electron demand, which might be correlated by σ^+ in the benzene series. However, the various $\sigma\rho$ correlations suggest that the resonance interaction is probably intermediate between those from the *meta* and *para* positions of a benzene ring in reactions which do not have a strong electron demand, and a model allowing for only inductive transmission through the ring–metal bonds correlates the data quite well. Singer and Cram[24] reached a similar conclusion for electron-withdrawing, transannular substituent effects in π–π complexes of paracyclophanes.

The excellent correlation between the solvolysis rate data and the $\Delta E_{1/4}$ values for the corresponding substituted ferrocenes depicted in Figure 2 is especially noteworthy. Computation 1 in Table III shows the rate data correlate better with $\Delta E_{1/4}$ than they do with any of the other parameters tested. Thus, at least for the case of the solvolysis reaction, the quarter-wave potentials constitute a standard reference for substituent effects, much as the ionization constants of benzoic acids do for side-chain reactions in the benzene series. This correlation implies that considerable positive charge is probably carried by the metal atom in α-metallocenylcarbonium ions, a situation which is predicted by both theoretical models[2–4] for these ions. Whether or not quarter-wave potentials would accurately predict substituent effects in other side-chain reactions of ferrocene remains an open question.

Hall and Russell[11] reported that ferrocenes bearing acetamido or urethano substituents possessed unusually low quarter-wave phenomenon, *i.e.*, the carbonyl oxygen atom of these groups coordinated with the positively charged iron atom in the oxidized species. Even if the iron atom does acquire a significant positive charge in the solvolysis of methylferrocenylcarbinyl acetates, it seems unlikely that appropriate substituents would lead to an unusually high solvolysis rate because of an internal solvation effect. This is so because the aqueous acetone solvent employed in these studies would likely compete with the substituent for coordination sites on the metal atom. Komenda and Tirouflet[25] observed no unusual effect when acetamidoferrocene was oxidized polarographically in ethanol–water.

Acknowledgment. This investigation was supported by a grant from the National Science Foundation (NSF-CP 5190) and the Paint Research Institute.

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[24] L. A. Singer and D. J. Cram, *J. Amer. Chem. Soc.*, **85**, 1082 (1963).

[25] J. Komenda and J. Tirouflet, *Compt. Rend.*, **254**, 3093 (1962).

Reaction of Nickelocene with Diazoalkanes[1,2]

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Abstract: Nickelocene catalyzes the reaction of diazomethane to produce polymethylene; even in the presence of carbene acceptors polymethylene is the only product formed. Nickelocene catalyzes the reaction of ethyl diazoacetate, giving diethyl maleate and diethyl fumarate. In the presence of cyclohexene, ethyl norcaranecarboxylate is also formed. Nickelocene is recovered unchanged from these reactions. The catalytic effects of nickelocene seem to be unique to it; for example, neither ferrocene nor dicyclopentadienylchromium have similar properties. A mechanism for these reactions is proposed.

In continuing our studies on reactions and properties of electron-deficient metallocene derivatives (for example, carbonium ions[4]) we have studied the interaction of potential carbenoid reagents, for example, diazomethane, with metallocenes such as nickelocene. We were particularly attracted to nickelocene because it is a paramagnetic substance with two unpaired electrons[5] and might have a novel interaction with a carbene, which in the triplet state would also have two unpaired electrons.

A great many substances have been previously investigated as catalysts for the decomposition of diazomethane, *e.g.*, Cu,[6–9] CuX (Br, Cl, I),[7,10] $CuCl_2$,[7,10] $CuSO_4$,[7] copper(II) stearate,[7,9,11] BF_3,[9–12] $B(OCH_3)_3$,[9,13] $AlCl_3$,[7,9,10,14] Et_2AlCl,[7,14] GaI_3,[10] $BeCl_2$,[10] $MgCl_2$,[10] $FeCl_3$,[9,10] $Fe(DPM)_3$,[6] $AgNO_3$,[7] Ag,[7] $PtCl_4$,[7] ZnI_2,[7,10] and $Ni(CO)_4$.[15] In addition, the photolysis of diazomethane has been extensively studied and both singlet

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[1] Supported by the National Science Foundation, Grant No. GP-5190, and the Paint Research Institute.

[2] Reported at the Cincinnati Symposium on Organometallic Chemistry, June 12–15, 1963; see also *Off. Dig. Federation Soc. Paint Technol.*, **36**, 1433 (1964).

[3] Anorganisch-Chemisches Laboratorium der Technischen Hochschule München, 8 München 2, Germany.

[4] E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, **83**, 4216 (1961).

[5] G. Wilkinson, P. L. Pauson, J. M. Birmingham, and F. A. Cotton, *ibid.*, **75**, 1011 (1953); E. O. Fischer and R. Jira, *Z. Naturforsch.*, **8b**, 217 (1953).

[6] K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **83**, 2397 (1961); **84**, 1015 (1962).

[7] E. Müller and H. Fricke, *Ann.*, **661**, 38 (1963).

[8] G. D. Buckley, L. H. Cross, and N. H. Ray, *J. Chem. Soc.*, 2714 (1950).

[9] C. E. H. Bawn and T. B. Rhodes, *Trans. Faraday Soc.*, **50**, 934 (1954).

[10] G. Wittig and K. Schwarzenbach, *Ann.*, **650**, 1 (1961).

[11] J. Feltzin, A. J. Restaino, and R. B. Mesrobian, *J. Amer. Chem. Soc.*, **77**, 206 (1955).

[12] S. W. Kantor and R. C. Osthoff, *ibid.*, **75**, 931 (1953).

