Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

BONDING STUDIES IN GROUP IV SUBSTITUTED ANILINES

II*. THE STABILITIES OF THE CATION RADICALS

MICHAEL J. DREWS and PAUL RONALD JONES**
Department of Chemistry, North Texas State University, Denton, Texas 76203 (U.S.A.)

(Received May 12th, 1972)

SUMMARY

The relative stabilities of the cation radicals of several Group IV substituted anilines have been determined by cyclic voltammetry. They are *p*-tert-butyl- $>$*m*-trimethylsilyl- $>$*p*-trimethylsilyl- $>$*p*-trimethylgermyl- $\gg$*N*,*N*-dimethylaniline radical cation. The order of stability parallels that of the compounds towards protodemetalation. CNDO/2 calculations of the charge distribution in the ground states and cation radicals of the molecules resolve the apparent anomaly in the rates of protodesilylation of *m*- and *p*-trimethylsilyl-*N*,*N*-dimethylaniline. A mechanism for the chemical reactions of the radical cations which is consistent with the experimental and theoretical results is proposed. It involves nucleophilic displacement of the metal from the cation radical prior to the coupling of the radicals. The relative stabilities of the radical cations of the silicon compounds are in the same order as the amount of π character of the Si–C bond in the radical cation. The CNDO/2 calculations indicate that this π character is due to both $(p\text{–}p)\pi$ and $(p\text{–}d)\pi$ interactions in the neutral molecules and in the radical cations.

INTRODUCTION

In our studies of the ground state properties of Group IV substituted anilines we observed a small but significant increase in the ionization potential of the molecules when silicon or germanium was substituted for carbon. The results indicated a stabilization of the highest filled molecular orbital (HFMO) for *p*-trimethylsilyl-, and *p*-trimethylgermyl-*N*,*N*-dimethylaniline of 0.30 and 0.24 eV respectively relative to the *p*-tert-butyl compound[1]. This is consistent with electron withdrawal from the HFMO by the trimethylsilyl or trimethylgermyl group. Such stabilizations of ground state orbitals are common to unsaturated Group IV organometallic compounds and have been generally attributed to interaction between the *d* orbitals of the metal and the π system[2]. However, CNDO/2 calculations which we have performed indicate significant overlap between silicon's *p* orbitals and the ring carbon $p\pi$ orbital. Because the

---

* For Part I see ref. 1.
** Address correspondence to this author.

silicon p orbitals are predominantly involved in σ bonds with methyl groups, this interaction amounts to a σ–π or hyperconjugative stabilization of the ground state[3]. Similar types of interactions have been suggested by Pitt[4] and by Curran and co-workers[5].

Latta and Taft have reported the ESR spectra for a series of substituted *N*,*N*-dimethylaniline radical cations generated electrolytically[6]. Because, in a radical cation, the unpaired electron resides in the molecular orbital most appropriate for the study of ground state interactions and because of the potential accessibility of the radical cations of Group IV substituted anilines we chose this series of compounds for our study.

In order to determine the feasibility of ESR studies of these radicals, it was necessary to first determine the relative stabilities of the Group IV substituted cation radicals. This paper deals with the results of that investigation.

RESULTS AND DISCUSSION

The relative stabilities of the radical cations of *N*,*N*-dimethylaniline, (I); *p*-tert-butyl-, (II); *p*-trimethylsilyl-, (III); *p*-trimethylgermyl-, (IV) and *m*-trimethylsilyl-*N*,*N*-dimethylaniline, (V) were measured using stationary electrode cyclic voltammetry and the analytical techniques developed by Nicholson and Shain[7]. A single sweep cyclic voltammogram of a solution of *p*-trimethylsilyl-*N*,*N*-dimethylaniline is shown in Fig. 1. If multiple sweeps of the same samples were employed, two additional anodic and cathodic peaks appeared at +0.35, +0.53 and +0.29, +0.47 V, respectively. These additional peaks were attributed to the oxidation and reduction of *N*,*N*,*N'*,*N'*-tetramethylbenzidine formed by chemical reaction of the initially formed radical cations[1,8]. Benzidine formation was demonstrated in the case of (I), (II) and (IV). Under conditions in which excess unoxidized compound was present in the electrolytic ESR cell during electrolysis, (II) and (III) initially gave rise to the spectrum of their corresponding cation radicals. With continued electrolysis, the spectrum decays and the spectrum of *N*,*N*,*N'*,*N'*-tetramethylbenzidine radical cation[9] develops[3]. In the case of (I) the initial radical cation was not observed. The follow-up reactions of (II) and (V) were not determined.

