between the carbene carbon shieldings and parameters which provide a measure of the overall σ and π properties that para substituents transmit through a simple aromatic system. For example, the Brown–Okamoto σ^+ [15a] substituent constants have been usefully compared with ^{13}C shieldings of C_i in compounds of type A[11] and with the ^{13}C coordination shifts $\Delta\delta_{C_i}$ and $\Delta\delta_{C_{ii}}$ in series B.[16]



A



B

Reasonably good *linear* correlations were shown to exist between the σ^+ substituent constants and the shieldings of C_i and $\Delta\delta_{C_i}$ for both series A and B, respectively. In contrast, a *nonlinear* relationship was observed in a similar plot between σ^+ and $\Delta\delta_{C_{ii}}$ for series B. This latter feature is probably related to the fact that C_{ii} is two carbons removed from the aromatic ring, while the Brown–Okamoto σ^+ parameters are derived for systems which have the carbon atom of interest *directly* bonded to the aromatic ring.

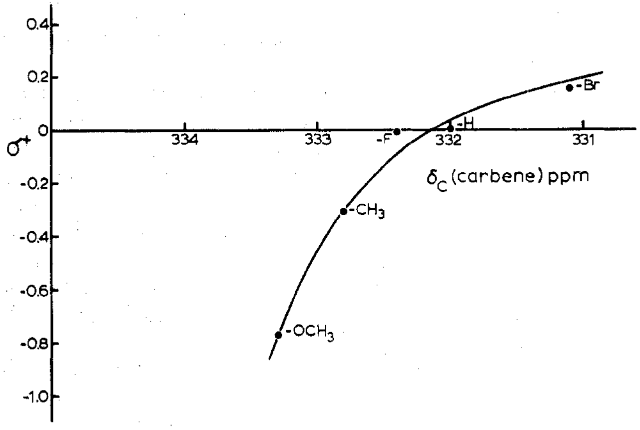


Figure 1. Plot of σ^+ *vs.* δ_C(carbene) for complexes **2–6**.

A plot of σ^+ *vs.* δ_C(carbene) for the tungsten carbene complexes **2–6** is shown in Figure 1. The nonlinear relationship is reminiscent of that observed for σ^+ *vs.* $\Delta\delta_{C_{ii}}$,[16] in B. This result is consistent with and supports the idea that the carbene carbon shieldings of **2–6** are sensitive to the *overall* variations in electron density induced by changes in the para substituent X.

The σ^+ parameters have been developed for systems in which a full positive charge is generated at a carbon atom directly attached to a phenyl ring. It is not clear that such a situation exists in the carbene derivatives **1–6**. However, the σ^n constants,[15a] which have been derived for series of meta- and para-substituted benzoic acids, will reflect somewhat reduced charge development at the adjacent carbon atom. In particular, $\sigma^n{}_{para}$, which reflects the *overall* charge density changes through aryl rings, may provide a more meaningful measure of the charge density variations in **1–6**.

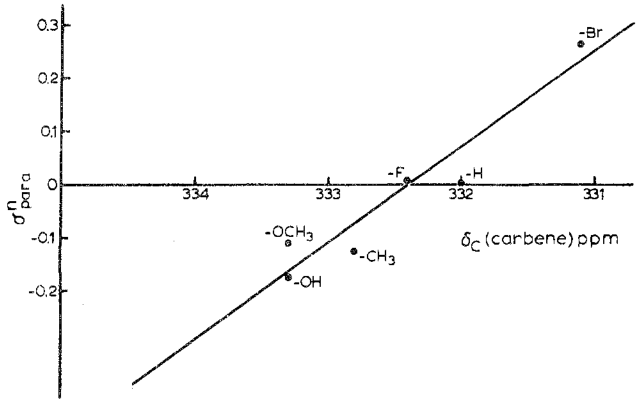


Figure 2. Plot of σ^n_{para} *vs.* δ_C(carbene) for complexes **1–6**.

A plot of σ^n_{para} *vs.* δ_C(carbene) for the tungsten complexes **1–6** is shown in Figure 2.

