

## HEAVIER ALKALI METALS

ANNUAL SURVEY COVERING THE YEAR 1978\*

EDWIN M. KAISER

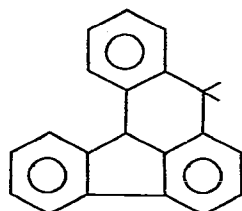
Department of Chemistry  
 University of Missouri-Columbia  
 Columbia, Missouri 65211, U.S.A.

## TABLE OF CONTENTS

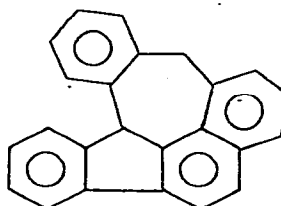
1. PHYSICAL ORGANIC CHEMISTRY . . . . .	107
2. SYNTHETIC ASPECTS . . . . .	119
3. INORGANIC AND ORGANOMETALLIC COMPOUNDS . . . . .	127
4. REFERENCES . . . . .	133

1. PHYSICAL ORGANIC CHEMISTRY

An even larger number of papers appeared in 1978 than in 1977 which discussed the acidities of a variety of active-hydrogen organic materials. Thus, the  $pK_a$  of hydrocarbon 1 has been found to be 15.45 using the cesium cyclohexylamide system with compound 2 serving as a reference [1]. The difference in the  $pK_a$  of 1 and fluorene itself is ascribed to about one-third polar and two-thirds conjugation effects.



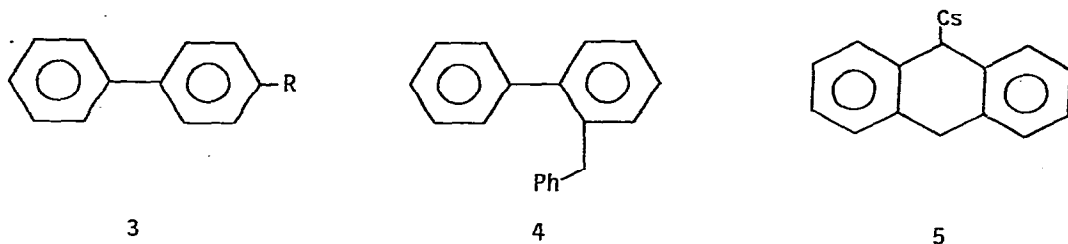
1



2

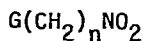
The cesium system was also employed to determine the following  $pK_a$  values: 3 (R = Me), 38.95 (a corrected value) [2]; 3 (R = Et), 38.8 [2]; 3 (R = i-Pr), 38.6 [2]; 4, 33.5 [3]; 3 (R =  $CH_2Ph$ ), 31.8 [3]; 9,10-dihydroanthracene, 30.3 [4]; and 5, 34.1 [4].

\* Heavier alkali metals; Annual Survey covering the year 1977 see J. Organometal. Chem., Vol. 163 (1978) p. 1 - 16.

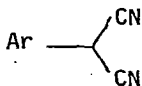


Tritium quenching by titrated benzenesulfonic acid of equilibrium mixtures of phenylacetylenes and sodium methoxide in methanol has been employed to determine directly the acidity of the hydrocarbons [5]. The method gave pKa values for phenylacetylene itself of 18.50 to 18.15 at temperatures of 0° and 25°, respectively. Such values are compared to those obtained in cyclohexylamine (23.2) and DMSO (28.8). Another paper listed pKa values of a variety of acetylenes,  $RC\equiv CH$ , in DMSO using dimethyl ion as studied by dynamic  $^1H$  and  $^{13}C$  NMR spectroscopy [6]. The following numbers are provided: R = Ph, 22.6; R =  $MeOCH_2$ , 23.5; R =  $Me_2NCH_2$ , 24.2; R = H, 25.5; R = n-Bu, 26.7; R = Me, 27.4; and R = t-Bu, 27.6.

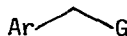
A series of full papers dealing with the acidities of carbon acids substituted with carbonyls, nitro groups, and others appeared in 1978. First, the effect of substitution of methyl for hydrogen upon acidities has been divided into four categories: 1) acid-weakening hyperconjugative and polar methyl effects illustrated by formic acid-acetic acid, 3-nitropropene-1-nitro-2-butene, and others; 2) acid-strengthening hyperconjugative and polar methyl effects, e.g., acetophenone-propionophenone, nitromethane-nitroethane, and others; 3) acid-weakening polar methyl effects illustrated by methyl phenyl sulfone-ethyl phenyl sulfone, malonitrile-1,1-dicyanoethane, and others; and 4) acid-weakening steric methyl effects, e.g., 1-nitro-2-butene-4-nitro-2-pentene and others [7]. The data are compared with data obtained from gas-phase studies. Second, the equilibrium acidities of 25 nitroalkanes 6 ( $n = 1, 2, 3$ ; G =  $SO_2Ph$ , CN, SPh, OPh, etc.) have been determined and correlated with Taft  $\sigma^*$  constants [8]. It is concluded that "although  $\sigma_{CH_2G}^*$  (or  $\sigma_1$ ) constants give an approximate measure of polar effects, their size and sometimes even their relative order change as the geometry of the system is changed." The other papers discuss both equilibrium and kinetic acidities in terms of the substituent effects for 20 nitroalkanes [9], a variety of  $C_3$ - $C_8$  and  $C_{12}$  nitrocycloalkanes [10], and 3-nitropropene and certain derivatives [11]. Changes in alkyl substitution of the nitroalkanes caused larger effects in kinetic than in equilibrium acidities. A linear correlation between the Hammett  $\rho$  and the size of the  $\alpha$ -phenyl effect has been realized in a related study on the equilibrium acidities of 7 and 8 (G = Ph, CN, COMe,  $NO_2$ ) [12].



6



7

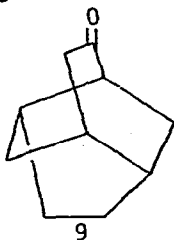


8

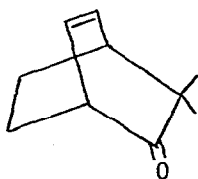
The pKa values and oxidation potentials of 44 cyanoaldehydes, cyanoketones, cyanoesters,  $\beta$ -diketones,  $\beta$ -ketoaldehydes, and others have been determined [13]. A correlation between the two values has been found for many of the compounds which has enabled the authors to define a stability range of the carbanions in solution.

A linear correlation in the plot of the reported pKa values of 14 meta- and para-substituted acetophenones versus Hammett  $\sigma$  constants with  $\rho = 3.55 \pm 0.05$  has been realized [14]. Since only slightly greater deviations were found for the nine other compounds studied, the authors conclude that  $\sigma$  constants derived from benzoic acids in water are applicable with remarkable precision for most acetophenones in DMSO."

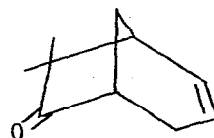
Additional studies of the rates of hydrogen isotope exchange of several polycyclic ketones, effected by alkali alkoxides or deuterioxide, were reported in 1978. Thus, a kinetic selectivity of 290:1 has been observed in such exchange of the  $\alpha$ -diastereotopic protons of twistan-4-one (9) [15].  $^1H$  NMR spectroscopy was employed to determine that the more rapidly exchanging  $\alpha$ -proton is the one with a dihedral angle of  $80^\circ$  with the bridgehead proton at C-6. The results are ascribed to stereoelectronic control. The rates and stereoselectivity of this exchange in ketones 10-12 have been similarly studied using  $^2H$  NMR spectroscopy [16]. The presence of the double bond in 10 has been found to enhance  $\beta$ -enolate formation and subsequent rearrangement to 11 and 12. The rates of both allylic and vinylic exchange are enhanced by the carbonyl groups. Finally, both the exo and endo  $\alpha$ -protons of thio-camphor (13) undergo more rapid exchange than those of camphor itself [17]. The results are explained by a ground state effect and the ability of sulfur to support a negative charge.



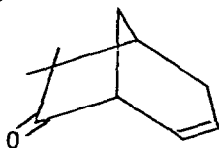
9



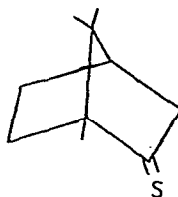
10



11

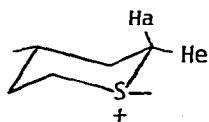


12

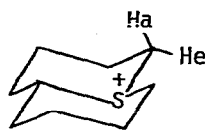


13

A similar study of the kinetic acidity of the  $\alpha$ -diastereotopic protons of sulfonium salts such as 14 and 15 has revealed that  $k_{\text{He}}/k_{\text{Ha}}$  for these compounds is 0.5 and 35, respectively [16]. The authors conclude that "the dependence of acidity on geometrical factors is related to the reacting system ability to achieve a conformation where the incipient lone pair orbital at  $\text{C}_\alpha$  is either syn or anti aligned with one of the vicinal bonds at sulfur."



14



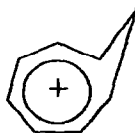
15

Two other papers which deserve mention in this area discussed the stopped-flow kinetics of proton transfer of cyclopentadiene derivatives [19], and the effects of adjacent lone pairs in heteroaromatic systems applied to isotope exchange of ring hydrogens in alkylimidazoles [20].

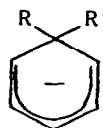
Turning to the area of spectroscopy, the use of  $^{23}\text{Na}$  NMR spectroscopy has been reviewed [21]. In contrast to cations 16 and 17,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy has revealed that potassium salts 18 ( $\text{R}, \text{R}' = \text{H}$  and/or  $\text{Me}$ ) in ammonia are planar species [22]. MINDO/3 calculations on 18 ( $\text{R} = \text{R}' = \text{H}$ ) indicated the planar form constituted a shallow energy minimum.



16

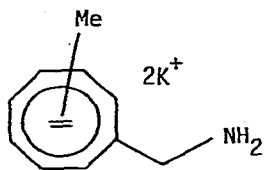


17

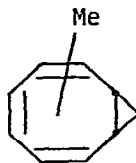


18

$^1\text{H}$  NMR spectra of the 1-, 2-, 3- and 4-methyl derivatives of 19, prepared from 20 and potassium amide in liquid ammonia, have been obtained to aid in the determination of the regioselectivities in such reactions [23]. It is believed that the reactions first proceed via proton abstraction of a bridgehead proton.

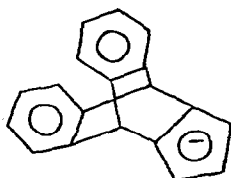


19

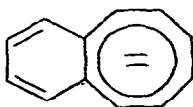


20

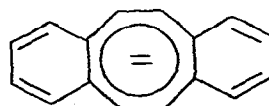
The  $^1\text{H}$  NMR spectra of a variety of other carbanions have been recorded including triptycene analog 21 [24], benzo systems 22 [25], 23 [26], and 24 [26], annulene 25 [27] including a discussion of its topomerization [28], and annulene 26 and its methyl derivative [29].