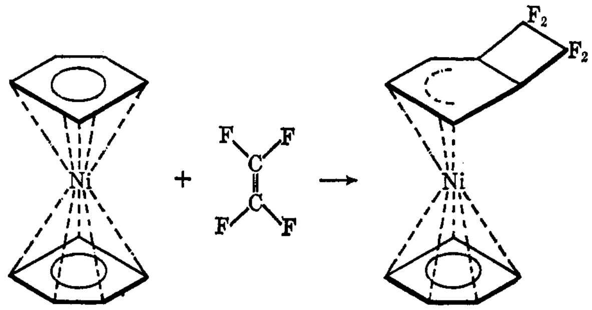
[13] G. D. Buckley and N. H. Ray, *J. Chem. Soc.*, 3701 (1952).

[14] H. Hoberg, *Ann.*, **656**, 1 (1962).

[15] C. Ruechardt and G. S. Schrauzer, *Chem. Ber.*, **93**, 1840 (1960).

and triplet methylene have been produced under appropriate conditions.[16] In general, the catalytic agents are Lewis acids and they effect the conversion of diazomethane to polymethylene and bring about carbene addition to double bonds (for example, copper catalyzes the formation of norcarane from cyclohexene and diazomethane, considerable polymer being formed at the same time),[6] insertion in aromatic rings (for example, $CuCl_2$ catalyzes the formation of cycloheptatriene from diazomethane and benzene[7]), and insertion in a wide variety of carbon–hydrogen bonds.

Of the metallocenes, ferrocene has probably received the greatest attention and shows many reactions characteristic of highly reactive aromatic systems.[17] Though aromatic diazonium compounds are known to react with ferrocene to give products of the anticipated type, studies of the interactions of metallocenes with diazo compounds have not been reported, though one of the attractive possibilities for the reaction of nickelocene might be addition of a carbene fragment to one of the cyclopentadienyl rings analogous to that observed by Stone, *et al.*,[18] who added fluorinated ethylenes to nickelocene.



Results

a. Ferrocene. Diazomethane does not react with ferrocene, nor is the sensitized or unsensitized photoreaction of diazomethane with cyclohexene affected by ferrocene. Table I gives some examples of this assertion. From all reaction mixtures containing ferrocene the ferrocene was recovered in practically quantitative yield, nor was there any evidence for the formation of methylferrocene. (In this respect, the "aromatic" ferrocene is quite different from benzene.) These results accord with those of Hammond showing that iron complexes, such as ferric dipivaloylmethide, or heavy atoms, such as iodine, do not change the product distribution in the photoreaction of diazomethane in the presence of cyclohexene.[6]

Table I. Effect of Ferrocene on Photoreaction of Diazomethane with Cyclohexene

	Products (rel amounts)		
Reaction mixture	3- and 4-methylcyclohexane	2-Methylcyclohexene	Norcarane
Diazomethane–cyclohexene[a]	1.5	0.3	1.0
Diazomethane–cyclohexene–ferrocene	1.43	0.17	1.0

[a] For comparison, see ref 6.

Ferrocene also does not affect the product distribution in the photoreaction of diazomethane with ether (Table II).

Table II. Effect of Ferrocene on Photoreaction of Diazomethane with Ether at 0°

	Products (rel amounts)		
Reaction mixture	Methyl ethyl ether	Isopropyl ethyl ether	*n*-Propyl ethyl ether
Diazomethane–ether[a]	0.23	1.0	1.12
Diazomethane–ether–ferrocene	0.21	1.0	1.10

[a] For comparison, see V. Franzen and L. Fikenscher, *Ann.*, **617,** 1 (1958); W. von E. Doering, L. H. Knox, and M. Jones, Jr., *J. Org. Chem.*, **24,** 136 (1959).

b. Nickelocene. In sharp contrast to the inertness of ferrocene toward diazomethane, mixing solutions of diazomethane and nickelocene in ether at −78° results in an instantaneous release of nitrogen and formation of a flaky white precipitate of polymethylene. The polymethylene contains no nickel or nitrogen within the limits of analysis. There is no ethylene formed, nor any other volatile, low molecular weight product, nor is there any addition or insertion of methylene. For example, the reaction can be carried out in cyclohexene and the only product is still polymethylene, no norcarane or methylcyclohexene being formed. This result contrasts, for example, the decomposition of diazomethane in cyclohexene catalyzed by copper powder or ferric chelates in which cases some norcarane is produced in addition to polymeric products. There is also no reaction of the intermediate in the decomposition of diazomethane catalyzed by nickelocene with ethylene, 2-butene, or aromatic hydrocarbons. In all these, as in all later cases, the nickelocene is recovered in practically quantitative yield and there is no evidence for reaction products incorporating nickelocene. Moreover, the rate of reaction of diazomethane catalyzed by nickelocene is very much greater than the rates of reaction of diazomethane with other catalysts (*e.g.*, copper powder or ferric chelates).

The effect of nickelocene on other diazo compounds was also studied. The list includes diazopropene, phenyldiazomethane, diphenyldiazomethane, diazofluorene, and ethyl diazoacetate.

Nickelocene catalyzes the decomposition of diazoprop-2-ene, though the reaction is much slower than in the case of diazomethane. After 1 hr about 80% of the diazopropene is decomposed. Some polymerization product (probably polycyclopropane) is formed but this reaction differs from that with diazomethane in that addition to olefins was observed. In cyclopentadiene as solvent *endo*-tricyclo[3.2.1.0^{2,4}]octa-6-ene is formed, a product that is effectively the Diels–Alder adduct of cyclopentadiene and cyclopropene and which is also formed in the photoreaction of diazopropene in cyclopentadiene.[19]

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[16] For a summary, see W. B. DeMore and S. W. Benson in "Advances in Photochemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1964, pp 219–261.

[17] M. Rosenblum, "Chemistry of the Iron Group Metallocenes, Ferrocene, Ruthenocene, and Osmocene," Part I, Interscience Publishers Inc., New York, N. Y., 1965.