The linear regression analysis parameters[17] for these data are summarized in eq 1. The good linear fit supports our

$$\sigma^n_{para} = (-0.18 \pm 0.02)\delta_C(\text{carbene}) + (60.0 \pm 6.2) \qquad r = 0.940 \qquad (1)$$

conclusion that the carbene carbon shieldings of **1–6** are sensitive to both σ *and* π effects, as was shown for the plot with σ^+ values. Moreover, the σ^n_{para} values appear to provide a better model than do the σ^+ parameters, since a curved relationship is observed when the latter substituent constants are used.

Finally, we should note that while the carbene carbons of **1–6** are one atom removed from the aromatic ring, the σ^+ and σ^n values have been developed for carbons directly bonded to aromatic rings. In order to test the effect of the intervening sulfur atom, we compared the δ_C(carbene) values with σ^0 constants[15a] derived for a series of para-substituted α-toluic acids, in which the carbonyl carbon is insulated from the aromatic ring by a methylene group. A plot of the appropriate data revealed no discernible relationship. Thus, it appears that α-toluic acids are not good models for the carbene complexes **1–6**; the transmission of electron density through the sulfur atom does not seem to parallel electron density transmission through a methylene group. This result is reasonable in view of the obvious difference in electron insulating or transmission properties of sulfur and saturated carbon atoms.

At this point it is interesting to reconsider the ^{13}C-nmr data for the carbene complexes[9] of the sort $R(R')CM(CO)_5$ (C), where R = p-C_6H_4X, R' = OCH_3, and M = Cr or W. By analogy with the relationships between σ^+ and $\delta(C_i)$ for series A, we might expect a linear relationship between σ^+ and δ(C carbene) for these derivatives, because the aromatic ring is directly bonded to the carbene carbon. The linear regression analysis parameters derived from a plot of the data for the tungsten complexes,[9] where X = CF_3, H, CH_3, Br, Cl, F, and OCH_3, are summarized in eq 2.

$$\sigma^+ = 0.12\delta_C(\text{carbene}) - 38.4 \qquad r = 0.834 \qquad (2)$$

This poor linear relationship is strikingly similar to the analogous plot of Ray, *et al.*,[11] for the shieldings of the central carbons of the carbonium ions A. In contrast to the results obtained for the phenylthiocarbene complexes *vs.* σ^n_{para} a much poorer correlation is observed.

A direct comparison between the shieldings of the carbonium ion carbons of A and the carbene carbons of C (tungsten) is even more informative. The appropriate plot is shown in Figure 3.[18] Linear regression analysis of the data affords the parameters included in eq 3.

$$\delta_{C^+}(A) = 2.03\delta_C(C) - 443.1 \qquad r = 0.989 \qquad (3)$$

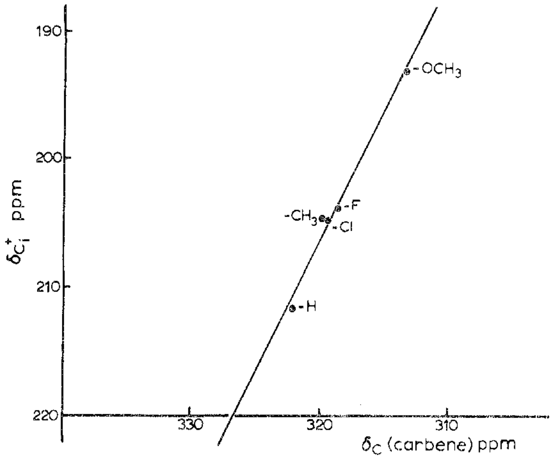
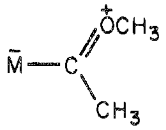


Figure 3. Plot of δ_{C_i}(series A) *vs.* δ_C(carbene, series C, M = W) for complexes sharing common para substituents X.

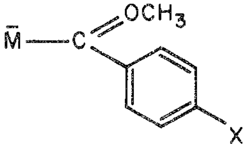
This interesting relationship[19] demonstrates that the shielding trends of the carbonium ion and carbene carbons are closely related, for derivatives with the same para substituents. The shieldings of the central carbonium ion carbons are only *ca.* twice as sensitive to variations in X as the shieldings of the carbene carbons. This behavior would be anticipated on the basis of the attenuation of the electronic effects of an individual substituent experienced upon progressive substitution at a given carbon atom. It is also consistent with Stothers'[14b] idea that steric congestion permits coplanarity of two, but not three, aryl rings in A. This feature would effectively eliminate the resonance interactions arising from one of the aromatic rings.