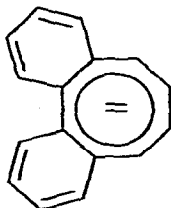
21



22



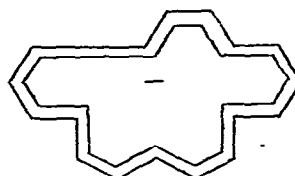
23



24

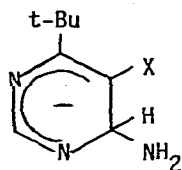


25

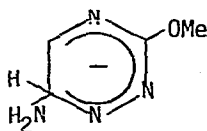


26

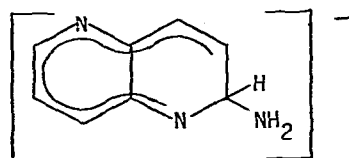
NMR spectroscopy has been employed to verify the existence of  $\sigma$ -adducts in the reaction of certain nitrogenous heterocycles with potassium amide in liquid ammonia. The types of adducts observed included 27 from pyrimidines ( $^1\text{H}$  NMR) [30], 28 from triazines ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) [31], and 29 and others from naphthyridines ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) [32,33].



27



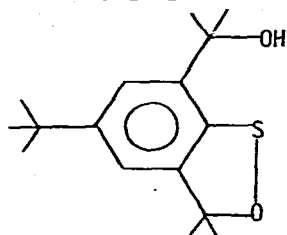
28



29

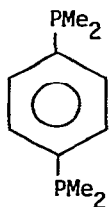
Other NMR studies have been concerned with the shape and inversion of allenic anions derived from disubstituted adamantanes ( $^1\text{H}$  NMR) [34], the detection of dialkali salts derived from carboxylic acids, esters, and ketones ( $^{13}\text{C}$  NMR) [35], the structure of the tricoordinate hypervalent sulfuranide anion derived from 30 and potassium hydride ( $^1\text{H}$  NMR) [36], and ionic mobility and contact ion pairing in a

perfluorosulfonate ionomer ( $^{23}\text{Na}$  NMR) [37].

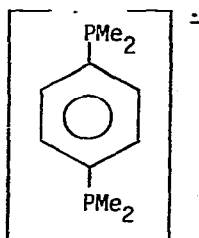


30

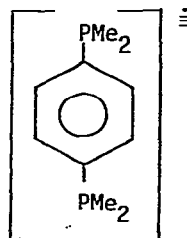
Reduction of bisphosphine 31 by sodium, potassium, or electrochemically has been shown by ESR to afford radical anion 32 which, with further metal, gives radical trianion 33 [38,39]. The ESR spectrum of the latter compound is also described. Attempts to oxidize 31 to the radical cation have been unsuccessful [39].



31

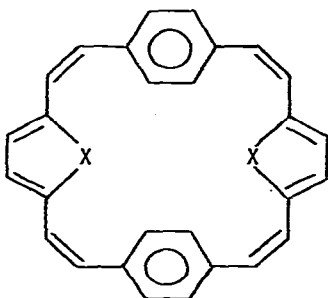


32



33

ESR and ENDOR spectra have been obtained for paracyclophanes 34 ( $X = \text{O}, \text{S}$ ) and related ones possessing four benzene and four thiophene rings as well as their deuterated derivatives [40]. The hyperfine data are consistent with conformations which should minimize deviations of the macrocyclic  $\pi$ -systems from planarity.



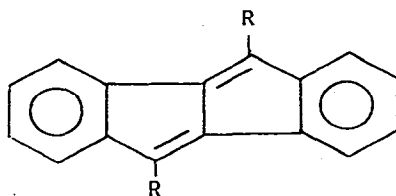
34

ESR spectroscopy on the *cis* and *trans* isomers of 35 ( $G = H, CN, CHO, NO_2$ ) has been employed to study the conformational behavior of such compounds [41]. This technique has revealed that the conformational rigidity of the radical anions is greater than that of the corresponding diamagnetic compounds.



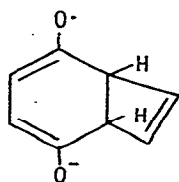
35

Proton hyperfine data have been obtained for the radical anions and cations of pentalenes 36 ( $R = H, Me$ ) [42] and compared with reexamined, higher resolution ESR spectra of the radical anions and cations of 1,3,5-tri-*t*-butylpentalene [43]. A simple MO model was employed to allow assignment of the coupling constants to pairs of equivalent protons.

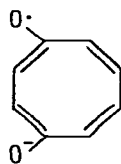


36

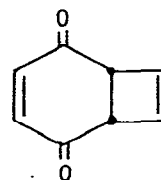
A chapter from a symposium on organic free radicals dealing with the semidione spin probe to study molecular rearrangements was published in 1978 [44]. Specific papers dealing with this area discussed the preparation of 37 rather than its valence isomer 38 by reduction of 39 and 40 and by oxidation of 41 [45], the presence of only the more stable *trans* semidiones such as 42 ( $Me = Li, Na, K$ ) in the presence of cryptands and crown ethers [46], and the existence of two types of ion pairs such as 43 and 44 as a function of cryptands [47]. Another paper described intramolecular migration of the metal ion between the two carbonyl groups of 45 and the formation of alkali cationic triple ions such as 46 [48]. The latter compounds afforded very high resolution in their ESR spectra which was ascribed to their unusual thermal stability.



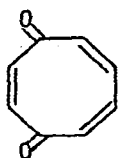
37



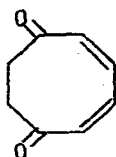
38



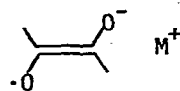
39



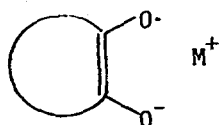
40



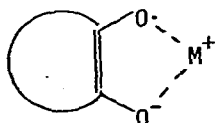
41



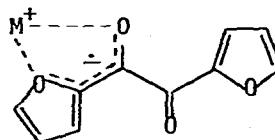
42



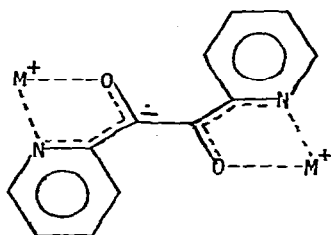
43



44

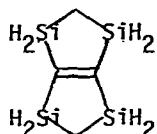


45

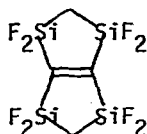


46

Other papers describing the results of investigations employing ESR spectroscopy were concerned with the blue solutions obtained from potassium, ammonia, and 18-crown-6 [49] and the radical anions of 47 and 48 [50].



47

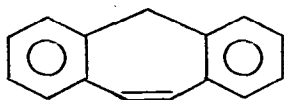


48

That the disproportionation constant of sodium *trans*-stilbenide is about 100 times smaller than that of the *cis*-radical anion is due to release of steric strain has been confirmed by the finding that the disproportionation constant of 49 is similar to the former stilbenide as determined by UV spectroscopy [51]. This same



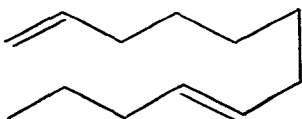
type of spectroscopy was employed in the laser-pulse photolysis of sodium trans-stilbene dianion to afford, at least partially, sodium cis-stilbenide [52]. This compound then reacts with the trans dianion to give cis dianion and trans stilbenide; the cis dianion then rapidly yields the trans dianion.



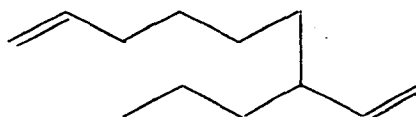
49

Finally, in the area of spectroscopy, IR techniques have been applied to the determination of the structure of potassium ethyl acetoacetate in the presence of a cryptand [53], to ascertain the presence of three ion sites for  $\text{NaCo}(\text{CO})_4$  in oxetane [54], and to characterize the reaction products of alkali halide and cyanide with ammonia in argon matrices [55].

Users of the 5-hexenyl probe for alkyl radical intermediates have been warned that prototropic isomerization to afford 1-propylallyl anions has been observed [56]. Thus, for example, 5-hexenyl chloride and cesium metal in ethers gives 50 and 51 in combined yields of up to 69%.



50



51

In an effort to establish the thermodynamic stability of 52 ( $\text{R} = \text{sodium}$ ) relative to other  $(\text{CH})_9^-$  isomers, reduction of both 52 ( $\text{R} = \text{I}$ ) and 53 by sodium in ammonia gives hydrocarbon 52 ( $\text{R} = \text{H}$ ) [57]. Since opposite isomerizations of carbonium ions derived from systems related to 52 and 53 have also been realized, the two carbon skeletons are interconvertible by merely controlling the formal charge on the systems.