For the kinetic studies the overall reaction was treated as an ECE process: a chemical reaction coupled between two electrochemical steps[8];

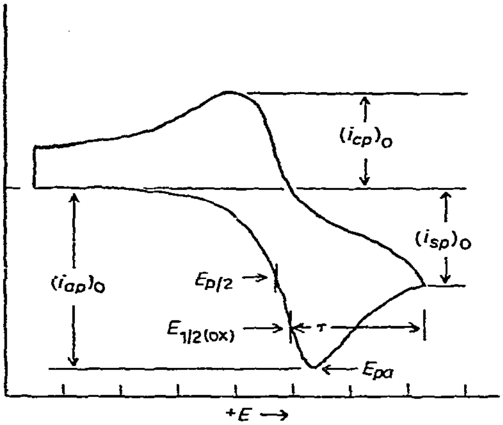
$$\mathrm{Ar} \rightleftarrows \mathrm{Ar}^{+} + e^{-} \qquad \text{(E)}$$

$$\mathrm{Ar}^{+} + \mathrm{Nu} \xrightarrow{k_f} \mathrm{B} \qquad \text{(C)}$$

$$\mathrm{B} \rightleftarrows \mathrm{B}^{+} + e^{-} \qquad \text{(E)}$$

in which the initially produced cation radical reacts with a nucleophile, Nu, in a chemical step to produce a new species, B. In general, the intermediate, B, is more easily oxidized than the parent compound. This description has been demonstrated to apply to the anodic oxidation of *N*,*N*-dimethylaniline[10].

It has been shown that for this type of process a plot of a current function, $i_p/v^{\frac{1}{2}}$, as a function of the scan rate, v, serves as a simple qualitative means for determining the reaction mechanism[7]. The electrochemical data, listed in Table 1, are plotted in this manner in Fig. 2. Comparison of the curves in Fig. 2 with the diagnostic



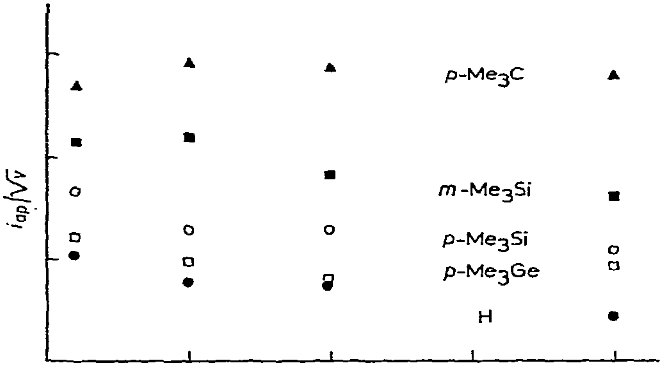


Fig. 1. Cyclic voltammogram of *p*-trimethylsilyl-*N*,*N*-dimethylaniline in acetonitrile, 1.00 V scan, 2.00 V/sec, 1 division = 0.10 volts.

Fig. 2. Diagnostic curves for the Group-IV-substituted-*N*,*N*-dimethylanilines from cyclic voltammetry.