Coordinated carbenes have been commonly referred to as "metal stabilized carbonium ions"[3b,4,9] and thus the relationships we have just noted are perhaps not surprising. However, we have also noted[3b] that in alkoxy(alkyl)carbene derivatives, a resonance form with double bond character in the carbene carbon–oxygen bond, as in D, may have considerable importance.



D

In view of this formulation, it is interesting to recall the behavior of the shieldings of the carbonyl carbons of a series of para-substituted phenyl ketones[20] and methyl benzoates.[21] For these derivatives, it was found that the carbonyl carbon shieldings are much less sensitive than the carbene carbon shieldings[9] for a wide variety of para substituents. It is tempting to suggest that in view of this lack of similarity, the contribution from resonance forms of the carbene complexes of type E is not significant. However, because the electron density of the aryl rings in the carbene complexes can in principle delocalize to the metal atom and *cis*- and *trans*-carbonyls, it is not clear that such comparisons are valid.



E

Finally, it is interesting to compare directly the carbene carbon shieldings of the two series of tungsten complexes p-$XC_6H_4S(CH_3)CW(CO)_5$ and p-$XC_6H_4(CH_3O)CW(CO)_5$.

A plot of these parameters for corresponding X analogs yielded a scattered array of points. Thus, it seems that while both series may reflect overall electron density changes produced by altering X, they obviously have differing sensitivities to these properties. Alternatively, some other parameters are varying sufficiently to mask any such relationship.

(c) **Aryl Carbon Shieldings**. Next, we considered the aryl carbon shieldings in order to determine whether any interactions of the carbene carbon with the SC_6H_4X group were revealed. We reasoned that differences in the bonding of a carbene carbon, which can employ σ and π bonding, and a proton, which employs only σ bonding, would be reflected in quantitative comparisons between the individual aryl carbons of **1–6** and **7–12**.

Before proceeding with a detailed discussion of the ^{13}C shieldings of the aromatic carbons of **1–12**, the qualitative origins[14a] of the ^{13}C shieldings in substituted benzenes should be considered. In monosubstituted benzenes, both quaternary and ortho carbons appear to be susceptible to inductive, resonance, and neighborhood anisotropy effects of the substituent. In contrast, substituent effects (possibly only σ-inductive properties) contribute minimally to meta carbon shieldings. Para carbon shieldings are viewed to be primarily governed by substituent resonance effects, although it is possible[22] that σ-inductive effects may also be substantially reflected by these shieldings. Finally, the differences of the para and meta carbon shieldings are believed to reflect pure resonance interactions within the aromatic ring.

First, we note that carbons C_1 of the carbene complexes **1–6** are deshielded by an average of *ca.* 8 ppm with respect to the corresponding carbons in the parent thiols **7–12**. Assuming that the neighborhood anisotropies of the sulfur atoms are similar in both series of compounds, it appears that there is an appreciable shift of electronic density out of the aromatic ring to the sulfur atom and most probably to the carbene carbon (*vide supra*). The nature of this delocalization is revealed by considering the shieldings of C_4.

Those carbons of the carbene complexes are again deshielded by an average of *ca.* 4 ppm with respect to the thiols. Since para carbon shieldings are believed to be mainly governed by resonance effects, it follows that a substantial π delocalization from the aromatic ring may be occurring. This notion can be further substantiated by reviewing the differences $[\delta_{C_4} - \delta_{C_{3,5}}]$ for **1–6** and **7–12**. The average value of $[\delta_{C_4} - \delta_{C_{3,5}}]$ for the carbenes is *ca.* 3 ppm higher than the average value for the thiols. Assuming that $C_{3,5}$ and C_4 equally reflect σ-inductive properties, this value is a measure of the additional π delocalization that occurs from the aromatic rings in the carbene complexes compared to the thiols. It is also interesting to note that the shieldings of $C_{3,5}$ of the carbene derivatives shift an average of only *ca.* 1 ppm downfield of the meta thiol carbons. This is in accordance with our expectations, since meta shieldings are normally minimally effected by substituent changes. Finally, the 2,6 carbons of **1–6** vary in a small range and are deshielded by an average of *ca.* 1.5 ppm from the thiols. Both of these results are consistent with similar observations made for a series of σ-bonded phenylplatinum derivatives of the type *trans*-$[(C_6H_5)Pt(As(CH_3)_3)_2L]^+PF_6^-$, where L is a neutral ligand.[22] In that study it was found that variations in ligands one bond removed from the aromatic ring resulted in very small changes in the ortho carbon shieldings. In summary then, our comparisons of the shieldings in analogous carbene and thiol compounds reveal that probably both σ and π electron density variations are transmitted from the aromatic ring to the sulfur and carbene carbon atoms.