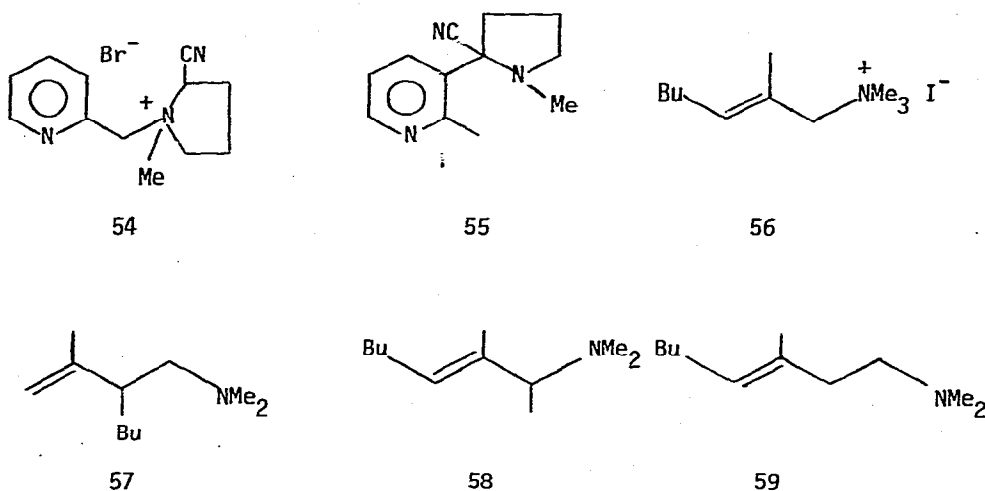


52

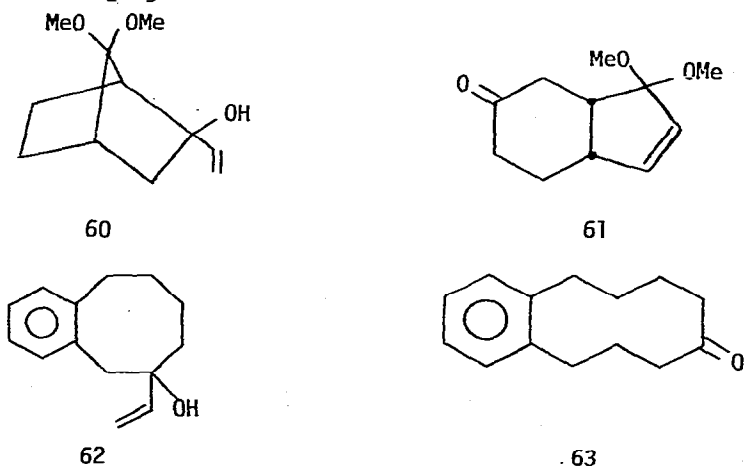


53

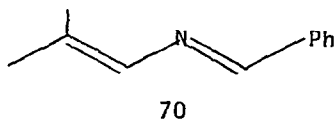
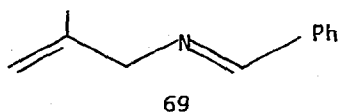
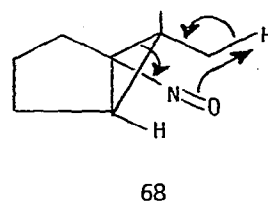
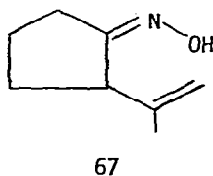
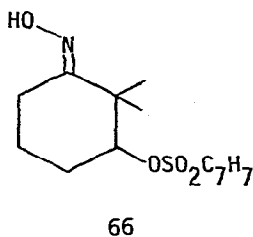
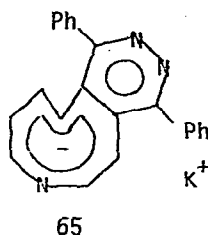
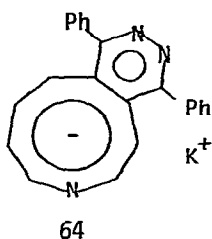
Sommelet-Hauser rearrangements have been successfully employed in the preparation of nicotine analogues [58]. For example, 54 and potassium *t*-butoxide gave 55 which was converted to 2-methylnicotine by LAH. Another paper revealed that [3,2]- rather than [1,2]-Stevens rearrangements of certain 2-alkenylquaternary ammonium salts can be obtained depending upon the choice of base [59]. For example, while 56 and dimethyl sodium affords only [3,2]-product 57, 56 and *n*-butyllithium give 57 as well as the [1,2]-products 58 and 59.



A large number of additional examples of the anionic oxy-Cope rearrangement of alkoxides was reported in 1978. The substrates were derived from bicyclo[2.2.1]-heptenes [60], bis-allylic tricyclo systems [61], medium ring systems [62], dienols [63], and bicyclo[3.2.0]heptenes [64]. The process is illustrated by the conversion of 60 to 61 and 62 to 63. Examples are described which include aromatic rings as the olefinic component [60]. The dienols are conveniently converted to 1,6-dicarbonyl derivatives [63].



Three other papers deserve mention at this point. First, anion 64, prepared from the ethyl carbamate and potassium amide in liquid ammonia, has been found to isomerize to 65 at 0° [65]. Reversion of such isomerization by heat is described. Secondly, treatment of oxime tosylates with potassium t-butoxide has been shown to cause such systems to undergo intramolecular C-alkylation [66]. For example, 66 affords 67 apparently via 68. Finally, N-allylic imines and  $\alpha,\beta$ -unsaturated imines have been found to undergo facile prototropic isomerization to N-alkenylimines by potassium t-butoxide [67]. The process is illustrated by the conversion of 69 to 70. The latter reagent and others are conveniently metalated by t-butyllithium.

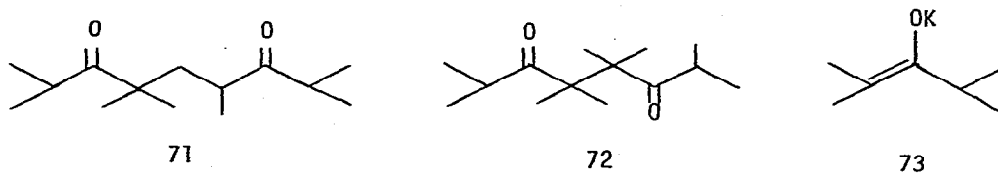


Kinetic studies reported in 1978 were concerned with the isomerization of *cis,cis,cis,trans*-[9]annulene anion 25 into the more thermodynamically stable all-*cis*-[9]annulene anion [68], substituent effects on the reductive cleavage of *N*-methyl-arenesulfonanilides by sodium anthracenide [69], differences in epoxide cleavage rates by organoalkali salts as a function of the alkali cations [70], and the propagation step in the anionic polymerization of methyl methacrylate with cumylcesium and  $\alpha$ -methylstyrylsodium [71]. An unrelated paper described a set of equilibrium

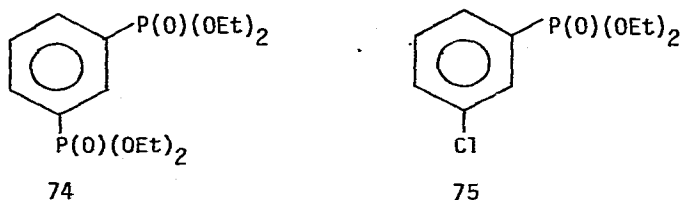
constants for aldol condensations of several simple aldehydes and ketones [72].

Nucleophilic aromatic substitutions continued to be studied in 1978. Review articles discussed the  $S_N$ (ANRORC) mechanism [73] and the  $S_{RN}1$  mechanisms [74,75] in such reactions.

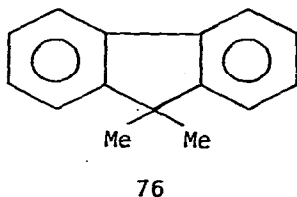
The formation of side-product diketone 71 rather than the previously described 72 in the photostimulated reaction of 73 with iodobenzene has been ascribed to a novel intermolecular hydrogen atom transfer between phenyl radicals and 73 [76].



Three full papers were concerned with photostimulated condensations of alkali diethyl phosphite ion with aryl halides [77-79]. Thus, while *m*-bromiodobenzene gave mostly 74, *m*-chloriodobenzene afforded 75 with 74 present in some but not all reactions. Mechanistic aspects are discussed.



Halogen derivatives of phenanthrene, naphthalene, and biphenyl have been converted to phenyl selenide derivatives by alkali phenyl selenide in ammonia under irradiation [80]. Dimethyl sodium has been phenylated similarly [81]. Incidentally, photolysis of several resonance delocalized anions in DMSO in the presence of catalytic amounts of iron(III) chloride have been found to yield methylated derivatives of the anions [82]. For example, the 9-methylfluorene anion gave 9,9-dimethylfluorene (76) (48%). Photocyclization of certain enolates of  $\beta$ -ketoesters has also been described [83].



A review appeared in 1978 which discussed nucleophilic displacement of aromatic nitro groups [84].

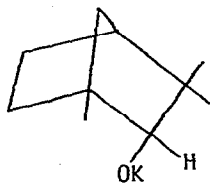
One entire issue of The Journal of Physical Chemistry devoted to radical ions was published in honor of Professor Michael Szwarc. The papers therein appropriate for inclusion in this survey discussed solvation of the radical anion of 2-chloroquinone [85], the molecular and magnetic structure of the paramagnetic ion pair of bis(tetraglyme)potassium biphenyl [86], kinetics of protonation of potassium anthracenide by ethanol in THF including the effect of crown ethers and cryptands [87], competitive reaction modes of the 1,3-cyclohexadiene radical anion [88], EPR studies of the formation of propanol solvated ion pairs of 2,5-di-*t*-butylbenzoquinone [89], an experimental estimate of the lower bound on the energy separation between the ground and first excited states of the *p*-xylene radical anion [90], ion-pair formation in alkali metal salts of 1,2-semidiones [91], and picosecond time-resolved spectroscopic study of solvated electron formation from the photoexcited  $\beta$ -naphthoate ion [92].

Other papers in this section were concerned with a perturbational interpretation of C-versus O-alkylation selectivity and electrophile leaving group effect [93], the interaction of carbanions with phenylchloroacetylene [94], a review of the use of cryptates [95], enhanced reactivity of potassium *t*-butoxide towards electrophiles by crown ethers [96], stereochemical control of Michael condensations by crown ethers and cryptands [97], the effect of crown ethers on the reductive dimerization of alkali derivatives of Schiff bases [98], the effect of poly(vinylmonobenzo-18-crown-6) and other crown ethers on the reaction of sodium phenoxide with allyl chloride [99], substituent effects on alkene-forming eliminations from carbanions [100], a dispute about the source of hydrogen gas from the radical anions of certain aromatic hydrocarbons and water [101,102], the crystal and anion structure of sodium cyanamide [103], and the chemistry of 2-methylpentadienyl- and 2,4-dimethylpentadienyl-potassium, the first examples of U-shaped, through open-chain, organometallics [104].

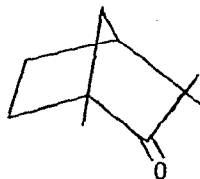
## 2. SYNTHETIC ASPECTS

The synthesis of benzocyclopropenes has been reviewed [105].

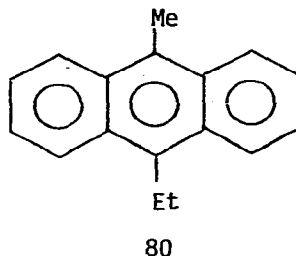
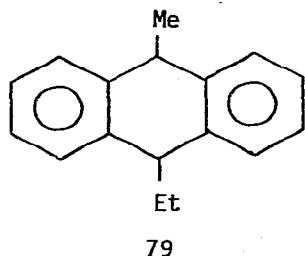
Two more papers appeared in 1978 which discussed deprotonation-hydride elimination as a method of dehydrogenation [106,107]. For example, potassium fencholate (77) and fenchone (78) convert 79 to 80 (92%) after 30 hr.