[18] D. W. McBride, P. L. Pruett, E. Pitcher, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **84,** 497 (1962).

[19] A. A. Lamola, private communication.

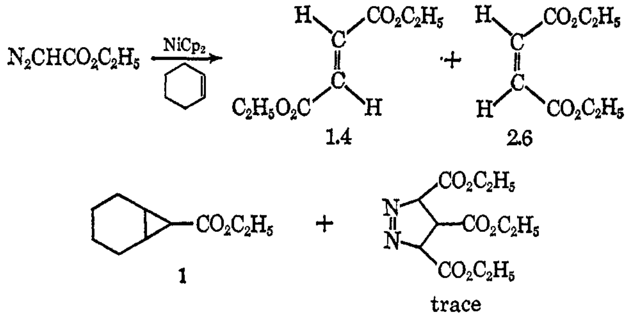
As the degree of substitution and steric bulk at the carbon bearing the diazo function increase, the reactivity in the presence of nickelocene sharply diminishes. On addition of phenyldiazomethane to nickelocene in ether no noticeable reaction occurs at first, but after some minutes a slow evolution of nitrogen commences and continues for about 3 hr. Only a small amount of polymeric product is formed, and the major product from phenyldiazomethane is benzyl ethyl ether which is also formed on photolysis of phenyldiazomethane in ether.

Nickelocene has no effect on diphenyldiazomethane or on diazofluorene; addition of nickelocene to an ether solution of these substances causes no gas evolution, and both the diazo compounds and nickelocene can be recovered unchanged. Photolyses of these substances in the presence of nickelocene yields as the main reaction products benzophenone azine (from diphenyldiazomethane) and α,β-bisdiphenyleneethylene.

The action of nickelocene on ethyl diazoacetate in cyclohexene was also studied and the major products were found to be diethyl fumarate, diethyl maleate, and ethyl norcaranecarboxylate in relative amounts of about 1.4:2.6:1 (see Table III). Nickelocene does not catalyze the conversion of maleic to fumaric ester or *vice versa.* A small amount of the triethyl ester of pyrazoline-3,4,5-tricarboxylic acid formed from either diethyl maleate or diethyl fumarate and ethyl diazoacetate[20] can also be isolated.

Table III. Ratio of Products from Catalyzed Decomposition of Ethyl Diazoacetate

Catalyst	Diethyl fumarate	Diethyl maleate	Ethyl norcaranecarboxylate
$NiCp_2$	1.4	2.6	1.0
$Ni(CO)_4$	6.0	...	1.0
Cu	0.57	0.67	1.0
CuBr	0.5	0.5	1.0
$CuSO_4$	0.7	0.5	1.0
ZnI_2	1.4	0.6	1.0
$CrCp_2$	1.5	0.6	1.0



The effects of several other catalysts (copper powder, cuprous bromide, cuprous sulfate, nickel carbonyl, and, zinc iodide) on ethyl diazoacetate were also studied; the catalysts except nickelocene and nickel carbonyl produced product mixtures which contained about as much ethyl norcaranecarboxylate as the total amount of diethyl maleate and diethyl fumarate. However, nickelocene had one dramatic difference from the other catalysts, all of which showed induction periods of varying lengths; in the case of nickelocene as catalyst, nitrogen evolution began instantaneously and the reaction was very much more rapid than with any of the other catalysts. The reaction seems to be first order in nickelocene and first order in ethyl diazoacetate; doubling the concentration of either doubled the rate of nitrogen evolution.

Many of the substances known to catalyze the formation of polymethylene from diazomethane are Lewis acids. Nickelocene is not; its spectrum is unchanged in the presence of aliphatic amines such as triethylamine. On the other hand, nickelocene does form complexes with Lewis acids; addition of boron trifluoride to nickelocene in ether yields a black precipitate which is assumed to be a 1:1 complex of nickelocene and boron trifluoride.

c. Dicyclopentadienylchromium. The effect of dicyclopentadienylchromium, which, like nickelocene, has two unpaired electrons,[21] was also studied. Its effect is very different from that of nickelocene. It does not rapidly catalyze the decomposition of diazomethane, and no polymethylene, ethylene, or volatile hydrocarbons are formed. Dicyclopentadienylchromium reacts rapidly with 1 mol of ethyl diazoacetate in the presence of cyclohexene. Additional ethyl diazoacetate is decomposed very slowly and the product distribution is quite similar to that in the presence of zinc iodide and differs from that when nickelocene is the catalyst.

d. Effect of Diphenylpicrylhydrazyl. The possibility that radical intermediates might intervene in the nickelocene-catalyzed decomposition of diazomethane was studied by adding 2,2-diphenyl-1-picrylhydrazyl to reaction mixtures of nickelocene and diazomethane. There was no effect until the molar concentration of diphenylpicrylhydrazyl exceeded the molar concentration of nickelocene. In the case when there was 2 mol of diphenylpicrylhydrazyl present for 1 mol of nickelocene, the decomposition of diazomethane proceeded (as evidenced by gas evolution) but the production of polymethylene ceased. Diphenylpicrylhydrazyl alone catalyzes the decomposition of diazomethane, but this reaction does *not* produce polymer. Other radicals such as the triphenylmethyl radical or aryloxy radicals also react with diazomethane.[22]

Discussion

Nickelocene differs from all other previously studied substances, either in degree or kind, in its effect on diazo compounds. The results with diazomethane and ethyl diazoacetate show nickelocene to be a very active catalyst; the results with diphenyldiazomethane, diazofluorene, phenyldiazomethane, and diazopropene indicate that the catalytic effect of nickelocene is also strongly influenced by the nature of the diazo compound with which it interacts.