We can also compare the shieldings of the aromatic carbons of series **1–6** and **7–12** in a slightly different way. By graphically comparing the shielding parameters of the individual carbons and $[\delta_{C_4} - \delta_{C_{3,5}}]$ for the carbenes and thiols, we may obtain a measure of the consistencies of the bonding interactions, as well as a measure of the average changes. A plot of $\delta_{C_4}(p\text{-}XC_6H_4S(CH_3)CW(CO)_5)$ *vs.* $\delta_{C_4}(p\text{-}XC_6H_4SH)$ is a typical example which is shown in Figure 4.

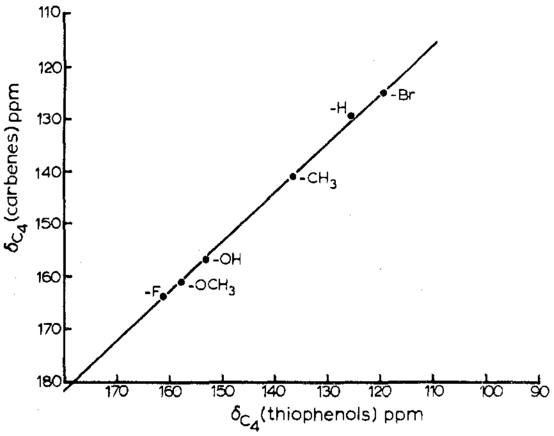


Figure 4. Plot of δ_{C_4}(carbenes) *vs.* δ_{C_4}(thiophenols) for compounds sharing common para substituents X.

The parameters derived from linear regression analyses of the compared ^{13}C shieldings of C_1, $C_{2,6}$, $C_{3,5}$, and C_4, as well as the shielding difference $[\delta_{C_4} - \delta_{C_{3,5}}]$ of **1–6** and **7–12** are summarized in eq 4-8.

$$\delta_{C_1}(\text{carbene}) = (0.76 \pm 0.04)\delta_{C_1}(\text{thiol}) + (38.1 \pm 4.5) \quad r = 0.995 \tag{4}$$

$$\delta_{C_{2,6}}(\text{carbene}) = (0.79 \pm 0.15)\delta_{C_{2,6}}(\text{thiol}) + (28.5 \pm 20.0) \quad r = 0.890 \tag{5}$$

$$\delta_{C_{3,5}}(\text{carbene}) = (1.04 \pm 0.03)\delta_{C_{3,5}}(\text{thiol}) - (3.2 \pm 3.3) \quad r = 0.999 \tag{6}$$

$$\delta_{C_4}(\text{carbene}) = (0.93 \pm 0.01)\delta_{C_4}(\text{thiol}) + (14.3 \pm 1.6) \quad r = 0.999 \tag{7}$$

$$[\delta_{C_4} - \delta_{C_{3,5}}](\text{carbene}) = (0.96 \pm 0.01)[\delta_{C_4} - \delta_{C_{3,5}}](\text{thiol}) + (4.0 \pm 0.2) \quad r = 0.999 \tag{8}$$

The sensitivities of the various carbons to changes at the sulfur atom are generally reflected in the slopes of the lines. For example, meta carbon shieldings ($C_{3,5}$) are believed to be most insensitive to these changes, and we would therefore expect an ideal 1:1 correspondence between the two series, that is, a plot with unity slope and intercept through the origin. Indeed, these predictions are almost attained by eq 6 where the slope is 1.04 ± 0.03 and the intercept −3.2 ± 3.3 ppm. In contrast, eq 7 and 8, which should mainly reflect resonance effects, should differ from the ideal case just mentioned. Again, as we had anticipated, both the slope and intercept deviate significantly from unity and zero, respectively. The excellent linear correlations also indicate that overall electron density variations are smoothly transmitted through the aromatic rings. The ortho carbons, $C_{2,6}$, fall within a restricted range of *ca.* 2 and 3 ppm for the carbenes and thiols, respectively. Thus, we would expect that the larger *relative* errors would result in a distinctly poorer linear correlation. The parameters in eq 5 bear this prediction out, since the correlation coefficient (0.89) is much lower than that (*ca.* 0.99) for the remainder of the equations. Also, the errors in the slope and intercept are extremely large. Finally, the parameters in eq 4, which should reflect π-inductive, σ-inductive, and neighborhood anisotropy effects, have pronounced deviations from unit slope and zero intercept. Thus, all of eq 4–8 are in accord with the results that would be expected for differing σ and π donation from the aryl ring when the thiol proton is replaced by a carbene carbon atom.