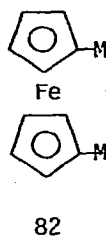
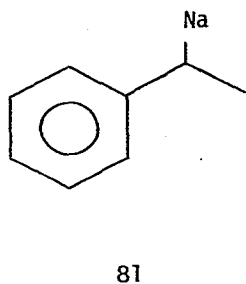
77



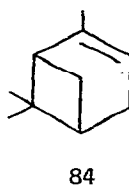
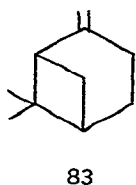
78



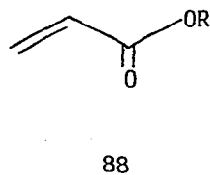
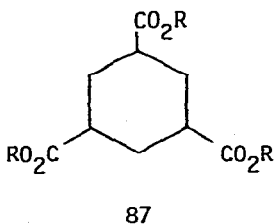
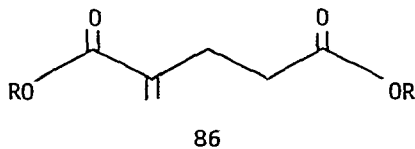
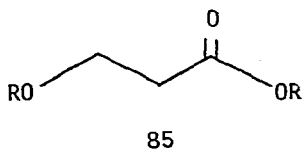
The rate of metalation of ethylbenzene with *n*-pentylsodium has been dramatically increased by TMEDA to afford 81 (>95%) after only 1 hr. [108]. Similar enhanced rates were also realized with this system on ferrocene to give mostly 82 (M=Na) [109]. 1,1'-Dipotassioferrocene (82, M=K) has been obtained from ferrocene and *n*-butylpotassium, prepared from potassium (-)(1*R*)-menthoxide and *n*-butyllithium [110]. Ferrocenes containing up to eight metal atoms have been prepared using an excess of *n*-butylpotassium.



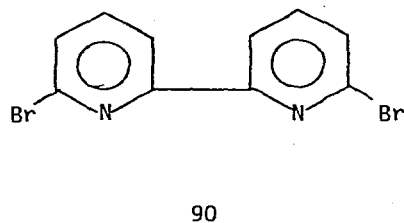
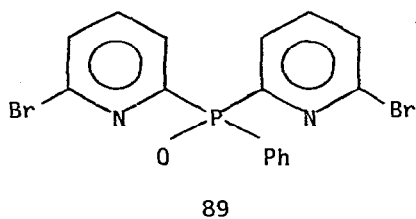
Terminal alkenes may be conveniently isomerized to internal ones by treatment with catalytic quantities of potassium 3-aminopropylamide in the parent amine [111]. For example, 83 is converted into 84 (>99.5% isomeric purity, optical yield  $\geq$  99%).



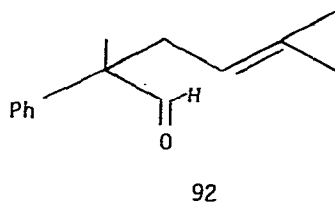
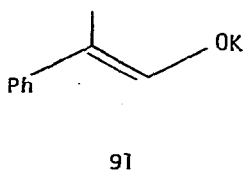
Lower molecular weight products 85-87 have been obtained from 88 and potassium-benzylpotassium [112]. In each case, R=2-ethyl-1-hexyl. The catalytic activities of related sodium and lithium systems are discussed. An unrelated paper discussed the use of complex base systems  $\text{NaNH}_2\text{-RONa}$  in anionic polymerization where R = a variety of alkyl groups [113].



A convenient phosphorus expulsion reaction which allows for the formation of heteroaryl-heteroaryl bonds has been described [114]. The process is illustrated by the conversion of 89 to 90 by sodium ethoxide in toluene at 100°C. The paper also describes the preparation of several such bipyridyls which comprise a portion of macrocycles containing seven oxygen atoms as part of the ring systems.

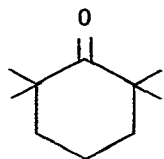


Direct C-alkylations of aldehyde enolates, prepared from potassium hydride in THF, have been effected in excellent yield [115]. For example, 91 affords 92 (94%).

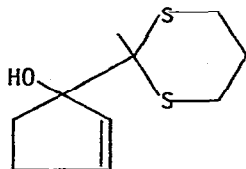


Cyclohexanone has been found to undergo mostly enolization rather than reduction by sodium hydride in a variety of solvents and by potassium hydride in dioxane as evidenced by silylation with chlorotrimethylsilane [116]. The latter base in THF

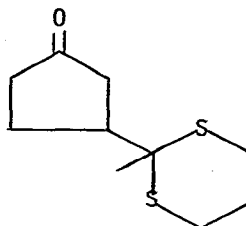
has been employed to permethylate cyclic ketones (e.g., cyclohexanone yields 93) using methyl iodide [117], and in 80% HMPA/THF to effect the conversion of 1,2-adducts such as 94 to 1,4-adducts such as 95 [118]. The latter procedure has been employed as a portion of the synthesis of d,l-muscone.



93



94

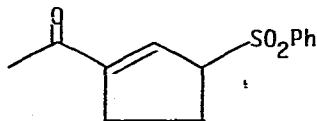


95

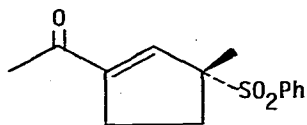
$\gamma$ -Alkylation of  $\alpha,\beta$ -unsaturated ketones has been effected by the use of the phenylsulfonyl moiety as a regiospecific control element [119]. Thus, for example, methylation of enolate 96, prepared from 97 and sodium hydride in THF-HMPA, gave mostly 98 (62%). Other examples are described. Another paper discussed conjugate additions of ketone enolates to nitroenamines such as 99 as a means of extending active hydrogen compounds by an even number of methylene groups [120].



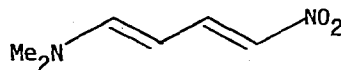
96



97



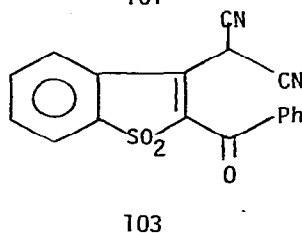
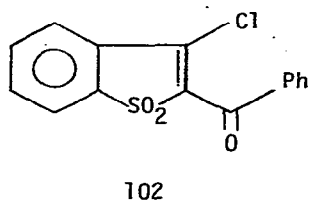
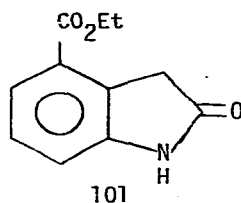
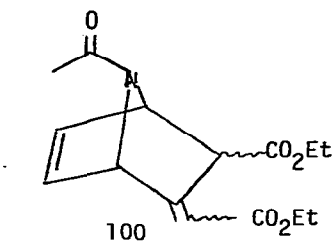
98



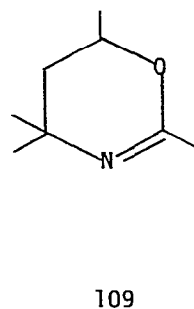
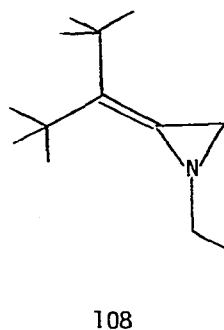
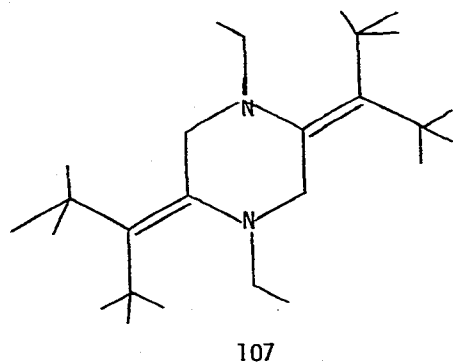
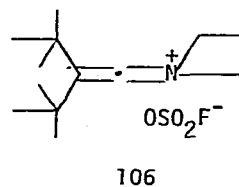
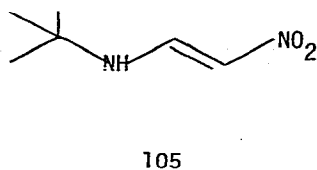
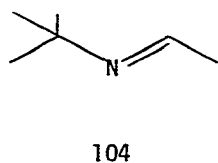
99

Oxindoles and benzofurans have been synthesized by potassium hydride induced  $\beta$ -elimination of the heteroatom bridge of certain 7-heterobicyclo[2.2.1]heptenes [121]. The procedure is illustrated by the conversion of 100 to 101. Another paper described displacement of the vinyl chloride of 102 by a variety of metal enolates to afford products such as 103 [122].



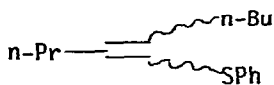


Alkyl nitration of carbanions using nitrate esters has been applied to aldimines [123] and alkylphosphonate esters [124]. For example, 104, potassium amide, and ethyl nitrate in ammonia gave 105. Deprotonation of hindered keteniminium salt 106 with sodium bis(trimethylsilyl)amide has been reported to yield piperazine dimer 107 rather than desired aziridine 108 [125]. Potassium-graphite has been shown to metalate imines and oxazine 109 in synthetically useful yields; [126]. Reactions of potassium-graphite with alkyl halides to afford alkanes and with alcohols to give alkoxides have been reported [127].

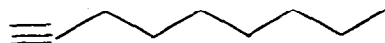


Potassium *t*-butoxide-*n*-butyllithium-diisopropylamine has been found to metalate nitrosamines more rapidly than lithium diisopropylamide (LDIPA) [128]. Moreover, the resulting potassium nitrosamines are more reactive than previously described metal derivatives of such compounds.

Vinyl sulfides such as 110 have been converted to acetylenes such as 111 by potassium 3-aminopropylamide [129]. Vinyl ethers behave similarly.

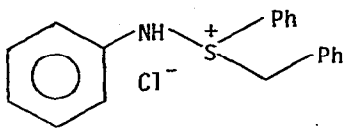


110

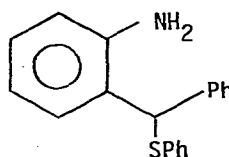


111

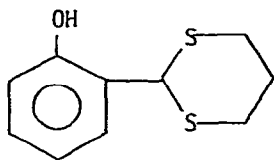
A full paper described the details about specific ortho functionalization of aromatic amines via intramolecular rearrangement of ylides derived from azasulfonium salts [130]. Among the many examples listed was the conversion of 112 to 113 effected by sodium methoxide. Similar rearrangements have been realized on phenolic systems as illustrated by the preparation of 114 from 115 [131].