We take the absence of any addition products when nickelocene decomposes diazomethane in the presence of cyclohexene to indicate that no *free* methylene (either in the singlet or in the triplet state) is formed in this re-

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[20] E. Buchner and H. Witter, *Ann.*, **273**, 239 (1893); **284**, 219 (1895).

[21] F. Engelmann, *Z. Naturforsch.*, **8b**, 775 (1953); G. Wilkinson, *J. Amer. Chem. Soc.*, **76**, 209 (1954); E. O. Fischer and H. Leipfinger, *Z. Naturforsch.*, **10b**, 353 (1955).

[22] E. Müller, A. Moosmayer, and A. Rieker, *ibid.*, **18b**, 982 (1963).

action and extrapolate this conclusion to the other diazo compounds the reactions of which are catalyzed by nickelocene.

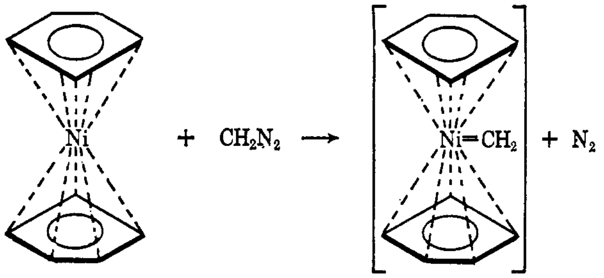
The experiments with diphenylpicrylhydrazyl lead us to the conclusion that no free-radical type intermediates are involved. Up to 1 mol of this reagent can be neutralized by the nickelocene, either by reaction or complexation; at higher concentrations of DPPH the reaction observed is that between diazomethane and diphenylpicrylhydrazyl itself.

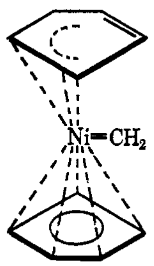
The very different behavior of dicyclopentadienylchromium in its interactions with diazo compounds indicates that the mere presence of two unpaired electrons in a transition metal complex does not make the complex an active catalyst like nickelocene.

The fact that nickelocene has none of the properties of a Lewis acid eliminates a mechanism for its catalytic action which mimics that of other Lewis acids such as boron trifluoride.

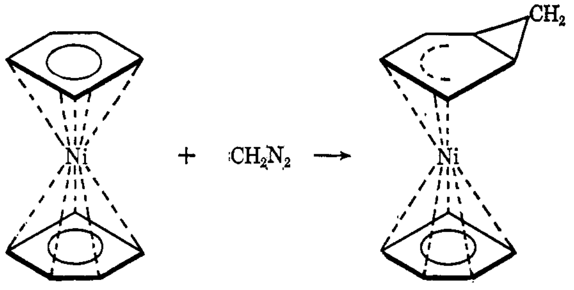
We attribute the absence of any reaction in the case of diphenyldiazomethane, for example, to steric reasons and suggest, in line with other proposals for the mechanisms of reactions of metallocenes with electron-deficient species,[4] that the primary interaction may be between the central nickel atom of the nickelocene and the diazo compound or the carbene type species formed on loss of nitrogen. Such an interaction which might resemble that of a charger-transfer complex would place severe steric demands on the substrates with which nickelocene could efficiently interact.[23] Such complexation could also greatly lower the energy of the "hot" methylene.

Thus the first step in the nickelocene-catalyzed decomposition of diazomethane might well be the formation of a nickelocene–methylene complex, and the structure of this complex is open to speculation. Nickelocene has two unpaired electrons which might conceivably form two bonds with methylene in such a way that the nickel atom would have 22 electrons in its valence shell, or, more probably, the nickel could partially release one of the cyclopentadienyl rings which would then be linked like a π-allyl system, and acquire the methylene fragment in its place; the electronic configuration of the reacting intermediate would then be the same as in nickelocene. The Ni=CH_2 bond may be considered to be made up from one σ bond resulting from the donation to the nickel of the two unshared electrons of the methylene fragment and one π bond resulting from back donation of electrons from the metal to the vacant p_z orbital of the methylene.

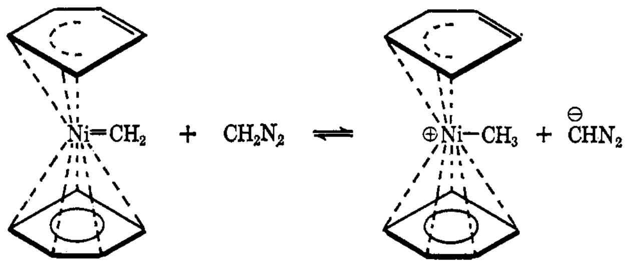




The addition of tetrafluoroethylene to nickelocene causes the molecule to give up two of the ring-carbon bonds without decomposition of the metallocene.[8] In direct analogy to this reaction the methylene could add to the cyclopentadienyl ring to give an intermediate with a cyclopropane ring. We tend to disfavor this possibility, however, because no alkylated nickelocenes are isolated which one might anticipate would be formed if a carbon–carbon bond is once established between the carbenoid reagent and one of the cyclopentadienyl rings of nickelocene.