TABLE I

DATA AND RESULTS FOR THE CYCLIC VOLTAMMETRIC DETERMINATION OF THE STABILITIES OF THE RADICAL CATIONS OF GROUP IV SUBSTITUTED-*N*,*N*-DIMETHYLANILINES

Substituent	$i_{ap}/v^{\frac{1}{2}}$	i_{cp}/i_{ap}	τ *(sec)*	$k_f\tau$	k_f *(sec^{-1})*
H	222	[a]			$>10^2$
(I)	212				
	210				
	197				
	160				
p-Me₃C	288	0.526	3.900	0.891	0.20[b]
(II)	297	0.893	0.760	0.110	
	295	0.942	0.357	0.078	
	290	1.042	0.174	0.004	
p-Me₃Si	247	0.432	3.050	1.450	0.92[b]
(III)	231	0.644	0.547	0.525	
	232	0.716	0.263	0.363	
	223	0.902	0.121	0.104	
p-Me₃Ge	228	0.418	3.150	1.560	1.53[b]
(IV)	219	0.529	0.610	0.871	
	210	0.628	0.284	0.550	
	219	0.735	0.139	0.331	
m-Me₃Si	266	0.493	3.680	0.631	0.68[b]
(V)	269	0.720	0.695	0.355	
	253	0.781	0.337	0.275	
	245	0.821	0.153	0.190	

[a] i_{cp} not observed. [b] Slope of least squares plot of $k_f\tau$ *versus* τ.

curves presented by Nicholson and Shain[7] indicate that the electron transfer steps are reversible, and that, at least for (I), (III) and (IV), the overall paths of the reactions are the same. For this type of mechanism the ratio i_{cp}/i_{ap} of the cathodic and anodic peak currents is a constant for a given value of the parameter $k_f\tau$, where k_f is the forward rate of the chemical step, and τ is the time in seconds as shown in Fig. 1. The values of $k_f\tau$ for each peak current ratio are determined using the theoretical working curve for the process[7]. In our work, the reverse peak currents, i_{cp}, were calculated using the method suggested by Nicholson[11] from the equation:

$$\frac{i_{cp}}{i_{ap}} = \frac{(i_{cp})_0}{(i_{ap})_0} + \frac{0.485(i_{sp})_0}{(i_{ap})_0} + 0.086$$

where all the quantities are defined in Fig. 1. The values of k_f listed in Table 1 are the slopes of the least squares fitted lines obtained from a plot of $k_f\tau$ *versus* τ. Although the uncertainty in the experimental measurements results in an uncertainty of about ± 0.1 sec^{-1} in the values of the rate constants[7], the trend in the relative stabilities of the radical cations is clear. It is *p*-tert-butyl- >*m*-trimethylsilyl- >*p*-trimethylsilyl- >*p*-trimethylgermyl- ≫*N*,*N*-dimethylaniline.

It is not unreasonable to assume, on the basis of the fact that we observe benzidine formation *only* under conditions where excess parent compound co-exists with oxidized species[3], that the chemical step of the ECE pathway is first order in radical cation. On this basis one may estimate half-lives of the radicals as (II), 3.4 sec; (V), 1.0 sec; (III), 0.74 sec; (IV), 0.45 sec; and (I), < 0.007 sec.

It is interesting to compare the relative stabilities of the cation radicals with the stabilities of similar compounds to acid catalyzed cleavage of the C–M bond*. Eaborn found that *p*-triethylgermylanisole is cleaved 15 times faster than *p*-triethylsilylanisole by perchloric acid in ethanol[12]. Benkeser and Krysiak reported yields of trimethylchlorosilane of 8% and 94% for *meta*- and *para*-trimethylsilyl-*N*,*N*-dimethylaniline respectively, in their reactions with dry hydrogen chloride in glacial acetic acid[13]. Combining these data one may arrive at a qualitative order of stability toward protodemetalation of *m*-Me_3Si > *p*-Me_3Si > *p*-Me_3Ge; identical with the order of stability we have observed for the radical cations. It is rather intriguing that in both reactions the *m*-trimethylsilyl species is more stable than the *p*-trimethylsilyl species.

