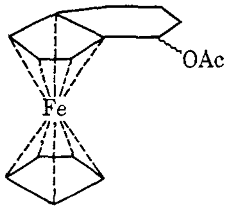
Nucleophilic Substitution on Ferrocenylmethyl Chloride[1]

Sir:

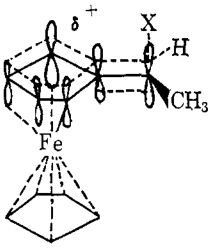
Hill and Richards[2] have shown that α-ferrocenylethyl derivatives (I) solvolyze with retention of configuration at rates of about 5–500 times those of the trityl derivatives.[3] Moreover, *exo*-II, having the leaving group *trans* to the iron, solvolyzes 2500 times as fast as the *endo* isomer.[2b,6] Both Hill and Richards[2] and Trifan and Bacskai[6] attributed these phenomena to a combination of resonance stabilization (III) and neighboring group participation (IV); the latter was considered to be the predominant effect.[7]

$$\overset{\displaystyle CH_3}{\overset{|}{\text{FerCHX}}}$$

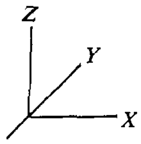
I

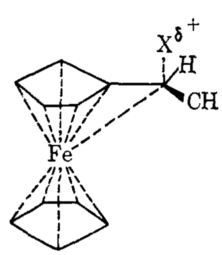


II



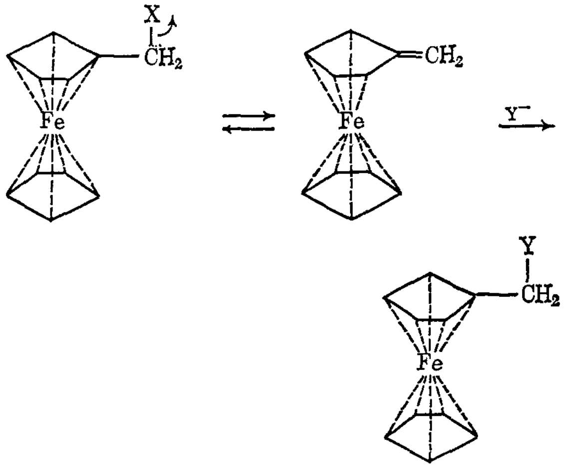
III





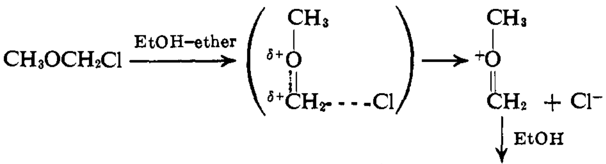
IV

More recently Ware and Traylor[4] have compared the effect of the ferrocenyl group with that of the methoxyl group, both in the α position (where neighboring group participation is possible) and in the *para* position (where neighboring group participation is not possible[10]), on the solvolysis rates of alkyl chlorides. Finding the ratio of rate constants to be about the same for the α-substituted and *para*-substituted derivatives, *i.e.*, $k_{\text{FerCHClCH}_3}/k_{\text{MeOCHClCH}_3} \cong 0.5$, $k_{p\text{-FerC}_6\text{H}_4\text{CHClCH}_3}/k_{p\text{-MeOC}_6\text{H}_4\text{CHClCH}_3} \cong 0.5$, they concluded that neighboring d_{xz},d_{xy} participation in the sense of IV did not contribute significantly to the reported rate enhancements.[2,4,6] They suggested that all these facts could be accounted for by elimination followed by readdition.[4,11a,b]



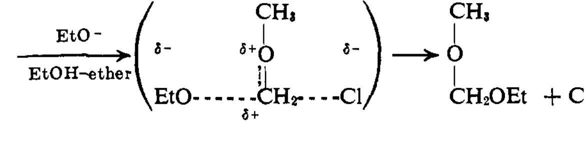
(1)