As diazomethane and other diazoalkanes are weakly acidic[25] the next step in the reaction might be a proton transfer which produces an intermediate with more Lewis acid-like properties which can attack another molecule of diazomethane to yield a cationic species with two new groups attached to nickel. An ionic species similar to $^-CHN_2$ cannot be formed with diphenyldiazomethane or with diazofluorene, and this might be another reason they do not react with nickelocene. Rearrangement can now lead to an ethyl derivative with formation of a new carbon–carbon bond. The species so generated is also able to accept another methylene group from diazomethane and repetitions of these two steps, reaction with diazomethane followed by migration of the alkyl group from nickel to carbon, extends the growing polymer chain. In this regard, it is known that copper alkyls (for example, CuC_2H_5) react with diazoalkanes producing polymers.[26] Ejection of the chain by an E_2-type process



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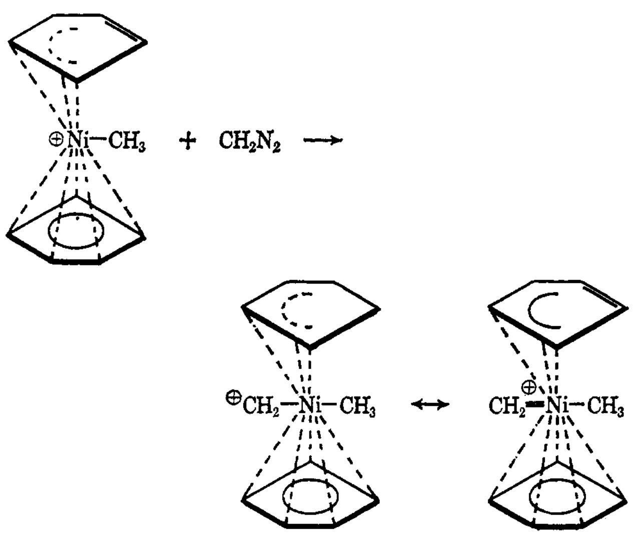
[23] The intermediate formation of transition metal methylene complexes has also been postulated by Ruechardt and Schrauzer[15] and more recently by Jolly and Pettit.[24]

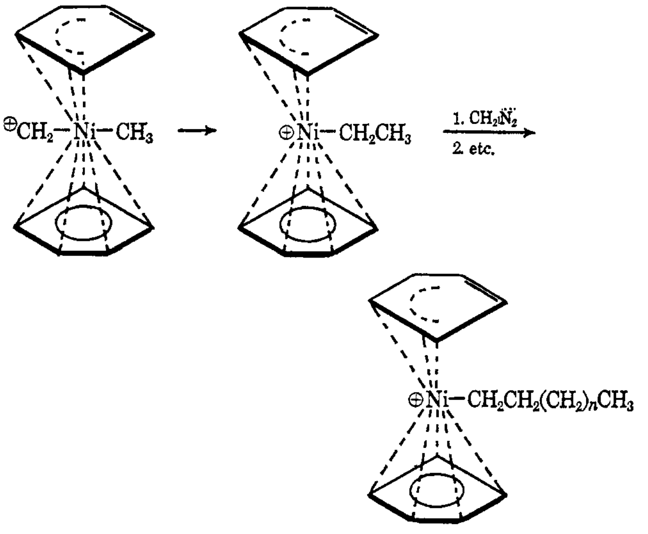
[24] P. W. Jolly and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 5044 (1966).

[25] E. Müller and H. Disselhoff, *Ann.*, **512**, 250 (1934); E. Müller and D. Ludsteck, *Chem. Ber.*, **87**, 1887 (1954); for a summary of reactions of diazomethane with Lewis bases, see R. Huisgen, *Angew. Chem.*, **67**, 439 (1955).

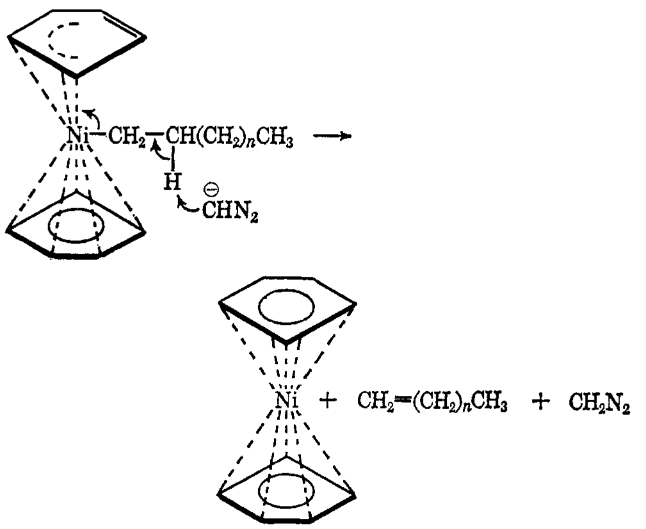
[26] C. E. H. Bawn, A. Ledwith, and J. Whittleston, *ibid.*, **72**, 115 (1960).



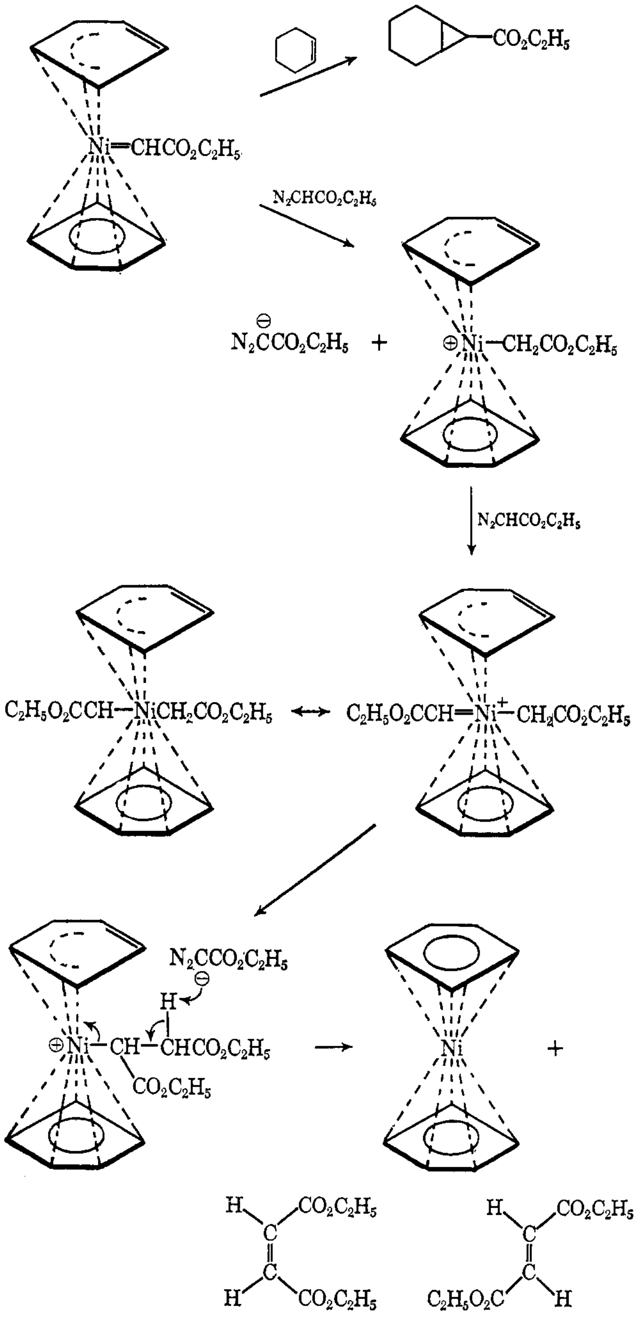
regenerates nickelocene and liberates a molecule of polymethylene.