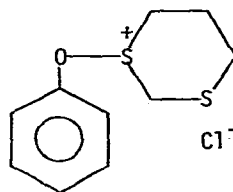
112



113

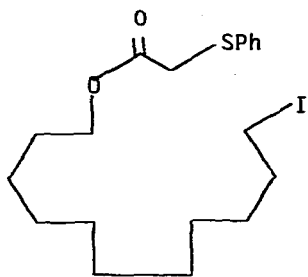


114

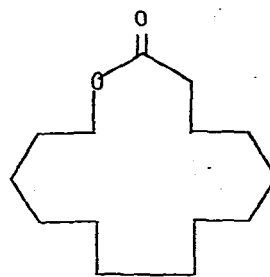


115

Intramolecular alkylations of haloalkyl phenylthioacetates such as 116, effected by potassium bis(trimethylsilyl)amide, have been employed to prepare macrolides such as 117 [132].

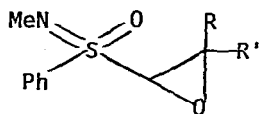


116

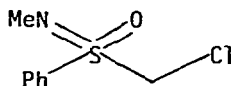


117

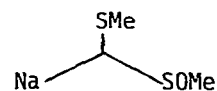
Epoxy sulfoximines 118 have been synthesized from 119, benzaldehyde or ketones, and potassium *t*-butoxide in DMSO [133]. Sodio salt 120 has been condensed with aliphatic and aryl nitriles to afford  $\alpha$ -ketoesters and  $\alpha$ -ketothioesters [134].



118

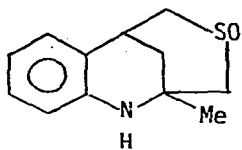


119

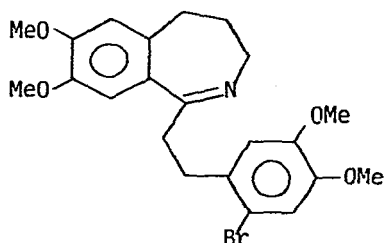


120

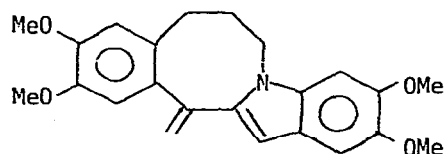
Dimethyl anion has been added to 2-methylquinoline to give 121 [135] and with 122 to yield mostly 123 [136].



121

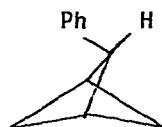


122

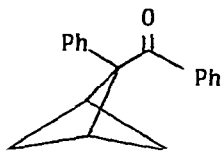


123

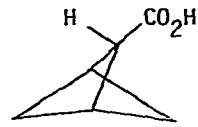
Bicyclo[1.1.1]pentane 124 has been obtained in quantitative yield from 125 and sodium amide [137]. Subsequent conversion of 124 to 126 by ruthenium dioxide/sodium periodate (>85%) allows the synthesis of 2-substituted bicyclo[1.1.1]-pentanes.



124



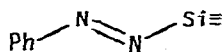
125



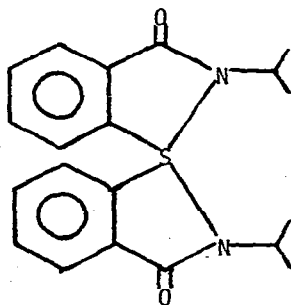
126

The scope and limitations of the reduction of carbonyl compounds by "NaH-t-AmONa-Ni(OAc)<sub>2</sub>" have been delineated in a full paper [138]. Other papers concerned with reductions described the conversion of 4-phenylbenzoic acids to alcohols and hydrocarbons by alkali metal-ammonia solutions [139] and the reduction of alkyl esters to alkanes by sodium in HMPA [140].

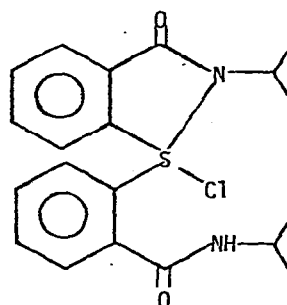
Other papers in this area were concerned with the conversion of aryl halides to arenes by sodium methoxide/Pd(PPh<sub>3</sub>)<sub>4</sub> in DMF [141], the mild synthesis of phenylsodium by interaction of 127 and sodium methoxide [142], the preparation of the first example of a sulfurane with two apical nitrogen ligands, 128, from 129 and potassium hydride [143], the synthesis of 130 from 131 and malononitrile [144], alkoxy exchange and/or alcohol elimination in β-oxoacetals by alkoxides [145], and the preparation of C-fluorophosphaethyne (132) by treatment of trifluoromethylphosphine vapor and potassium hydroxide [146].



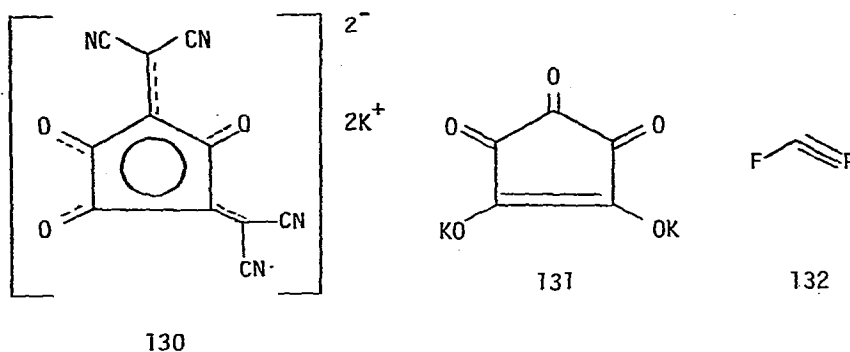
127



128

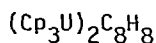


129



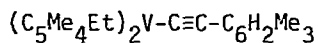
### 3. INORGANIC AND ORGANOMETALLIC COMPOUNDS

A gray powder obtained from praseodymium(III)chloride and potassium has been found to convert *cis,cis*-1,5-cyclooctadiene to  $C_8H_8^{2-}$  [147]. Actinide complex 133 has been obtained from the reaction of tris(cyclopentadienyl)chlorouranium(IV) and dipotassium cyclooctatetraenide [148].

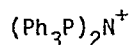
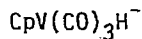


133

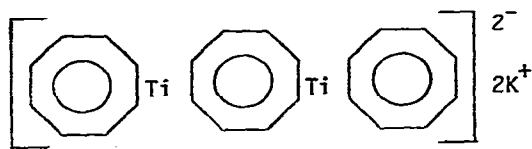
Stable  $\sigma/\pi$ -complex 134 has been prepared from peralkylated vanadocene bromide and sodiomesitylacetylene [149]. The MS,  $^1H$ -NMR, and X-ray data for 134 are reported. Anionic vanadium carbonyl hydride 135 has been synthesized from  $CpV(CO)_4$  and sodium followed by water, then  $(Ph_3P)_2N^+Cl^-$  [150]. Reagent 135 converts alkyl bromides to alkanes and acid chlorides to aldehydes apparently via a radical chain mechanism. Niobium-containing reagent,  $C_8H_8NbCl_2 \cdot THF$ , prepared from niobium(V) chloride and  $K_2C_8H_8$ , has been combined with cyclopentadienyl sodium to afford  $Cp_2NbC_8H_8$  in which the  $C_8H_8$  is bonded to the metal in an unusual dihapto mode [151]. Reduction of tris(cyclooctatetraene)ditanium with potassium is suggested to afford 136 [152].



134

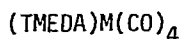


135

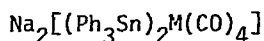


136

Other "superreduced" organometallics,  $\text{Na}_4\text{M}(\text{CO})_4$ , ( $\text{M}=\text{Cr}, \text{Mo}, \text{W}$ ) have been prepared by reduction of 137 using sodium in liquid ammonia [153]. The compounds have been converted to 138 by chlorotriphenylstannane.

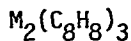


137

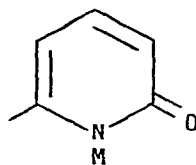


138

Quadruply bonded 139 ( $\text{M}=\text{Mo}, \text{W}$ ) have been prepared by interaction of  $\text{K}_2\text{C}_8\text{H}_8$  with molybdenum(IV) and tungsten(IV) chlorides, then characterized by X-ray crystallography [154]. Similar quadruple bonds have been realized in condensations of 140 with chromium and molybdenum acetates and hexacarbonyltungsten [155].

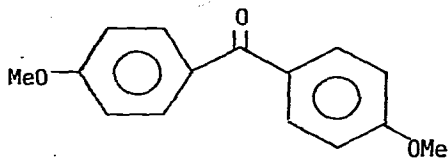


139

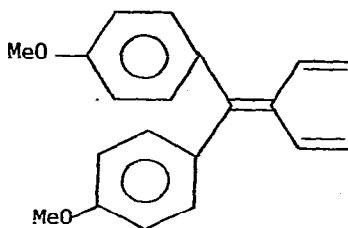


140

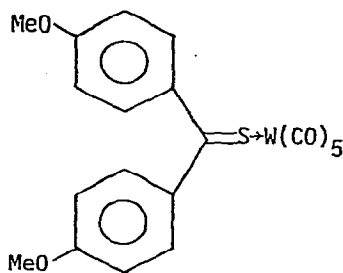
Certain transition metal anions have been found to add to thioketones in a thiophilic fashion to afford fulvenes [156]. For example,  $\text{NaCpW}(\text{CO})_3$  and 141 gives 142. Similar results have been realized with related iron and molybdenum species. In contrast,  $\text{Na}_2\text{W}_2(\text{CO})_{10}$  and 141 yields 143 [157].



141

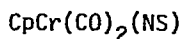


142

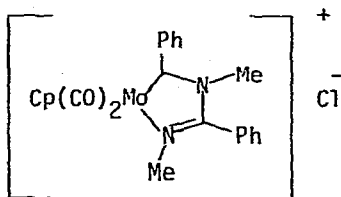


143

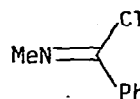
The thionitrosyl functionality has been introduced directly into organometallic complexes as illustrated by the preparation of 144 from  $\text{NaCpCr}(\text{CO})_3$  and  $\text{S}_3\text{N}_3\text{Cl}_3$  [158]. Another paper described the synthesis of chelate 145 from  $\text{NaCpMo}(\text{CO})_3$  and 146 [159].



144



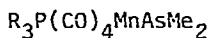
145



146

Other papers in this triad discussed the synthesis, structures, and reactions of  $\eta^5$ - and  $\eta^6$ -derivatives of fluorenyl- and indenyl-transition metal complexes [160], and the chemical and electrochemical reduction of  $\text{C}_7\text{H}_8\text{W}(\text{CO})_3$  [161].