We wish to report[12] a second test for neighboring group participation which is applicable in cases of large acceleration (rate increases of $>10^4$ in solvolysis). Resonance-stabilizing groups such as the methoxyl group which increase SN1 reactivity by large factors ($>10^8$) also measurably increase SN2 reactivity in the same compounds by stabilizing the positive carbon in the transition state.[15a,b,i,16]



$$\text{CH}_3\text{OCH}_2\text{Cl} \xrightarrow{\text{EtOH–ether}} \left(\begin{array}{c} \text{CH}_3 \\ | \\ {}^{\delta+}\text{O} \\ \| \\ {}^{\delta+}\text{CH}_2\text{---Cl} \end{array} \right) \longrightarrow \begin{array}{c} \text{CH}_3 \\ | \\ {}^{+}\text{O} \\ \| \\ \text{CH}_2 \end{array} + \text{Cl}^- \qquad (2)$$

$$\big\downarrow \text{EtOH}$$



$$\xrightarrow[\text{EtOH–ether}]{\text{EtO}^-} \left(\begin{array}{ccc} \delta- & \begin{array}{c} \text{CH}_3 \\ | \\ {}^{\delta+}\text{O} \\ \| \end{array} & \delta- \\ \text{EtO------} & \underset{\delta+}{\text{CH}_2} & \text{---Cl} \end{array} \right) \longrightarrow \begin{array}{c} \text{CH}_3 \\ | \\ \text{O} \\ | \\ \text{CH}_2\text{OEt} \end{array} + \text{Cl}^- \qquad (3)$$

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[1] This work was supported by the Air Force Office of Scientific Research (Grant AF-AFOSR-514-64).

[2] (a) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 3840 (1961); (b) *ibid.*, **83**, 4216 (1961).

[3] Another comparison[4] indicates that the rate of solvolysis of α-ferrocenylethyl chloride exceeds the estimated rate[5] of SN1 solvolysis of ethyl chloride by about 10^{14}. This is based upon a rate ratio of 10^6 for α-phenethyl chloride over ethyl chloride.

[4] J. C. Ware and T. G. Traylor, *Tetrahedron Letters*, 1295 (1965).

[5] S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 828 (1948).

[6] D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, **No. 13**, 1, (1960).

[7] It was estimated that "delocalization of the charge into the ring" would afford stabilization approximately equivalent to delocalization into a phenyl group[6] (or 0.6β to 0.99β).[2a] The remainder of the stabilization was attributed[2] to overlap between d_{xz} (or d_{yz}) and the d_{xy} (or $d_{x^2-y^2}$) orbitals and the appropriate fulvene orbitals. These interactions were presumed to comprise sufficient overlap of the d orbitals with the α carbon to afford the extra stabilization and stereospecificity. (For the α-ferrocenylethyl system under discussion this extra stabilization accounts for a rate factor of about 10^{8}.[8]) The MO treatment used[2] assumed that the d_{xz},d_{yz} are bonding and the $d_{xy},d_{x^2-y^2}$ are nonbonding in ferrocene. Thus, the d_{xz}–α-carbon interaction is analogous to carbon participation and the d_{xy}–α-carbon interaction is analogous to sulfur participation since the former uses bonding and the latter uses nonbonding reactant orbitals. If these d-orbital interactions may be assigned the property of maintaining configuration as do nonbonding electrons on sulfur or bonding electrons on neighboring carbon, then they must also be assigned the other properties of neighboring sulfur or carbon, *e.g.*, relationship of anchimeric ability to nucleophilicity, ring size, etc.

[8] Later[2b] Hill and Richards discussed the d_{xy},d_{xz} participation in terms of the *exo/endo* ratio of 2500 found in solvolysis of II and it is not entirely clear what fraction of the total 10^{14} acceleration would be assigned to this effect. Reviewers[9a] of their work indicate that both Hill and Richards and Trifan and Bacskai favor this interaction over that of delocalization into the ring.

[9] M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part 1, Interscience Publishers, Inc., New York, N. Y., 1965: (a) p 133; (b) p 139.