The generally accepted pathway for the protodesilylation reaction involves a rapid reversible proton transfer to the substrate before the rate determining step followed by the slow nucleophilic attack on the protonated species[14]. The analogy between this process and the ECE process discussed above is clear.

$$Me_3SiAr + H^+ \rightleftarrows [Me_3SiArH]^+$$
$$[Me_3SiArH]^+ + Nu \longrightarrow \text{Products}$$

In order to account for the large difference in reactivity of (III) and (V) towards protodesilylation, Benkeser and Krysiak assumed that the equilibrium between the free *m*-amine and its salt lies largely in the direction of the salt form, while that of the *p*-amine lies principally in the direction of the free base. This assumption, at first

---

* Protodemetalation.

appearances, seems to be at odds with the small differences in the basicities of (III) and (V); pK_a of 3.98 and 4.41 respectively in 50% aqueous ethanol[15].

In order to get a better understanding of the bonding interactions in these group IV substituted anilines we have performed CNDO/2 calculations[16] for both their neutral molecules and the radical cations. The CNDO/2 approximation has been shown to give very good agreement with experiment for charge distributions in molecules, as in the calculation of dipole moments for wide varieties of molecules[17]. In Fig. 3 we have indicated the "formal charges" obtained in our calculations for *p*-trimethylsilyl-, and *m*-trimethylsilyl-*N*,*N*-dimethylaniline and their respective radical cations. These "formal charges" were determined by subtracting the CNDO/2 calculated electron density for each atom from the normal number of valence electrons for that atom. The hydrogens and methyl groups were included in the calculations but are omitted from the figure for clarity.

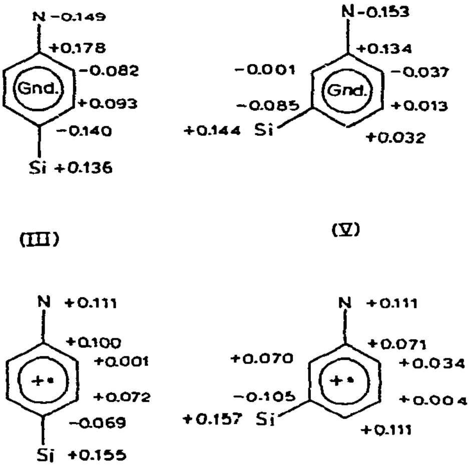


Fig. 3. CNDO/2 calculated charge distributions for the ground states and cation radicals of *p*-, and *m*-trimethylsilyl-*N*,*N*-dimethylaniline.

The charges on the nitrogens in the ground state are clearly in agreement with the known basicities of the compounds, the *meta* amine being slightly more basic than the *para* compound*. More pertinent to this discussion is the large accumulation of negative charge at the *para* carbon of *p*-trimethylsilyl-*N*,*N*-dimethylaniline, which is nearly equal to that on the nitrogen itself. Clearly the protonation of (III) should occur with nearly equal facility at either nitrogen or the carbon bonded to silicon. Since protodesilylation occurs *via* protonation of the metal carbon, one would expect the cleavage of this compound to be facile. If one considers the charge distribution in the cation radical to approximate to that of an *N*-protonated aniline the calculations also suggest that the non-*N*-protonated form of (III) is the species which undergoes protodesilylation. The lower half of Fig. 3 indicates the calculated charges for the cation radicals. It can be seen that upon protonation of nitrogen the accumulation of negative