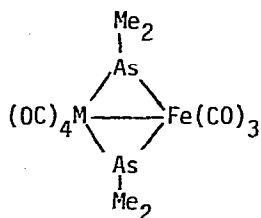
Metal carbonylate anions may now be conveniently prepared by reductive cleavage of dinuclear carbonyls with potassium hydride in THF or HMPA/THF [162]. Such reductions of  $[\text{Mn}(\text{CO})_5]_2$ ,  $[\text{Co}(\text{CO})_4]_2$ ,  $[(\text{Ph}_3\text{P})\text{Co}(\text{CO})_3]_2$ ,  $[\text{CpMo}(\text{CO})_3]_2$ , and  $[\text{CpFe}(\text{CO})_2]_2$  afford  $\text{KMn}(\text{CO})_5$ ,  $\text{KCo}(\text{CO})_4$ ,  $\text{K}(\text{Ph}_3\text{P})\text{Co}(\text{CO})_3$ ,  $\text{KCpMo}(\text{CO})_3$ , and  $\text{KCpFe}(\text{CO})_2$ , respectively. Manganese arsenides 147 ( $\text{R}=\text{Ph}$ ,  $\text{OPh}$ ,  $\text{Me}$ ,  $\text{OMe}$ ) have been prepared from  $\text{Me}_2\text{AsCl}$  and  $\text{M}(\text{R}_3\text{P})\text{Mn}(\text{CO})_4$  [163].



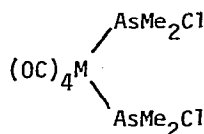
147

Turning to the iron family, analytically pure  $\text{K}_2\text{Fe}(\text{CO})_4$  may now be conveniently prepared from pentacarbonyl iron and potassium tri-*s*-butylborohydride [164]. A full paper described a detailed kinetic and mechanistic study of alkyl migration reactions of  $\text{RFe}(\text{CO})_4\text{M}$  [165]. The acyl group has been implicated as the cation

binding site in  $RC(O)Fe(CO)_4M$ . It is suggested that tight ion paired transition states are more favorable than more dissociated ones in such alkyl migrations. Condensations of  $Na_2Fe(CO)_4$  with phosgene [166] and chlorotrimethylgermane [167] have been reported to afford  $Fe(CO)_4(CS)$  and  $(Me_3Ge)_2Fe(CO)_4$ , respectively. New heterodinuclear complexes 148 ( $M=Cr, Mo, W$ ) have been obtained from  $K_2Fe(CO)_4$  and 149 [168]. Full synthetic and mechanistic details of the reduction of the carbon-carbon double bond of a variety of  $\alpha,\beta$ -unsaturated carbonyl and related compounds by  $NaHFe_2(CO)_8$  were disclosed in 1978 [169].



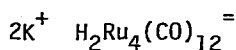
148



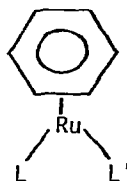
149

Several additional condensations of  $CpFe(CO)_2M$  were reported in 1978. Thus, this species was combined with carbon dioxide to give  $[CpFe(CO)_2]_2$  [170], with sulfur dioxide to afford  $CpFe(CO)_2S(O_2)Na$  [171], and with  $(PhO)_2CS$  to yield  $Cp_2Fe_2(CO)_3(CS)$  [172].

Ruthenium cluster  $H_4Ru_4(CO)_{12}$  has been sequentially ionized by potassium hydride in THF to give mono-, di-, and tripotassio salts illustrated by 150 [173]. Half-sandwich 151 ( $L$  and  $L'$  = phosphines) has been prepared from  $C_6H_6RuCl_2$ ,  $L'$ , and sodium naphthalenide [174]. The ruthenium atom of 151 is a nucleophile since it undergoes methylation with methyl iodide.



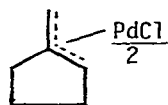
150



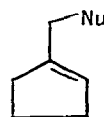
151



While  $\text{NaCo(CO)}_4$  combines with chlorosilanes in ether by nucleophilic attack on silicon to afford species such as  $\text{Me}_3\text{SiCo(CO)}_4$ , similar reactions in THF give acyltetracarbonylcobalt derivatives which have been trapped by triphenylphosphine [175]. Finally, in the area of transition metals, palladium complex 152 has been found to react with a series of soft nucleophiles (for example, sodiodimethyl malonate) to yield 153 [176].

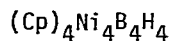


152

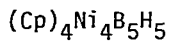


153

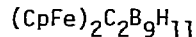
The previously described polyhedral nickel-boron cluster systems have been extended to tetranickel species 154 and 155, prepared from  $\text{NaB}_5\text{H}_8$ ,  $(\text{Cp})_2\text{Ni}$ , and sodium amalgam [177].  $^1\text{H}$ - and  $^{11}\text{B}$  NMR spectra for both 154 and 155 are reported. Biferracarboranes 156-158 have been obtained by sodium reduction of 159 followed by treatment with cyclopentadienyl sodium [178].



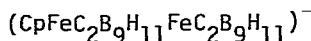
154



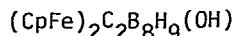
155



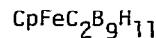
156



157

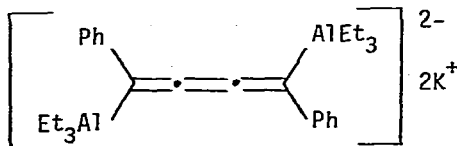


158

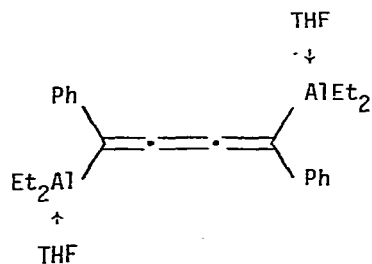


159

Di-ate complex 160 has been prepared from 1,4-diphenylbutadiyne, triethylaluminum, and potassium [179]. Compound 160 is converted to 161 by chlorotrimethylsilane.

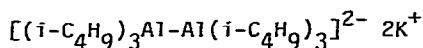


160



161

The novel dialuminate 162 has been prepared in the reaction of tri-isobutylaluminum with potassium in hexane [180]. Another paper reported the X-ray structure of bis(3,8-cis-cyclooctenyl)aluminate, synthesized from 1,3-cyclooctadiene, potassium, and trimethylaluminum [181].



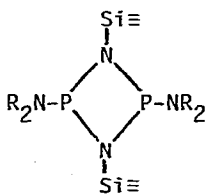
162

Reactions of trimethylstannylsodium with aryl halides to afford aryl tin systems have been shown by kinetic studies, deuteration, and trapping experiments with 1,3-diphenyl-1-propanone to proceed via nucleophilic displacement on halogen to give arylsodium and tin halogen intermediates [182]. This same sodiotin reagent has also been added in a 1,4-fashion to several  $\alpha,\beta$ -unsaturated esters, ketones, and nitriles [183].

In contrast to earlier reports, reaction of KHPPh with 1,2-dibromoethane has been shown to give 163 [184]. Phosphides 164 ( $n=4, 3, 2$ ) have been obtained by ring cleavage of  $(t-BuP)_4$  by potassium in THF or dioxane [185]. Diazadiphosphetidines 165 have been prepared from  $(R_2N)_2PCl$  and sodium bis(trimethylsilyl)amide [186]. Nortricyclene 166 has been synthesized from white phosphorus, Na/K alloy, and dichlorodimethylsilane [187].

PhPH-PPH

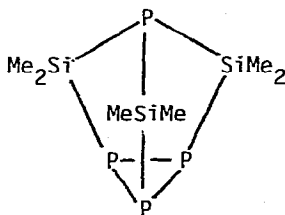
163



165

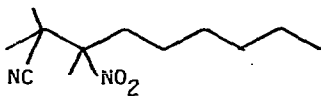
 $K_2(t-BuP)_n$ 

164

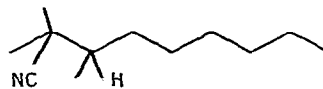


166

Finally, the nitro group of a variety of tertiary and benzylic nitroparaffins has been replaced by hydrogen using sodium methylmercaptide [188]. The reaction proceeds via radical anion intermediates and is illustrated by the conversion of 167 to 168 (92%).



167



168

#### 4. REFERENCES

1. A. Streitwieser, Jr. and L. L. Nebenzahl, *J. Org. Chem.*, 43 (1978) 598.
2. A. Streitwieser, Jr. and F. Guibe', *J. Am. Chem. Soc.*, 100 (1978) 4532.
3. E. Juaristi and A. Streitwieser, Jr., *J. Org. Chem.*, 43 (1978) 2704.
4. A. Streitwieser, Jr., C. M. Berke, and K. Robbers, *J. Am. Chem. Soc.*, 100 (1978) 8271.
5. J. O. Stoffer, D. R. Strait, D. L. Filger, E. T. Lloyd, and C. Crain, *J. Org. Chem.*, 43 (1978) 1812.
6. J. Chrisment and J.-J. Delpuech, *J. Chem. Research(S)*, (1978) 340; *J. Chem. Research(M)*, (1978) 3701.
7. F. G. Bordwell, J. E. Bartmess, and J. A. Hautala, *J. Org. Chem.*, 43 (1978) 3095.
8. F. G. Bordwell and J. E. Bartmess, *J. Org. Chem.*, 43 (1978) 3101.
9. F. G. Bordwell, J. E. Bartmess, and J. A. Hautala, *J. Org. Chem.*, 43 (1978) 3107.
10. F. G. Bordwell, J. E. Bartmess, and J. A. Hautala, *J. Org. Chem.*, 43 (1978) 3113.
11. F. G. Bordwell and J. A. Hautala, *J. Org. Chem.*, 43 (1978) 3116.
12. D. Algrim, J. E. Bares, J. C. Branca, and F. G. Bordwell, *J. Org. Chem.*, 43 (1978) 5024.
13. J. M. Kern and P. Federlin, *Tetrahedron*, 34 (1978) 661.
14. F. G. Bordwell and F. J. Cornforth, *J. Org. Chem.*, 43 (1978) 1763.
15. R. R. Fraser and P. J. Champagne, *J. Am. Chem. Soc.*, 100 (1978) 657.
16. A. K. Cheng and J. B. Stothers, *Can. J. Chem.*, 56 (1978) 1342.
17. N. H. Werstiuk and P. Andrews, *Can. J. Chem.*, 56 (1978) 2605.
18. G. Barbarella, P. Dembech, A. Garbesi, F. Bernardi, A. Bottoni, and A. Fava, *J. Am. Chem. Soc.*, 100 (1978) 200.
19. T. Okuyama, Y. Ikenouchi, and T. Fueno, *J. Am. Chem. Soc.*, 100 (1978) 6162.
20. Y. Takeuchi, H. J. C. Yeh, K. L. Kirk, and L. A. Cohen, *J. Org. Chem.*, 43 (1978) 3565.
21. P. Laszlo, *Angew. Chem. Int. Ed. Engl.*, 17 (1978) 254.