[10] This proposal, previously assumed, has now been established (unpublished results).

[11] (a) This suggestion in a slightly modified form was independently made by Rosenblum.[9a] (b) Because most of the driving force for ionization comes from delocalization into the ring, the indicated *trans* elimination is only 10^3–10^4 as fast as *cis* elimination, which is ~10^{10} as fast as solvolysis of primary derivatives.

[12] The recently reported[13,14] nuclear magnetic resonance spectra of a variety of metallocenylmethyl cations have been interpreted as evidence for[13] and against[14] metal participation. These conflicting interpretations encourage us to report our findings at this time.

[13] M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Letters*, 1695 (1966).

[14] J. D. Fitzpatrick, L. Watts, and R. Pettit, *ibid.*, 1299 (1966).

[15] A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962: (a) p 26; (b) p 103; (c) p 17; (d) p 109; (e) p 115; (f) p 151; (g) p 12; (h) p 75; (i) p 176.

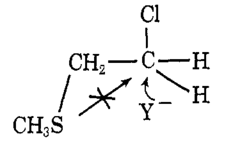
[16] C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press, New York, N. Y., 1962, p 9.

Table I. Relative Rates[a] of Unimolecular and Bimolecular Reactions on Substrates Displaying Resonance or Anchimeric Acceleration

Compound	S_N1 Rel rate[b,c]	S_N1 Ref	S_N2 Rel rate	S_N2 Ref	Type of S_N1 acceleration
$EtSCH_2CH_2Cl$	3200[c,f]	15d	0.8	15c	Anchimeric
$RCOOCH_2CH_2X$	630[e]	15e	0.45[d]	15c	Anchimeric
p-$MeOC_6H_4CH_2CH_2X$	94	15f, 19	0.9	15c	Anchimeric
$C_6H_5CH_2X$	2200[g]	15h	120	15g	Resonance
CH_3SCH_2Cl	6×10^9	16	5×10^3	16	Resonance
CH_3OCH_2Cl	$1 \times (10^{13})$[j]	15b This work[i]	$1 \times (10^6)$[j]	15a This work[i]	Resonance
$FerCH_2Cl$[h]	$7.6 \times (10^{13})$[j]	This work[i]	$8.6 \times (10^6)$[j]	This work[i]	?

[a] Relative to the ethyl derivative unless noted otherwise. [b] Relative rates of solvolysis in the most ionizing and least nucleophilic solvent for which data are available. [c] Since these are observed rates, corrections for inductive effects would make the participation much larger. For example, Winstein and Grunwald estimate the neighboring group acceleration by the EtS group to be 10^7 after correcting for inductive effects and for S_N2 contribution to ethyl chloride solvolysis. [d] $R = C_6H_5$, $X = Cl$. [e] Rate difference between *cis*- and *trans*-2-acetoxycyclohexyl brosylates. [f] Relative to *n*-hexyl chloride. [g] Benzyl tosylate in acetic acid. [h] Ferrocenylmethyl chloride was prepared by passing dry HCl into a cold ether solution of ferrocenylmethyl alcohol[20] containing calcium chloride and recrystallizing the product from pentane. Infrared and nmr spectra, titration for acid following hydrolysis, and production of the ethyl ether in ethanol confirm the structural assignment. [i] The kinetics of reaction of both ferrocenylmethyl chloride and methoxymethyl chloride with ethanol or with ethoxide ion in 90% ether–10% ethanol and 50% ether–50% ethanol at various temperatures were followed by aliquot titration or intermittant (*in situ*) titration. Our results agree well with those recorded for methoxymethyl chloride. At −17° retardation of rate was observed indicating external return. Kinetic data are: in 90 vol. % ethyl ether–10% ethanol at 0.0°, $k_1(FerCH_2Cl) = 1.02 \times 10^{-4}\ sec^{-1}$, $\Delta H^* = 14.3$ kcal, $\Delta S^* = -24$ eu; $k_2(FerCH_2Cl) = 0.60\ M^{-1}\ sec^{-1}$, $\Delta H^* = 12$ kcal, $\Delta S^* = -15$ eu; $k_1(CH_3OCH_2Cl) = 1.34 \times 10^{-5}\ sec^{-1}$, $\Delta H^* = 13$ kcal (lit.[21] 12.7), $\Delta S^* = -32$ eu (lit.[21] −35); $k_2(CH_3OCH_2Cl) = 0.070\ M^{-1}\ sec^{-1}$, $\Delta H^* = 13$ kcal, $\Delta S^* = -15$ eu. Average deviations between runs were ±5% for first-order rate constants and ±10% for second-order rate constants. [j] The numbers in parentheses are crude extrapolations. However, the ratios 1 to 7.6 and 1 to 8.6 are accurate to ±5 or ±10% as stated in footnote *i*.