---

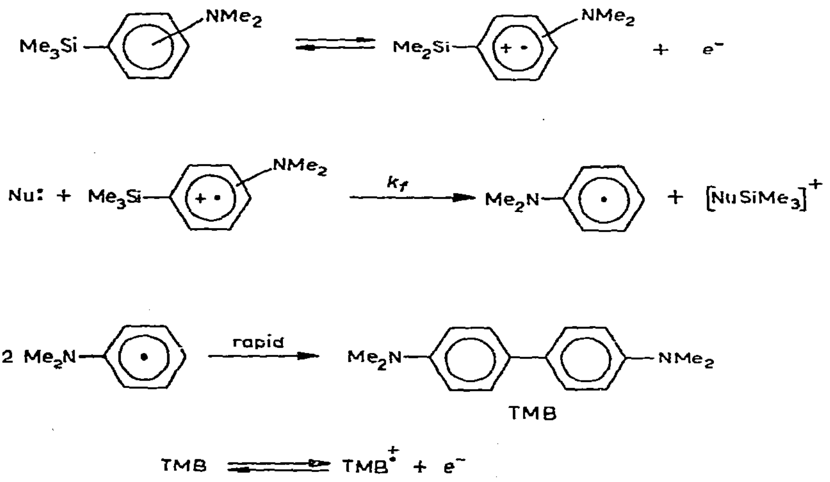
* Indeed, we have found an excellent correlation between base strength and the nitrogen charge density calculated using the CNDO/2 approximation for a wide variety of substituted anilines[1,3].

charge at the *para* position is drastically reduced. This is consistent with the stability toward protodesilylation of *p*-trimethylsilyl-*N*,*N*,*N*-trimethylanilinium ion[18], and Benkeser's suggestion that it is the free base form of (III) which undergoes cleavage[13].

With the *meta*-compound the calculated charge densities indicate the most basic site in the neutral molecule to be the nitrogen. Protonation of the nitrogen results in an increase of electron density at the carbon bonded to silicon. This is consistent with the *N*-protonated form of (V) being the species which undergoes the protodesilylation reaction. It might even be suggested on this basis that the reason for the great deviation of the *m*-trimethylsilyl compound from the linear free energy correlation of ease of protodesilylation[13] is that its cleavage is second order in acid while the cleavage of the other substituted phenyltrimethylsilanes is first order in acid.

It thus appears, on the basis of the CNDO/2 results that the great difference in reactivity of (III) and (V) towards protodesilylation is not a result of the differences of the basicities of the two amines. Instead (III) may be protonated directly at the reaction site in the first step of the cleavage while (V) is initially protonated at nitrogen and apparently its *N*-protonated form undergoes the cleavage reaction.

The chemical reactions of the radical cations present a much more complicated system than the protodesilylation reaction. On the basis of the fact that we can observe and resolve the ESR spectra of the radical cations of (II) through (V) it may be concluded that, under our conditions, the initial oxidation involves a transfer of one electron[8,*]. This also indicates that neither unimolecular decomposition nor simple coupling are predominant modes of reaction for the cation radicals of the Group IV substituted *N*,*N*-dimethylanilines. The parallel between the stability of the cation radicals and the stability of the anilines toward protodemetalation, coupled with the fact that we observe benzidine formation only under conditions where excess unoxidized amine is present suggests that the consumption of the radical cations involves nucleophilic attack by the unoxidized aniline.



---

* Adams and coworkers found that the anodic oxidation of (I) involved the transfer of two electrons prior to benzidine formation[10].

Inspection of the charge distributions in the radical cations illustrated in Fig. 3 reveals that silicon should be the site most susceptible to nucleophilic attack. A pathway consistent with these considerations is shown below. Because in our ESR experiments we observe only the initial radical cation and the benzidine cation radical we conclude that the coupling of the neutral radicals produced by the nucleophilic attack is very rapid.

On the basis of this pathway, the relative ease of cleavage of the trimethylsilyl group from the aromatic ring should be related to strength of the carbon-silicon bond in the radical cation*. In Table 2 we have listed the CNDO/2 calculated bond orders and bond densities for the bonding interactions between silicon and its ring carbon for (III) and (V) for both the neutral molecules and the radical cations. Comparison of the total bond orders for the neutral molecules indicates that the silicon–carbon bond is stronger for the *para* compound than for the *meta* substituted aniline. As might be anticipated, the silicon–carbon bond order is reduced for both compounds upon ionization. However, the relative bond orders for the *meta* and *para* cations are reversed. The silicon–carbon bond order for the *meta* cation radical is higher than that for the *para* cation radical, in agreement with the kinetic stabilities of the radicals.