22. G. A. Olah, G. Asensio, H. Mayr, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 100 (1978) 4347.
23. S. W. Staley, G. E. Linkowski, and M. A. Fox, *J. Am. Chem. Soc.*, 100 (1978) 4818.
24. D. N. Butler and I. Gupta, *Can. J. Chem.*, 56 (1978) 80.
25. H. Gunther, A. Shyoukh, D. Cremer, and K.-H. Frisch, *Liebigs Ann. Chem.*, (1978) 150.
26. H. Gunther, M.-E. Gunther, D. Mondeshka, and H. Schmickler, *Liebigs Ann. Chem.*, (1978) 165.
27. G. Boche, H. Weber, D. Martens, and A. Bieberbach, *Chem. Ber.*, 111 (1978) 2480.
28. G. Boche, H. Weber, and A. Bieberbach, *Chem. Ber.*, 111 (1978) 2833.
29. P. Hildenbrand, G. Plinke, J. F. M. Oth, and G. Schroder, *Chem. Ber.*, 111 (1978) 107.
30. C. A. H. Rasmussen and H. C. van der Plas, *Recueil*, 97 (1978) 288.
31. A. Rykowski, H. C. van der Plas, and A. van Veldhuizen, *Recueil*, 97 (1978) 273.
32. H. C. van der Plas, A. van Veldhuizen, M. Wozniak, and P. Smit, *J. Org. Chem.*, 43 (1978) 1673.
33. H. C. van der Plas, M. Wozniak, and A. van Veldhuizen, *Recueil*, 97 (1978) 130.
34. W. J. le Noble, D.-M. Chiou, and Y. Okaya, *J. Am. Chem. Soc.*, 100 (1978) 7743.
35. J. B. Lambert and S. M. Wharry, *J. Chem. Soc., Chem. Comm.*, (1978) 172.
36. P. H. W. Lau and J. C. Martin, *J. Am. Chem. Soc.*, 100 (1978) 7077.
37. R. A. Komoroski and K. A. Mauritz, *J. Am. Chem. Soc.*, 100 (1978) 7487.
38. W. Kaïm and H. Bock, *J. Am. Chem. Soc.*, 100 (1978) 6504.
39. W. Kaïm and H. Bock, *Chem. Ber.*, 111 (1978) 3843.
40. F. Gerson, W. Huber, and O. Wennerstrom, *Helv. Chim. Acta*, 61 (1979) 2763.
41. G. F. Pedulli, M. Tiecco, M. Guerra, G. Martelli, and P. Zanirato, *J. Chem. Soc., Perkin II*, (1978) 212.
42. P. Furderer, F. Gerson, M. Rabinovitz, and I. Willner, *Helv. Chim. Acta*, 61 (1978) 2981.
43. P. Furderer, F. Gerson, and K. Hafner, *Helv. Chim. Acta*, 61 (1978) 2974.
44. G. A. Russell, K. Schmidt, C. Tanger, E. Goettert, M. Yamashita, Y. Kosugi, J. Siddens, and G. Senatore in "Organic Free Radicals," W. A. Pryor, Ed., American Chemical Society, Washington, D. C., 1978, Chapter 23.

45. G. A. Russell, C. M. Tanger, and Y. Kosugi, *J. Org. Chem.*, 43 (1978) 3278.
46. G. A. Russell, G. Wallraff, and J. L. Gerlock, *J. Phys. Chem.*, 82 (1978) 1161.
47. G. A. Russell and C. E. Osuch, *J. Am. Chem. Soc.*, 100 (1978) 5979.
48. K. S. Chen and J. K. S. Wan, *J. Am. Chem. Soc.*, 100 (1978) 6051.
49. R. L. Harris and J. J. Lagowski, *J. Phys. Chem.*, 82 (1978) 729.
50. G. Fritz, E. Matern, H. Bock, and G. Brahler, *Z. anorg. allg. Chem.*, 439 (1978) 173.
51. F. Jachimowicz, G. Levin, and M. Szwarc, *J. Am. Chem. Soc.*, 100 (1978) 5426.
52. G. Levin, B. E. Holloway, C. R. Mao, and M. Szwarc, *J. Am. Chem. Soc.*, 100 (1978) 5841.
53. C. Cambillau, G. Bram, J. Corset, C. Riche, and C. Pascard-Billy, *Tetrahedron*, 34 (1978) 2675.
54. W. F. Edgell, S. Hegde, and A. Barbetta, *J. Am. Chem. Soc.*, 100 (1978) 1406.
55. B. S. Ault, *J. Am. Chem. Soc.*, 100 (1978) 5773.
56. J. F. Garst, J. A. Pacifici, C. C. Felix, and A. Nigam, *J. Am. Chem. Soc.*, 100 (1978) 5974.
57. L. A. Paquette, C. R. Degenhardt, and H. C. Berk, *J. Am. Chem. Soc.*, 100 (1978) 1599.
58. E. B. Sanders, H. V. Secor, and J. I. Seeman, *J. Org. Chem.*, 43 (1978) 324.
59. W. Dietrich, K. Schulze, and M. Muhlstadt, *J. Prakt. Chem.*, 320 (1978) 143.
60. M. E. Jung and J. P. Hudspeth, *J. Am. Chem. Soc.*, 100 (1978) 4309.
61. T. Miyashi, A. Hazato, and T. Mukai, *J. Am. Chem. Soc.*, 100 (1978) 1008.
62. R. W. Thies and E. P. Seitz, *J. Org. Chem.*, 43 (1978) 1050.
63. D. A. Evans, D. J. Baillargeon, and J. V. Nelson, *J. Am. Chem. Soc.*, 100 (1978) 2242.
64. S. R. Wilson and D. T. Mao, *J. Chem. Soc., Chem. Comm.*, (1978) 479.
65. A. G. Anastassiou, M. Sabahi, and R. Badri, *Tetrahedron Lett.*, (1978) 4755.
66. D. A. Clark, C. A. Bunnell, and P. L. Fuchs, *J. Am. Chem. Soc.*, 100 (1978) 7777.
67. P. A. Wender and J. M. Schaus, *J. Org. Chem.*, 43 (1978) 782
68. G. Boche and A. Bieberbach, *Chem. Ber.*, 111 (1978) 2850.

69. H. S. Quaal, S. Ji, Y. M. Kim, W. D. Closson, and J. A. Jubieta, *J. Org. Chem.*, 43 (1978) 1311.
70. S. Boileau, A. Deffieux, D. Lassalle, F. Menezes, and B. Vidal, *Tetrahedron Lett.*, (1978) 1767.
71. R. Kraft, A. H. E. Muller, V. Warzeihan, H. Hocker, and G. V. Schulz, *Macromolecules*, 11 (1978) 1093.
72. J. P. Guthrie, *Can. J. Chem.*, 56 (1978) 962.
73. H. C. van der Plas, *Acc. Chem. Res.*, 11 (1978) 462.
74. J. F. Bunnett, *Acc. Chem. Res.*, 11 (1978) 413.
75. J. F. Wolfe and D. R. Carver, *Org. Prep. and Procedures Int.*, 10 (1978) 225.
76. J. F. Wolfe, M. P. Moon, M. C. Sleevi, J. F. Bunnett, and R. R. Bard, *J. Org. Chem.*, 43 (1978) 1019.
77. J. F. Bunnett and R. P. Traber, *J. Org. Chem.*, 43 (1978) 1867.
78. J. F. Bunnett and S. J. Shafer, *J. Org. Chem.*, 43 (1978) 1873.
79. J. F. Bunnett and S. J. Shafer, *J. Org. Chem.*, 43 (1978) 1877.
80. A. B. Pierini and R. A. Rossi, *J. Organomet. Chem.*, 144 (1978) C12.
81. S. Rajan and K. Muralimohan, *Tetrahedron Lett.*, (1978) 483.
82. L. M. Tolbert, *J. Am. Chem. Soc.*, 100 (1978) 3952.
83. J. D. White and R. W. Skeeane, *J. Am. Chem. Soc.*, 100 (1978) 6296.
84. J. R. Beck, *Tetrahedron*, 34 (1978) 2057.
85. N. M. Atherton, A. J. Horsewill, and P. A. Kennedy, *J. Phys. Chem.*, 82 (1978) 1097.
86. J. H. Noordik, J. Schreurs, R. O. Gould, J. J. Mooij, and E. de Boer, *J. Phys. Chem.*, 82 (1978) 1105.
87. N. Papadakis and J. L. Dye, *J. Phys. Chem.*, 82 (1978) 1111.
88. G. G. Stroebel, D. Y. Myers, R. R. Grabbe, and P. D. Gardner, *J. Phys. Chem.*, 82 (1978) 1121.
89. K. S. Chen and N. Hirota, *J. Phys. Chem.*, 82 (1978) 1133.
90. M. T. Jones, *J. Phys. Chem.*, 82 (1978) 1138.
91. G. A. Russell, G. Wallraff, and J. L. Gerlock, *J. Phys. Chem.*, 82 (1978) 1161.
92. A. Matsuzaki, T. Kobayashi, and S. Nagakura, *J. Phys. Chem.*, 82 (1978) 1201.
93. J. M. Lefour, P. Sarthou, G. Bram, F. Guibe, A. Loupy, and J. Seyden-Penne, *Tetrahedron Lett.*, (1978) 3831.