On the other hand, even the best neighboring groups cause no acceleration of bimolecular substitution because of the limited coordination capacity of carbon.[15c]

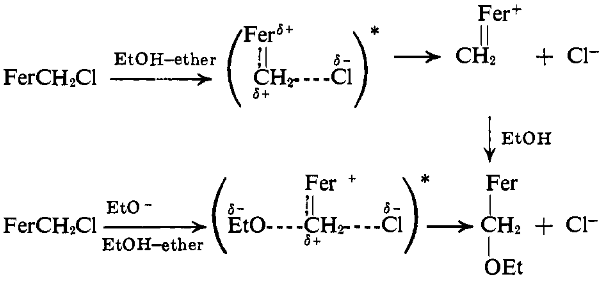


Indeed, one of the fundamental tenets of the theory[15] is that control of stereochemistry by neighboring group participation results from the interference of the bridging group to nucleophilic attack from the same side.

Thus, our test is a simple one. If ferrocenylmethyl chloride shows nearly the same reactivity as methoxymethyl chloride toward both S_N1 and S_N2 reactions, then neighboring group participation is excluded.[17] If, on the other hand, ferrocenylmethyl chloride reacts by an S_N1 process at the same rate as methoxymethyl chloride but much slower than methoxymethyl chloride by an S_N2 process, then there is neighboring group participation and we may estimate its importance.[18]

We have studied the solvolyses of methoxymethyl chloride and ferrocenylmethyl chloride in 90% ether–10% ethanol and in 50% ether–50% ethanol, as well as the reactions of both compounds with sodium ethoxide (eq 2–5).

Some of the relative rate data are shown in Table I, along with data for other resonance-stabilized and anchimerically accelerated systems.



(4)

(5)

The results are straightforward. For solvolysis in 90% ether–10% ethanol

$$k_{FerCH_2Cl}/k_{MeOCH_2Cl} = 7.6$$

(14.7 in 50% ether–ethanol), and for the reaction with sodium ethoxide in the same solvent

$$k_{FerCH_2Cl}/k_{MeOCH_2Cl} = 8.6$$

When it is remembered that these S_N1 rates are accelerated about 10^{14} and the S_N2 rates about 10^6 over ethyl chloride,[22] whereas neighboring groups such as $RS-CH_2-$ accelerate S_N1 rates by 10^6 but do not accelerate S_N2 reactions even a few per cent, it seems clear

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(17) It might be argued that this approach is inconclusive because either electron-withdrawing or electron-donating resonance groups accelerate S_N2 processes.[15] For small S_N1 accelerations this would be a valid criticism. However, it cannot be seriously contended that a group such as ferrocenyl which accelerates S_N1 processes by 10^{13} increases S_N2 reactions by electron withdrawal! See especially ref 15 where a quantitative correlation of S_N1 and S_N2 reactions is reported.

(18) It must be pointed out that this test, although rigorous, is rather inaccurate because a factor 10^{14} in the S_N1 reaction of ferrocenylmethyl chloride is reflected by only 10^7 in the S_N2 process. Thus $(\Delta\Delta F^*)_{S_N2}/(\Delta\Delta F^*)_{S_N1} = {}^7/_{14}$. A rate factor of 2500 in S_N1 rate corresponds to about a factor of 50 in the S_N2 process. We believe that we could have detected a meaningful factor much smaller than this.