Acknowledgment. We wish to thank the National Research Council of Canada for financial support in the form of an operating grant to C. V. S. and the award of an NRC postdoctoral fellowship to J. E. H. W. Thanks are also extended to Drs. H. C. Clark, J. B. Stothers, and C. R. Jablonski for helpful discussions.

Registry No. **1**, 52843-18-2; **2**, 52843-19-3; **3**, 52843-20-6; **4**, 52843-21-7; **5**, 52843-33-1; **6**, 52843-34-2; **7**, 637-89-8; **8**, 696-63-9; **9**, 106-45-6; **10**, 371-42-6; **11**, 108-98-5; **12**, 106-53-6; ^{13}C, 14762-74-4.

References and Notes

(1) For the previous paper in this series, see H. C. Clark, L. E. Manzer, and J. E. H. Ward, *Can. J. Chem.*, **52**, 1973 (1974).
(2) (a) University of Guelph; (b) The University of Western Ontario.
(3) (a) C. T. Lam, C. V. Senoff, and J. E. H. Ward, *J. Organometal. Chem.*, **51**, 273 (1974); (b) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Amer. Chem. Soc.*, **95**, 8574 (1973).
(4) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *Chem. Commun.*, 1627 (1971).
(5) L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971).
(6) C. G. Kreiter and V. Formack, *Angew. Chem., Int. Ed. Engl.*, **11**, 141 (1972).
(7) J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 2419 (1972).
(8) D. J. Ciappenelli, F. A. Cotton, and L. Kruczynski, *J. Organometal Chem.*, **50**, 171 (1973).
(9) G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Weiller, and L. J. Todd, *Inorg. Chem.*, **12**, 1071 (1973).
(10) D. J. Cardin, B. Cetinkaya, E. Cetinkaya, M. F. Lappert, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 1982 (1973).
(11) G. J. Ray, F. J. Kurland, and A. K. Colter, *Tetrahedron*, **27**, 735 (1971).
(12) G. C. Levy and J. D. Cargioli, *J. Magn. Resonance*, **6**, 1432 (1972).
(13) K. N. Scott, *J. Amer. Chem. Soc.*, **94**, 8564 (1972).
(14) (a) G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2427 (1965), and references therein; (b) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N.Y., 1972; (c) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N.Y., 1972.
(15) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N.Y., 1970, p 356; (b) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963); (c) R. W. Taft, E. Price, I. R. Fox, I. R. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963).
(16) D. G. Cooper, G. K. Hamer, J. Powell, and W. F. Reynolds, *J. Chem. Soc., Chem. Commun.*, 449 (1973).
(17) The average deviations of the slopes and intercepts for the linear equations presented here are calculated on the basis of the maximum possible error due to the inherent uncertainty of the experimental measurements. These errors have already been cited in Table I. It is worthwhile noting that these variations represent the maximum error in *precision* and that as such they may be generous estimates.
(18) Original data converted to ppm from TMS using $\delta_C(CS_2) = 193.7$.
(19) A similar relationship also holds for the chromium derivatives of series C, since the shieldings of the carbene carbons of the tungsten and chromium analogs are linearly related according to the equation $\delta_C(W(CO)_5) = 0.87\delta_C(Cr(CO)_5) + 16.5$, $r = 0.994$.
(20) J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964).
(21) K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **45**, 233 (1967).
(22) H. C. Clark and J. E. H. Ward, *J. Amer. Chem. Soc.*, **96**, 1741 (1974).