It is of interest to compare the relative contributions of σ and π bonding interactions to these bond orders. For this reason both the bond densities and bond orders listed in Table 2 have been separated into their σ and π components. It can be seen that the main difference between the *para* and *meta* species is in their π bond orders. As we have pointed out elsewhere[3] the trimethylsilyl group appears to be the perturbed substituent rather than the perturbing influence in these Group IV substituted anilines, and its π interactions are very sensitive to the π electron density at its position of attachment to the ring. The large decrease in the π bond order for the *para* compound compared with that for the *meta* compound is directly related to this phenomenon.

TABLE 2

CNDO/2 BOND DENSITIES[a] AND BOND ORDERS[b] FOR THE INTERACTION BETWEEN SILICON AND ITS RING CARBON FOR *p*- AND *m*-TRIMETHYLSILYL-*N*,*N*-DIMETHYLANILINE NEUTRAL MOLECULE AND RADICAL CATIONS

Silicon orbitals	*Para*		*Meta*	
	Neutral	*Cation*	*Neutral*	*Cation*
s	0.679	0.635	0.678	0.638
$p\sigma$	1.116	1.080	1.099	1.064
$d\sigma$	0.800	0.797	0.837	0.817
$p\pi$	0.209	0.172	0.192	0.176
$d\pi$	0.363	0.260	0.321	0.288
σBO	1.298	1.256	1.307	1.259
πBO	0.286	0.216	0.256	0.232
Total BO	1.584	1.472	1.563	1.491

[a] Total bonding density minus antibonding density for the orbitals indicated. [b] Bond density/2.

---

* The charge distributions shown in Fig. 3 for the *para* and *meta* cation radicals indicate that the susceptibility of silicon to nucleophilic attack is nearly equal for both cations.

The net π atomic charge[20] for the *para* carbon in *p*-trimethylsilyl-*N*,*N*-dimethylaniline changes from -0.027 to $+0.135$ upon ionization. For *m*-trimethylsilyl-*N*,*N*-dimethylaniline the change for the *meta* carbon upon ionization is only from $+0.057$ to $+0.062$. These changes in π density reflect the fact that on oxidation the electron is removed from a symmetric π molecular orbital which has large density at the *para* position but rather small density at the *meta* position.

Further examination of the CNDO/2 results listed in Table 2 indicate that the π interactions between silicon and the aromatic ring consist of both $p \rightarrow d\pi$ overlap and $p \rightarrow p\pi$ hyperconjugative effects. Both the p and d interactions with the π system are of the same order of magnitude. However the $d\pi$ bond density appears somewhat greater than the $p\pi$ bond density. This may be due, in part, to the spatial orientation of silicon's d orbitals which tends to favor $d\pi$ overlap. Our results are in substantial agreement with those recently reported by Kawamura and Kochi who concluded from a study of hfcc's* and g values for a series of neutral radicals [$(CH_3)_3MCH_2CH_2^{\bullet}$, M = C, Si, Ge, Sn] that both p–d and hyperconjugative interactions provide delocalization of the odd electron to the β C–M σ bond[21].

In summary, the relative stabilities of the radical cations are in the same order as the calculated amount of π character of the C–M bond in the radical cation. The CNDO calculations indicate that in both the ground states and radical cations, this π character is due to both $(p$–$p)\pi$ and $(p$–$d)\pi$ overlap. The ESR spectra of the radicals and the complete CNDO results for the neutral molecules will be discussed in a subsequent paper[3].

EXPERIMENTAL

Anilines, solvents and electrolytes

The synthesis and characterization of the anilines, (II) through (V), and the purification of the solvents and electrolytes have been described previously[1].

Electrochemical kinetics

The kinetic parameters were determined by cyclic voltammetry using a three electrode cell consisting of a platinum button stationary working electrode (Beckman, 39273), a saturated calomel reference electrode, and a platinum coil as the counter electrode. The potential sweep was provided by a Chemtrix 300 polarographic amplifier with type 205 polarographic time base plug-in units. A Keithley 602 electrometer was used to calibrate the starting potentials and the measurements were recorded using a Tektronix 564 storage oscilloscope equipped with a Polaroid camera.