(19) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Am. Chem. Soc.*, 75, 147 (1953).

(20) We are grateful to Dr. Donald Bublitz of the Dow Chemical Co. for the gift of this material and for helpful suggestions.

(21) P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Prestt, *J. Chem. Soc.*, 3641 (1955).

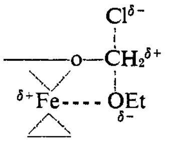
(22) Although this is the first kinetic study of S_N2 reactions on metallocenylmethyl derivatives, the extreme reactivity of such derivatives in S_N2 reactions has long been recognized in the wide use of displacement on metallocenylmethyltrimethylammonium ions.[9b]

that neighboring (d_{xz} or d_{xy}) participation as in IV cannot be significant.[23]

The significance of these results to other ferrocene reactions and the possible structure of α-ferrocenylcarbonium ions will be discussed in the full report.

Acknowledgment. We are grateful to the Air Force Office of Scientific Research (Grant AF-AFOSR-514-64) for financial support and to the National Institutes of Health for a Fellowship (T. T. T.).

[23] The similarity in the ratios of the SN1 and SN2 (7.6 *vs.* 8.6) reactions seems to indicate that the ethoxide must attack preferentially from the hindered side[24] or else suffer the *endo*/*exo* deceleration of 0.5 log (2500) = 1.7, or about 50-fold. That our SN2 reaction is "too fast" does not detract from the argument unless these results are obtained with, *e.g.*, chloride exchange. What this result possibly suggests is a small contribution from "merged" SN2-E2 mechanism.[25]



β-Metalloalkyl derivatives seem to us excellent substrates for such mechanisms because more charge will be developed on metals than on hydrogen.

[24] We previously suggested the possibility of steric hindrance contributing to the stereospecificity in solvolyses of metallocenylmethyl derivatives. However, the microscopic reverse of our proposed "elimination" must give the same stereospecificity as the elimination itself. Thus, any addition which is the microscopic reverse of E2 elimination will give high (E2-like) stereospecificity. The steric effect probably contributes only 5–10 to the *exo*/*endo* product ratio.

[25] S. Winstein, D. Darwish, and N. J. Holness, *J. Am. Chem. Soc.*, 78, 2915 (1956).

Thomas T. Tidwell, T. G. Traylor
Chemistry Department, Revelle College
University of California, San Diego, La Jolla, California
Received January 25, 1966

Valency Tautomerism in Metal–Olefin Complexes. Cyclooctatetraenemolybdenum, -chromium, and -iron Tricarbonyls[1]

Sir:

Several π-bonded cyclic olefin complexes of transition metals are known in which the free ligand has π electrons to offer in excess of the electronic requirements of the metal. In some of these complexes, part or all of the "excess" π electrons of the free olefin are diverted into C–C σ bonding, giving rise to a bicyclic ligand as in bicyclo[4.2.0]octa-2,4-dieneiron tricarbonyl[2a,b] or bicyclo[5.1.0]octa-2,4-dieniumiron tricarbonyl [from protonation of $C_8H_8Fe(CO)_3$].[2c,3a] A second possibility is that the metal takes up a coordination position relative to two or three of the available olefinic groups, leaving the others geometrically isolated as observed with $C_8H_8Fe(CO)_3$ in the crystal.[4a] A still conceivable third possibility is that the metal is simultaneously and symmetrically attached to all the olefinic carbon atoms with only a fraction of the olefinic π electrons involved in bonding.[5]