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14850

Dipseudohalobis(β-diketonato)titanium(IV) Complexes. Synthesis, Stereochemistry, Configurational Rearrangements, and Vibrational Spectra

ALAN F. LINDMARK and ROBERT C. FAY*

Received August 6, 1974 AIC40539K

Dipseudohalobis(β-diketonato)titanium(IV) complexes of the type $Ti(dik)_2(NCO)_2$ and $Ti(dik)_2(NCS)_2$, where dik = $CH_3COCHCOCH_3$ (acac) or *tert*-$C_4H_9COCHCO$-*tert*-C_4H_9 (dpm), have been prepared by reaction of $Ti(dik)_2Cl_2$ with AgNCO or NaSCN. Molecular weight, conductance, dipole moment, and nmr data demonstrate that these complexes and the previously unreported dichloro complex $Ti(dpm)_2Cl_2$ are monomeric nonelectrolytes which exist in solution as cis geometrical isomers. Variable-temperature nmr spectra show that the β-diketonate rings undergo rapid intramolecular configurational rearrangement which exchanges acac methyl groups (or dpm *tert*-butyl groups) between the two nonequivalent sites of the cis isomer. First-order rate constants (sec^{-1}), extrapolated to 25°, activation energies (kcal/mol), and activation entropies (eu) in dichloromethane solution are respectively as follows: 1.1×10^3, 11.0 ± 0.6, -9.3 ± 2.4 for $Ti(acac)_2(NCO)_2$; 6.7×10^3, 9.8 ± 0.3, -9.5 ± 1.5 for $Ti(dpm)_2(NCO)_2$; 3.5×10^3, 11.4 ± 0.4, -5.6 ± 1.5 for $Ti(dpm)_2Cl_2$. The $Ti(dik)_2(NCS)_2$ complexes rearrange faster (by a factor of $\sim 10^2$) than the $Ti(dik)_2(NCO)_2$ analogs, but precise kinetic data could not be obtained because of the low coalescence temperatures. Infrared frequencies are reported in the range 2300–300 cm^{-1}; band assignments are given. The spectra point to an N-bonded attachment of the pseudohalide ligands and indicate that the complexes exist as the cis isomer in the solid state as well as in solution.

Introduction

Previous papers from this laboratory have described the synthesis, stereochemistry, and configurational rearrangements of dihalobis(β-diketonato)titanium(IV) complexes, $Ti(dik)_2X_2$.[1-4] The difluoro, dichloro, and dibromo complexes exist in solution as stereochemically nonrigid cis octahedral isomers,[1-3] while the diiodo complex, $Ti(acac)_2I_2$,[5] is present in dichloromethane as an equilibrium mixture of rapidly isomerizing cis and trans isomers.[4] Reported herein are the results of related studies of new dipseudohalo analogs of the type $Ti(dik)_2(NCO)_2$ and $Ti(dik)_2(NCS)_2$ (dik = acac or dpm[5]).

Experimental Section

Reagents and General Techniques. Acetylacetone, bp 136–140°, and titanium tetrachloride (Matheson Coleman and Bell) were used as purchased without further purification. Dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione) was prepared by the method of Man, *et al.*,[6] and purified by conversion to the copper chelate. Sodium thiocyanate was dried *in vacuo* at 175° for 48 hr, with periodic grinding in a mortar during the drying. Silver cyanate was prepared in aqueous solution by reaction of potassium cyanate and silver nitrate. The product was washed with acetone and dried *in vacuo* at room temperature for 48 hr in the dark. Reaction mixtures containing this compound were well shielded from direct light. Solvents (benzene, hexane, dichloromethane, and deuteriochloroform) were dried by refluxing for at least 24 hr over calcium hydride. Nitrobenzene was purified for conductance measurements by a previously described method;[1] the specific conductance of the purified solvent was $<4 \times 10^{-8}$ ohm^{-1} cm^{-1}. Because the $Ti(dik)_2(NCO)_2$ and $Ti(dik)_2(NCS)_2$ complexes are readily hydrolyzed, especially in solution, all syntheses and subsequent handling of the compounds were conducted under anhydrous conditions in a dry nitrogen or argon atmosphere.

Diisocyanatobis(2,4-pentanedionato)titanium(IV). A mixture of $Ti(acac)_2Cl_2$[1] (4.0 g, 12.6 mmol) and dry silver cyanate (6.2 g, 41 mmol) was allowed to reflux for 48 hr in 75 ml of dichloromethane. The resulting brown solution was filtered, and 200 ml of hexane was