Methylene produced by photolysis of diazomethane reacts with *trans*-2-butene at a rate slower by a factor of 2.4 than the rate at which this methylene reacts with diazomethane.[27] Moreover, the rate of reaction of methylene with diazomethane is believed to be comparable to the collision rate.[28] Thus, the very high rate of reaction of nickelocene with diazomethane could be another reason that no reaction with olefins is observed. In the case of ethyl diazoacetate, the nickelocene–carbene intermediate can add to olefins or, once two units have been joined, eject a dimeric product. Because of activation by the carbethoxyl group, such an elimination reaction will be favored over the analagous nickelocene–polymethylene intermediate (Scheme I).



Scheme I



The steric requirements of the intermediates discussed above place severe restraints on the size of groups attached to the carbenoid carbon and account, we feel, in part at least for the inertness of diphenyldiazomethane and diazofluorene toward nickelocene.

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(27) H. M. Frey, *Proc. Roy. Soc.*, (London), **A251**, 575 (1959).

(28) G. Herzberg and J. Shoesmith, *Nature*, **183**, 1801 (1959).

Recently Mango and Dvoretzky[29] have studied the interaction of diazomethane with the iridium complex $IrCl(CO)(Ph_3P)_2$ in ether. They have been able to isolate a methylene-containing complex in which the methylene fragment is probably inserted between the iridium and the chlorine atoms. The authors assume that the complex is formed *via* an unstable intermediate containing a methylene group bound as a ligand to the metal. This isolated compound catalyzes decomposition of excess diazomethane to ethylene and nitrogen. In chloroform polymethylene is formed; in styrene the methylene fragment is transferred to the olefin yielding phenylcyclopropane. This behavior of the iridium complex has obvious similarities to the behavior of nickelocene, and the existence of a compound with an iridium–methylene bond supports the mechanism we propose for the reactions of nickelocene with potential carbenoid reagents.

Experimental Section

All reactions were carried out in a nitrogen atmosphere. The solvents, diethyl ether and cyclohexene, were refluxed over sodium wire and then fractionally distilled; their purity was confirmed by vpc analysis. Monomeric cyclopentadiene was obtained from dicyclopentadiene by heating at 200°. The cyclopentadienyl complexes $Ni(C_5H_5)_2$[30] and $Cr(C_5H_5)_2$[31] were prepared as described in the literature.

Photolysis of Diazomethane in Ether in the Presence of Ferrocene. Ferrocene (1.0 g, 5.4 mmol) was dissolved in 70 ml of ethereal diazomethane (prepared from 9 g of N-nitroso-N-methyl-*p*-toluenesulfonamide) and the solution irradiated in a nitrogen atmosphere for 1 hr at 0° with a 200-W Hanovia mercury lamp. The lamp was placed in a quartz waterjacket which was set inside a Pyrex reaction vessel of slightly larger diameter. Ice-water was circulated through the water jacket during the photolysis. Analysis of the reaction mixture by vpc (octyl phthalate column) gave the following products and their relative amounts (in parentheses): CH_2N_2 (trace), MeOEt (0.21), Et_2O (large), *i*-PrOEt (1.0), *n*-PrOEt (1.10).

Photolysis of a 25-fold excess of diazomethane in the presence of ferrocene led to the recovery of ferrocene in quantitative yield.

Photolysis of Diazomethane in Cyclohexene in the Presence of Ferrocene. A solution of ferrocene (1.0 g, 5.4 mmol) and diazomethane (prepared from 8 g of N-nitroso-N-methyl-*p*-toluenesulfonamide) in 80 ml of cyclohexene was irradiated as described above at room temperature. After 6 hr, gas evolution had ceased and the reaction mixture was analyzed by vpc (65°, octyl phthalate column) and was made up of the following substances and their relative amounts (duplicate runs at 0° are given in parentheses): 3- and 4-methylcyclohexene, 1.43, (1.46); 1-methylcyclohexene, 0.17 (0.21); norcarane, 1.0 (1.0).