Several compounds have been reported which display single sharp proton resonance for the olefinic group containing "excess" π electrons, most notably $C_8H_8Fe(CO)_3$ (I),[2a] $C_7H_7Mo(CO)_2(C_5H_5)$ (II),[6a] $C_7H_7Co(CO)_3$ (III),[6a] $C_7H_7{}^+Fe(CO)_3$ (IV),[7] $C_7H_7{}^+Fe_2(CO)_6$ (V),[7] $C_8H_8Fe_2(CO)_6$ (VI),[7c] and, most recently, $C_8H_8Mo(CO)_3$ (VII).[3a] As we have already indicated,[3a] VII is the first complex in this group whose proton nmr was observed to change from a single line at high temperatures to a multiplet pattern at low temperature. In this complex, therefore, the metal is involved in bonding with only six π electrons on six carbon atoms (6π6C) at any one time, and over a time average all eight carbon atoms of the ring become equivalent owing to valency tautomerism. The infrared spectrum of $C_8H_8Mo(CO)_3$, with three carbonyl stretching absorptions and a band attributable to an uncoordinated C=C, is in agreement with this interpretation. Metal–carbon valency tautomerism was suspected for the other compounds listed above which display single sharp resonances for the olefin groups containing "excess" π electrons; however, this can be proved only by the demonstration of temperature variation of the nmr or with other evidence obtained from a faster "camera" such as infrared spectroscopy.

Since our earlier report[3a] on VII, the temperature dependence of the nuclear magnetic resonance of the C_7H_7 protons in II has also been demonstrated.[6b] We now report on the temperature dependence of the nmr spectrum of VII and that of the analogous complex $C_8H_8Cr(CO)_3$ (VIII) which we have synthesized for the first time. Also, a reinvestigation of $C_8H_8Fe(CO)_3$ (I) has confirmed previous unpublished reports that the nmr spectrum remains essentially a single sharp line down to very low temperatures (*ca.* −100°). However, by using still lower temperatures, −140 to −150°, we have now been able to observe the nmr spectrum of the "frozen" complex.

The new compound $C_8H_8Cr(CO)_3$ (VIII) is obtained as red-brown crystals in 20% yield by stirring cyclooctatetraene with $(NH_3)_3Cr(CO)_3$[8] in refluxing *n*-hexane for 65 hr.

Anal. Calcd for $C_{11}H_8CrO_3$: C, 55.01; H, 3.36; Cr, 21.65. Found: C, 54.74; H, 3.62; Cr, 21.74, 21.89.

Three characteristic strong absorptions were noted for the metal carbonyls in the infrared for VIII (1996, 1940, and 1912 cm^{-1}; cyclohexane solution, LiF prism), analogous to but not superimposable on those (2006, 1945, and 1916 cm^{-1}) found for VII. A recognizable absorption at 1675 cm^{-1} for VII and 1668 cm^{-1} for VIII denotes the presence of an uncoordinated double bond. This excludes with certainty a complex containing the bicyclic[4.2.0] valency tautomer of C_8H_8.

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[1] Research sponsored by the U. S. Army Research Office (Durham) and the National Science Foundation, GP 4175 (H. D. K.) and GP 3780 (F. A. L. A.).

[2] (a) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960); (b) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961); (c) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *ibid.*, 4821 (1960).

[3] (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Am. Chem. Soc.*, **87**, 3267 (1965); (b) H. D. Kaesz, S. Winstein, and C. G. Kreiter, *ibid.*, **88**, 1319 (1966).

[4] (a) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962); (b) R. T. Bailey, E. R. Lippincott, and D. Steele, *J. Am. Chem. Soc.*, **87**, 5346 (1965).

[5] (a) D. A. Brown, *J. Inorg. Nucl. Chem.*, **10**, 39 (1959); (b) F. A. Cotton, *J. Chem. Soc.*, 400 (1960).

[6] (a) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964); (b) R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966); (c) R. B. King, *Inorg. Chem.*, **2**, 807 (1963).

[7] (a) J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Am. Chem. Soc.*, **86**, 3589 (1964); (b) G. F. Emerson, J. E. Mahler, R. Pettit, and R. Collins, *ibid.*, **86**, 3590 (1964); (c) C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, **87**, 1388 (1965).

[8] W. Hieber, W. Abeck, and H. K. Platzer, *Z. Anorg. Allgem. Chem.*, **280**, 252 (1955).