94. T. Izumi and S. I. Miller, *J. Org. Chem.*, 43 (1978) 871.
95. J.-M. Lehn, *Acc. Chem. Res.*, 11 (1978) 49.
96. S. A. DiBiase and G. W. Gokel, *J. Org. Chem.*, 43 (1978) 447.
97. S. Akabori and T. Yoshii, *Tetrahedron Lett.*, (1978) 4523.
98. J. G. Smith and Y. Chun, *Tetrahedron Lett.*, (1978) 413.
99. S. Akabori, S. Miyamoto, and H. Tanabe, *J. Polym. Sci., Polym. Lett. Ed.*, 16 (1978) 533.
100. R. P. Redman, P. J. Thomas, and C. J. M. Stirling, *J. Chem. Soc., Perkin II* (1978) 1135.
101. G. R. Stevenson, J. Valentin, C. Meverden, L. Echegoyen, and R. Maldonado, *J. Am. Chem. Soc.*, 100 (1978) 353.
102. H. C. Wang, G. Levin, and M. Szwarc, *J. Am. Chem. Soc.*, 100 (1978) 3969.
103. M. G. Barker, A. Harper, and P. Hubberstey, *J. Chem. Research(S)*, (1978) 432; *J. Chem. Research(M)*, (1978) 5310.
104. M. Schlosser and G. Rauchschalbe, *J. Am. Chem. Soc.*, 100 (1978) 3258.
105. W. E. Billups, *Acc. Chem. Res.*, 11 (1978) 245.
106. M. T. Reetz and F. Eibach, *Angew. Chem.*, 90 (1978) 285; *Angew. Chem. Int. Ed. Engl.*, 17 (1978) 278.
107. M. T. Reetz and F. Eibach, *Liebigs Ann. Chem.*, (1978) 1598.
108. T. F. Crimmins and E. M. Rather, *J. Org. Chem.*, 43 (1978) 2170.
109. E. W. Post and T. F. Crimmins, *J. Organomet. Chem.*, 161 (1978) C17.
110. A. G. Osborne and R. H. Whiteley, *J. Organomet. Chem.*, 162 (1978) 79.
111. C. A. Brown, *Synthesis*, (1978) 754.
112. J. Shabtai and E. Ney-Igner, and H. Pines, *J. Org. Chem.*, 43 (1978) 4086.
113. G. Coudert, G. Ndebeka, P. Caubere, S. Raynal, S. Lecolier, and S. Boileau, *J. Polym. Sci., Polym. Lett. Ed.*, 16 (1978) 413.
114. G. R. Newkome and D. C. Hager, *J. Am. Chem. Soc.*, 100 (1978) 5567.
115. P. Groenewegen, H. Kallenberg, and A. van der Gen, *Tetrahedron Lett.*, (1978) 491.
116. P. F. Hudrlik and J. M. Takacs, *J. Org. Chem.*, 43 (1978) 3861.
117. A. A. Millard and M. W. Rathke, *J. Org. Chem.*, 43 (1978) 1834.
118. S. R. Wilson and R. N. Misra, *J. Org. Chem.*, 43 (1978) 4903.

119. P. T. Lansbury and R. W. Erwin, *Tetrahedron Lett.*, (1978) 2675.
120. T. Severin and I. Ipach, *Chem. Ber.*, 111 (1978) 692.
121. A. P. Kozikowski and M. P. Kuniak, *J. Org. Chem.*, 43 (1978) 2083.
122. W. Ried, J. B. Mavunkal, and G. Oremek, *Liebigs Ann. Chem.*, (1978) 1274.
123. A. I. FeteII and H. Feuer, *J. Org. Chem.*, 43 (1978) 497.
124. H. Feuer, W. D. Van Buren II, and J. B. Grutzner, *J. Org. Chem.*, 43 (1978) 4676.
125. J. A. Deyrup and G. S. Kuta, *J. Org. Chem.*, 43 (1978) 501.
126. D. Savoia, C. Trombini, and A. Umani-Ronchi, *J. Org. Chem.*, 43 (1978) 2907.
127. D. E. Bergbreiter and J. M. Killough, *J. Am. Chem. Soc.*, 100 (1978) 2126.
128. B. Renger, H. Hugel, W. Wykypiel, and D. Seebach, *Chem. Ber.*, 111 (1978) 2630.
129. C. A. Brown, *J. Org. Chem.*, 43 (1978) 3083.
130. P. G. Gassman and H. R. Drewes, *J. Am. Chem. Soc.*, 100 (1978) 7600.
131. P. G. Gassman and D. R. Amick, *J. Am. Chem. Soc.*, 100 (1978) 7611.
132. T. Takahashi, S. Hashiguchi, K. Kasuga, and J. Tsuji, *J. Am. Chem. Soc.*, 100 (1978) 7424.
133. H. G. Corkins, L. Veenstra, and C. R. Johnson, *J. Org. Chem.*, 43 (1978) 4233.
134. K. Ogura, N. Katoh, I. Yoshimura, and G. Tsuchihashi, *Tetrahedron Lett.*, (1978) 375.
135. H. Kato, I. Takeuchi, Y. Hamada, M. Ono, and M. Hirota, *Tetrahedron Lett.*, (1978) 135.
136. S. Kano and T. Yokomatsu, *Tetrahedron Lett.*, (1978) 1209.
137. E. C. Alexander and T. Tom, *Tetrahedron Lett.*, (1978) 1741.
138. J. J. Brunet, L. Mordenti, and P. Caubere, *J. Org. Chem.*, 43 (1978) 4804.
139. D. Franks, M. C. Gossel, R. C. Hayward, and L. J. S. Knutsen, *J. Chem. Soc., Chem. Comm.*, (1978) 941.
140. H. Deshayes and J.-P. Pete, *J. Chem. Soc., Chem. Comm.*, (1978) 567.
141. A. Zask and P. Helquist, *J. Org. Chem.*, 43 (1978) 1619.
142. J. C. Bottaro, *J. Chem. Soc., Chem. Comm.*, (1978) 990.
143. L. J. Adzima, C. C. Chiang, I. C. Paul, and J. C. Martin, *J. Am. Chem. Soc.*, 100 (1978) 953.
144. A. J. Fatiadi, *J. Am. Chem. Soc.*, 100 (1978) 2586.



145. S. Antus, F. Boross, and M. Nogradi, *Liebigs Ann. Chem.*, (1978) 107.
146. H. W. Kroto, J. F. Nixon, N. P. C. Simmons, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 100 (1978) 446.
147. W. J. Evans, A. L. Wayda, C.-W. Chang, and W. M. Cwiria, *J. Am. Chem. Soc.*, 100 (1978) 333.
148. G. R. Sienel, A. W. Spiegl, and R. D. Fischer, *J. Organomet. Chem.*, 160 (1978) 67.
149. F. H. Kohler, W. Prossdorf, U. Schubert, and D. Neugebauer, *Angew. Chem.*, 90 (1978) 912; *Angew. Chem. Int. Ed. Engl.*, 17 (1978) 850.
150. R. J. Kinney, W. D. Jones, and R. G. Bergman, *J. Am. Chem. Soc.*, 100 (1978) 635.
151. C. P. Verkade, A. Westerhof, and H. J. de Liefde Meijer, *J. Organomet. Chem.*, 154 (1978) 317.
152. S. P. Kolesnikov, J. E. Dobson, and P. S. Skell, *J. Am. Chem. Soc.*, 100 (1978) 999.
153. J. E. Ellis, C. P. Parnell, and G. P. Hagen, *J. Am. Chem. Soc.*, 100 (1978) 3605.
154. F. A. Cotton, S. A. Koch, A. J. Schultz, and J. M. Williams, *Inorg. Chem.*, 17 (1978) 2093.
155. F. A. Cotton, P. E. Fanwick, R. H. Niswander, and J. C. Sekutowski, *J. Am. Chem. Soc.*, 100 (1978) 4725.
156. H. Alper and H.-N. Paik, *J. Am. Chem. Soc.*, 100 (1978) 508.
157. H. Alper and H.-N. Paik, *J. Organomet. Chem.*, 155 (1978) 47.
158. B. W. S. Kolthammer and P. Legzdins, *J. Am. Chem. Soc.*, 100 (1978) 2247.
159. H. Brunner and J. Wachter, *J. Organomet. Chem.*, 155 (1978) C29.
160. A. N. Nesmeyanov, N. A. Ustynyuk, L. G. Makarova, S. Andre, Y. A. Ustynyuk, L. N. Novikova, and Y. N. Luzikov, *J. Organomet. Chem.*, 154 (1978) 45.
161. N. El Murr, M. Riveccie, and A. Salzer, *Inorg. Chim. Acta*, 29 (1978) L213.
162. K. Inrott, R. Goetze, and G. S. Shore, *J. Organomet. Chem.*, 154 (1978) 337.
163. R. Muller and H. Vahrenkamp, *J. Organomet. Chem.*, 150 (1978) C11.
164. J. A. Gladysz and W. Tam, *J. Org. Chem.*, 43 (1978) 2279.
165. J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, 100 (1978) 4766.
166. W. Petz, *J. Organomet. Chem.*, 146 (1978) C23.

167. A. Bonny and K. M. Mackay, *J. Organomet. Chem.*, 144 (1978) 389.
168. A. Trenkle and H. Vahrenkamp, *J. Organomet. Chem.*, 155 (1978) C51.
169. J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, R. G. Komoto, and J. I. Brauman, *J. Am. Chem. Soc.*, 100 (1978) 1119.
170. G. O. Evans, W. F. Walter, D. R. Mills, and C. A. Streit, *J. Organomet. Chem.*, 144 (1978) C34.
171. P. Reich-Rohrwig, A. C. Clark, R. L. Downs, and A. Wojcicki, *J. Organomet. Chem.*, 145 (1978) 57.
172. R. E. Wagner, R. A. Jacobson, R. J. Angelici, and M. H. Quick, *J. Organomet. Chem.*, 148 (1978) C35.
173. K. E. Inkrott and S. G. Shore, *J. Am. Chem. Soc.*, 100 (1978) 3954.
174. H. Werner and R. Werner, *Angew. Chem.*, 90 (1978) 721; *Angew. Chem. Int. Ed. Engl.*, 17 (1978) 683.
175. B. K. Nicholson and J. Simpson, *J. Organomet. Chem.*, 155 (1978) 237.
176. B. M. Trost, L. Weber, P. Strege, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, 100 (1978) 3426.
177. J. R. Bowser and R. N. Grimes, *J. Am. Chem. Soc.*, 100 (1978) 4623.
178. C. G. Salentine and M. F. Hawthorne, *Inorg. Chem.*, 17 (1978) 1498.
179. H. Hoberg, V. Gotor, and R. Mynott, *J. Organomet. Chem.*, 149 (1978) 1.
180. H. Hoberg and S. Krause, *Angew. Chem.*, 90 (1978) 1013; *Angew. Chem. Int. Ed. Engl.*, 17 (1978) 949.
181. A. M. McPherson and G. Stucky, *J. Organomet. Chem.*, 152 (1978) 367.
182. K. R. Wursthorn, H. G. Kuivila, and G. F. Smith, *J. Am. Chem. Soc.*, 100 (1978) 2779.
183. H. G. Kuivila and G. H. Lein, Jr., *J. Org. Chem.*, 43 (1978) 750.
184. M. Baudler, B. Carlsohn, D. Koch, and P. K. Medda, *Chem. Ber.*, 111 (1978) 1210.
185. M. Baudler, C. Gruner, G. Furstenberg, B. Kloth, F. Saykowski, and U. Ozer, *Z. anorg. allg. Chem.*, 446 (1978) 169.
186. W. Zeiss, C. Feldt, J. Weis, and G. Dunkel, *Chem. Ber.*, 111 (1978) 1180.
187. G. Fritz and R. Uhlmann, *Z. anorg. allg. Chem.*, 440 (1978) 168.
188. N. Kornblum, S. C. Carlson, and R. G. Smith, *J. Am. Chem. Soc.*, 100 (1978) 289.