Decomposition of Diazomethane in Ether Catalyzed by Nickelocene. Nickelocene (190 mg, 1 mmol) was dissolved in 50 ml of ether and 50 ml of a solution of diazomethane (from 5.5 g of N-nitroso-N-methyl-*p*-toluenesulfonamide) added under nitrogen over a period of 10 min. Immediate gas evolution occurred and a flaky white precipitate formed. Nickelocene was recovered in almost quantitative yield from the solution. The infrared spectrum of the white precipitate, mp 132–136°, was identical with that of polymethylene and analyses revealed no nickel or nitrogen in the polymer. The entire volume of gas was condensed and analyzed by vpc under conditions where traces of ethylene or cyclopropane would have been detected (20°, 3% nitrobenzene, Firebrick column). The gas was entirely nitrogen except for a small amount of ether which was collected in the first trap. At a lower temperature (−78°) the rate of reaction of nickelocene and diazomethane decreased slightly; polymethylene was, again, the only reaction product.

Decomposition of Diazomethane in Cyclohexene Catalyzed by Nickelocene. In a similar way, a solution of nickelocene (190 mg, 1 mmol) dissolved in 50 ml of redistilled cyclohexene was treated under nitrogen with 50 ml of diazomethane (from 4 g of N-nitroso-N-methylurea) in cyclohexene. Again there was an immediate evolution of gas and a white flaky precipitate formed. Nickelocene (173 mg) was recovered and vpc analysis of the reaction mixture showed only cyclohexene. If the catalytic decomposition was carried out in the presence of ethylene (by bubbling the gas through the solution) no cyclopropane could be detected.

Decomposition of Diazopropene in Ether Catalyzed by Nickelocene. A solution of nickelocene (190 mg, 1 mmol) in 50 ml of ether was treated at room temperature with an ether solution of diazopropene (from 5 g of N-allyl-N-nitrosourea). After a few minutes gas evolution began and a small amount of gray precipitate (which contained no nitrogen or nickel) formed. The reaction was stopped after 1 hr. Vapor phase chromatography of the solution showed that about 20% of the diazopropene was unreacted. No volatile reaction product could be detected.

Decomposition of Diazopropene in Cyclopentadiene Catalyzed by Nickelocene. When the same reaction was carried out in cyclopentadiene, some precipitate still formed, but the major new product was C_8H_{10}, identical with the substance which is also formed when diazopropene is irradiated in cyclopentadiene solution in the absence of nickelocene.[21] The identity of both compounds was confirmed by their nmr spectra.

Decomposition of Phenyldiazomethane in Ether Catalyzed by Nickelocene. Addition of 100 ml of an ethereal solution of phenyldiazomethane (from 8 g of N-benzyl-N-nitrosourea) to 20 ml of an ethereal solution of nickelocene (190 mg, 1 mmol) at room temperature with stirring resulted in a very slow evolution of gas. A small amount of a polymeric product precipitated, but after 3 hr virtually all (90%) of the phenyldiazomethane remained.

Effect of Nickelocene on Diphenyldiazomethane. Nickelocene has no effect on ethereal solutions of diphenyldiazomethane. Mixtures of these two substances are stable and upon irradiation diphenyldiazomethane decomposes normally giving benzophenone azine, mp 161° (lit. mp 162°), as the major product. Nickelocene can be recovered almost quantitatively.

Effect of Nickelocene on Diazofluorene. Nickelocene has no effect on the decomposition of diazofluorene either in the dark or on irradiation. After photolysis the major product is α,β-bis-diphenyleneethylene, mp 187–189° (lit. mp 189–190°).

Reaction of Ethyl Diazoacetate with Nickelocene. Treatment of 100 ml of cyclohexene solution containing ethyl diazoacetate (0.1 mol) with nickelocene (0.1 mmol) resulted in a vigorous gas evolution. After 36 hr, 30% of unreacted ethyl diazoacetate could be recovered. In addition, four products were separated by vpc—diethyl fumarate, diethyl maleate, ethyl norcaranecarboxylate, and diethyl pyrazoline-3,4,5-tricarboxylate, mp 98° (lit.[32] mp 98–99°), which is formed in small yield (less than 5%). The ratio of diethyl fumarate–diethyl maleate is 1:1.85 and of the mixture of these esters to ethyl norcaranecarboxylate is 4:1. The reaction can be shown to be qualitatively first order in nickelocene; doubling the concentration of nickelocene doubles the rate of nitrogen evolution.

Reaction of Ethyl Diazoacetate with Other Catalysts. Solutions of ethyl diazoacetate (0.1 mol) in cyclohexene (100 ml) were treated with 0.001 mol of various catalysts: (a) nickel tetracarbonyl, (b) cuprous bromide, and (c) cupric sulfate. With nickel tetracarbonyl a vigorous gas evolution began after 30 sec, with cuprous bromide a slower gas evolution was apparent after 20 min, and cupric sulfate required 1.5 hr before appreciable gas was evolved. Copper powder also catalyzed the decomposition of ethyl diazoacetate above 80°. Zinc was also tried but only small amounts of the usual products were formed, most of the ethyl diazoacetate being unreacted. In all cases the rate of gas evolution was a linear function of the catalyst concentration. The products were isolated and Table III gives their ratios.

Dicyclopentadienylchromium as a Catalyst. Addition of dicyclopentadienylchromium (0.001 mol in 10 ml of ether) to diazomethane in ether (0.01 mol) gave only a slow evolution of gas and after standing several hours there was no precipitate, nor could any ethylene or cyclopropane be detected.

With ethyl diazoacetate (0.01 mol) in cyclohexene (100 ml), dicyclopentadienylchromium (0.001 mol) caused a rapid evolution of about 0.001 mol of nitrogen. There then ensued a slow de-

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(29) F. D. Mango and I. Dvoretzky, *J. Amer. Chem. Soc.*, **88**, 1654 (1966).

(30) J. F. Cordes, *Chem. Ber.*, **95**, 3084 (1962).

(31) J. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, **2**, 95 (1956).

(32) T. Curtius, *J. Prakt. Chem.*, (2) **91**, 47 (1915).

composition of the excess ethyl diazoacetate which produced diethyl fumarate, diethyl maleate, and ethyl norcaranecarboxylate in a ratio of 1.5:0.6:1.0.