The stationary platinum button working electrode was prepared in the same manner for each run. After standing overnight in cleaning solution (sodium dichromate/sulfuric acid) the electrode was rinsed and placed in distilled water for 24 h. Immediately prior to use the electrode was wiped dry with a lint-free disposable wiper.

Acetonitrile which was 0.1 *M* in tetrabutylammonium perchlorate was used as the solvent and supporting electrolyte for all the runs. In a typical run a sample

---

* hfcc = hyperfine coupling constants.

concentration of 10^{-4} M was used. The system was maintained under an atmosphere of dry argon throughout the runs.

Theoretical calculations

The CNDO/2 program was that of Pople[16] and includes basis functions for the 3*d* orbitals. It was obtained from the Quantum Chemistry Exchange Program, Indiana University, Bloomington, Indiana, 47401. Standard bond angles were used along with bond lengths from standard sources[19]. The same bond lengths and angles were used for both the neutral molecule and the radical. Various rotational orientations of the Me_3M group were used. It was found that although these different orientations had a slight effect on the overall calculated electronic energy of the molecule, there was a negligible effect on the resulting electronic distributions. The dimethylamino group was treated as a group with an sp^2 hybridized nitrogen coplanar with the aromatic ring.

ACKNOWLEDGEMENTS

The authors are grateful to the Robert A. Welch Foundation, the Research Corporation, and the North Texas State University Faculty Research Fund for support of this work. The assistance of Jerry H. Waldon of the North Texas computer center in helping with the overlay for the CNDO/2 program is gratefully acknowledged.

REFERENCES

1 P. R. Jones, M. J. Drews, J. K. Johnson, and P. S. Wong, *J. Amer. Chem. Soc.*, 94 (1972) 4595.
2 See, for example, C. J. Attridge, *Organometal. Chem. Rev. Sect. A.*, (1970) 323, and references therein.
3 M. J. Drews and P. R. Jones, *J. Amer. Chem. Soc.*, in press.
4 C. G. Pitt, *J. Organometal. Chem.*, 23 (1970) C35.
5 C. Curran, R. Witucki, and P. McCusher, *J. Amer. Chem. Soc.*, 72 (1950) 4471.
6 B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, 89 (1967) 5172.
7 R. S. Nicholson and I. Shain, *Anal. Chem.*, 36 (1964) 706; 37 (1965) 178, 190.
8 R. N. Adams, *Accounts Chem. Res.*, 2 (1969) 175.
9 J. M. Fritsch and R. N. Adams, *J. Chem. Phys.*, 43 (1965) 1887.
10 T. Mizoguchi and R. N. Adams, *J. Amer. Chem. Soc.*, 84 (1962) 2058; Z. Galus and R. N. Adams, *ibid.*, 2061; Z. Galus, R. M. White, F. S. Rowland and R. N. Adams, *ibid.*, 2065.
11 R. S. Nicholson, *Anal. Chem.*, 38 (1966) 1406.
12 C. Eaborn and K. C. Pande, *J. Chem. Soc.*, (1960) 1566.
13 R. A. Benkeser and H. R. Krysiak, *J. Amer. Chem. Soc.*, 75 (1953) 4528.
14 C. Eaborn, *J. Chem. Soc.*, (1953) 3148.
15 R. A. Benkeser and H. R. Krysiak, *J. Amer. Chem. Soc.*, 75 (1953) 2421.
16 J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970.
17 *Ibid.*, pp. 113–128.
18 F. B. Deans and C. Eaborn, *J. Chem. Soc.*, (1959) 2299.
19 *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Special Publication 11, The Chemical Society, Burlington House, London, 1958, pp. 140, 172–73; *Handbook of Chemistry and Physics*, Chemical Rubber Co., Cleveland, Ohio, 1966, p. F-126.
20 J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, 72 (1968) 716.
21 T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, 94 (1972) 648.