Effect of Diphenylpicrylhydrazyl. A solution of diazomethane (0.92 g, 22 mmol) in ether (50 ml) was dropped over a period of 20 min into (a) a solution of nickelocene (92 mg, 0.49 mmol) in ether (50 ml), (b) a solution of nickelocene (92 mg, 0.49 mmol) and diphenylpicrylhydrazyl (190 mg, 0.48 mmol) in ether (50 ml), (c) a solution of nickelocene (92 mg, 0.49 mmol) and diphenylpicrylhydrazyl (385 mg, 0.98 mmol) in ether (50 ml). The gas evolution from the three solutions was (a) 390 ml, (b) 375 ml, and (c) 370 ml and the yield of polymeric precipitate was (a) 275 mg (90%), (b) 292 mg (95%); in (c) only a trace of polymer was formed. Diphenylpicrylhydrazyl alone was also found to effect the decomposition of diazomethane in ether with the generation of only a small trace of polymeric product.

Intermediates in Nucleophilic Aromatic Substitution. I. Temperature-Jump Study of the Decomposition of 1,1-Dimethoxy-2,4-dinitrocyclohexadienate in Methanol[1]

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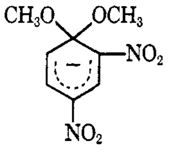
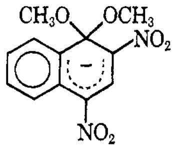
Abstract: The rate of decomposition of 1,1-dimethoxy-2,4-dinitrocyclohexadienate (I) into 2,4-dinitroanisole and methoxide ion has been determined by applying the temperature-jump technique to concentrated solutions of 2,4-dinitroanisole and sodium methoxide in methanol and methanol-o-*d*. An appreciable discrepancy between the equilibrium constant for equilibrium 1 derived from kinetic data and a value reported in the literature is found and discussed. The effect of sodium methoxide concentration on the rates of formation and decomposition of complex I is to increase k_1 and decrease k_{-1}. The activation energy of 11.8 ± 0.5 kcal/mol is found to agree reasonably well with a value of 12.5 kcal/mol predicted by Miller. The present results are discussed with reference to other available kinetic and equilibrium data on related Meisenheimer complexes. The solvent deuterium isotope effect on the equilibrium is $K^H/K^D = 0.38 \pm 0.02$, on the rates is $k_{-1}^H/k_{-1}^D = 1.34 \pm 0.10$ and $k_1^H/k_1^D = 0.51 \pm 0.06$ at 25°. It is interpreted as a secondary solvent isotope effect. Its significance with respect to the mechanism of general base catalyzed nucleophilic aromatic substitutions by amines is discussed.

A large body of evidence has accumulated establishing for nucleophilic aromatic substitution reactions a two-step mechanism involving the formation of an intermediate.[3-10] These intermediates, often referred to as Meisenheimer complexes,[11] aroused considerable interest as to their precise structures, their stabilities, and their rates of formation and decomposition.[12] Depending on the aromatic residue, the attacking nucleophile, the leaving group, and the solvent there is a great variation in the stability of these complexes. Typically the stability increases with any feature in the aromatic residue which brings about a more efficient delocalization of the negative charge, with increasing carbon basicity of nucleophile and leaving group, and with decreasing polarity and hydrogen bond donating ability of the solvent,[13] as long as anionic nucleophiles are involved.[14] The rates of formation and decomposition of these intermediates are expected to correlate with their stabilities.

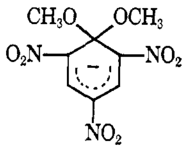
The three complexes designated by I, II, and III, which are formed by addition of methoxide ion to the respective aryl methyl ethers constitute an interesting series of increasingly stable structures with a stability order I ≪ II < III. Complete equilibrium and kinetic data in methanol solution have recently become available on systems II[15] and III,[16-18] as well as incomplete data on system I.[18,19] In this article a kinetic study of the decomposition of the Meisenheimer complex I in methanol is reported, filling the last gap in our knowledge of the rate–equilibrium relationships in series I–III.



I



II



III

The solvent deuterium isotope effect is also reported, and its significance with respect to the mechanistic de-

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[3] J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).

[4] J. F. Bunnett, *Quart. Rev.* (London), **12**, 1 (1958).

[5] J. F. Bunnett and J. J. Randall, *J. Amer. Chem. Soc.*, **80**, 6020 (1958).

[6] S. D. Ross, *Progr. Phys. Org. Chem.*, **1**, 31 (1963).

[7] J. F. Bunnett and R. H. Garst, *J. Amer. Chem. Soc.*, **87**, 3879 (1965).

[8] J. F. Bunnett and C. F. Bernasconi, *ibid.*, **87**, 5209 (1965).

[9] C. R. Hart and A. N. Bourns, *Tetrahedron Lett.*, 2995 (1966).

[10] B. O. Coniglio, D. E. Giles, W. R. McDonald, and A. J. Parker, *J. Chem. Soc., B*, 152 (1966).

[11] J. Meisenheimer, *Ann.*, **323**, 205 (1902).

[12] For a recent review, see R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966).

[13] It is realized that carbon basicity and the influence of the solvent are not independent of each other.

[14] Only Meisenheimer complexes derived from anionic nucleophiles will be our concern in the present paper.

[15] J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, **33**, 977 (1968).

[16] V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1687 (1964).

[17] T. Abe, T. Kumai, and H. Arai, *Bull. Chem. Soc. Jap.*, **38**, 1526 (1965).

[18] J. H. Fendler, *J. Amer. Chem. Soc.*, **88**, 1237 (1966).

[19] C. H. Rochester, *J. Chem. Soc.*, 2405 (1965).