HEAVIER ALKALI METALS

ANNUAL SURVEY COVERING THE YEAR 1977

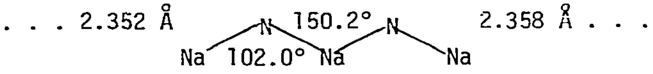
EDWIN M. KAISER

Department of Chemistry
University of Missouri-Columbia
Columbia, Missouri 65201, U.S.A.

TABLE OF CONTENTS

1. PHYSICAL ORGANIC CHEMISTRY

The crystal structures of several organoalkalies have been determined by X-ray diffraction. Thus, methylrubidium and methylcesium, prepared from methyllithium and rubidium and cesium alkoxides, respectively, were shown to possess hexagonal structures of the NiAs type [1]. The crystal structure of potassioethyl acetoacetate complexed with 18-crown-6 indicated the presence of a distinct molecule in which the cation is coordinated to the two oxygen atoms of the U-shaped enolate and to the six oxygen atoms of the ether [2]. Sodiohexamethyldisilazane has been shown to exist in a polymeric arrangement of sodium and nitrogen atoms (1) [3]. Each of the above papers lists specific crystallographic data.



1

A large number of papers in 1977 were concerned with the acidities of carbon acids. First, a review article described a scale of absolute equilibrium acidities of active hydrogen organics in DMSO [4]. Such acidities are compared with apparent acidities in solvents of low dielectric constants, absolute acidities in water, and relative acidities in the gas phase. The effect of m- and p-substituents of benzene derivatives upon acidity is discussed in terms of solvation effects and the Hammett equation. The equilibrium acidities of $PhCH_2G$ (G = CN, SO_2Ph, and other electron withdrawing groups) and Ph_2CHG have been compared with those of the non-phenylated componds in DMSO [5]. The progressive decrease

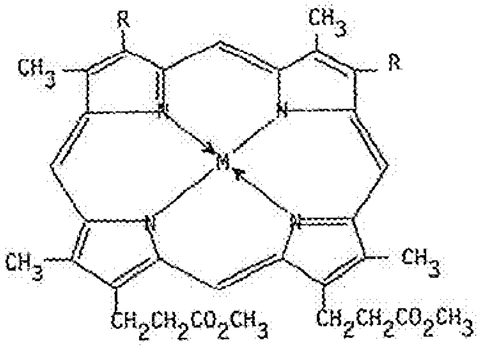
---

*Annual Survey covering the year 1976 see J. Organometal. Chem., Vol. 143(1977)p.99-127.

in the size of acid-strengthening effects by phenyl with a progressive increase in acidity of the parent H_3CG has been ascribed to a resonance saturation effect, a phenomenon believed to be general in chemistry. The importance in these compounds of steric inhibition to resonance and of the ratios of resonance to polar effects is discussed. Similar results have been realized when the methyl group of CH_3CH_2G has been replaced by a thiophenyl substituent where steric inhibition to resonance is unimportant [6]. It is suggested that strong conjugative interactions are present in carbanions stabilized not only by sulfones but also by sulfoxide and sulfide moieties. Other compounds studied in DMSO have included substituted toluenes and anilines [7], aliphatic carboxamides [8], acetylenes [9], and disulfonylmethanes [10].

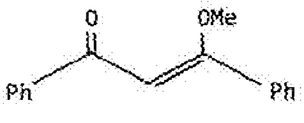
Metalations of a variety of polyarylmethanes by potassium hydride [11] and potassium amide [12] in THF have been employed to obtain apparent pKa values for hydrogen and ammonia of 35.3±0.3 and 37.8±0.2, respectively.

The methyl groups of rings A and B of protoporphyrin IV dimethyl ester (2, R vinyl, M = 2H) have been found to be acidic to sodium methoxide as evidenced by deuterium exchange [13]. As anticipated, the methylene protons adjacent to the esters also undergo such exchange. Interestingly, the methyl protons of 2 are not exchanged when R = ethyl instead of vinyl.



2

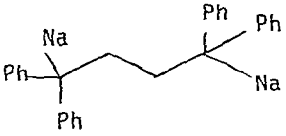
Kinetic studies have been performed on a variety of organometallic systems. Thus, alkylations of sodio- and potassiodibenzoylmethides with methyl iodide in DMSO to afford 1,1-dibenzoylethane are first order in each reagent [14]. In contrast, the use of dimethyl sulfate in DMSO to give 3 is first order in the alkylating agent but only 0.24 order in enolate, a result ascribed to substitutions on reactive intermediate 4. Calorimetric heats of methylation of alkali dibenzoylmethanes with methylfluorosulfonate in propylene carbonate and in THF are listed.



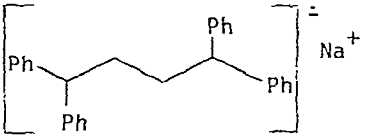
3

$Me_2\overset{+}{S}-OMe$ 4

1,4-Disodio-1,1,4,4-tetraphenylbutane (5) has been oxidized by perylene and tetracene in an effort to kinetically observe the conversion of radical anion 6 to 1,1-diphenylethene and the radical anions of the latter hydrocarbons [15]. However, the desired reaction was not observed due to the rapid transformation of 6 into 1,1-diphenylethene and its radical anion without the intervention of the perylene or the tetracene. On the other hand, flash photolysis of 5 was shown to give 6 by electron photoejection [16]. Subsequent thermal or photolytic decomposition of 6 into 1,1-diphenylethene and 1,1-diphenylethene radical anion is virtually completed within 100 usec.



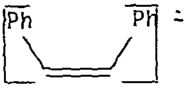
5



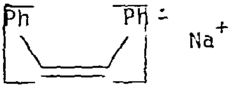
6

Because of a conflict between the kinetic conclusions and certain ESR spectra, additional research has been performed on cis-stilbene radical anion in HMPA [17]. Using flash photolysis and pulse radiolysis, the authors conclude that cis-species 7,8 and 9 are distinct compounds compared to the respective trans isomers. The ESR spectrum of 8 is discussed. Optical spectra have been obtained for the sodium salts of radical anions and dianions of 1,2-diphenylcycloalkenes, compounds which may be considered to be derivatives of cis-stilbene [18]. It was determined that K_{dispr} for the radical anions of the cyclobutene, -pentene, and -hexene rings is 0.15, 110, and 3000, respectively. The results are discussed in terms of steric strain.

7



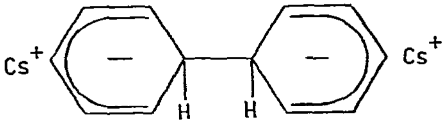
8



9

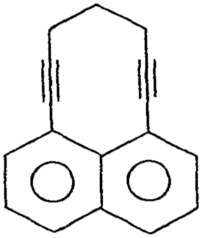
Kinetic studies have also been performed on the cleavage of picolyl- and quinolylmethylsilanes by sodium methoxide and the rates correlated with the acidity of the parent heterocycles [19], and on the oxidative-addition of alkyl halides and tosylates to $Na_2Fe(CO)_4$ to demonstrate two-electron, but not one-electron or radical chain mechanisms [20].

A large number of organometallic systems were studied by ESR spectroscopy. Thus, a detailed study of the benzene radical anion has been effected as a function of solvent, temperature, and metallic cation (K, Rb, and Cs) [21]. The authors propose a model for such compounds where the metal oscillates parallel to the plane of the ring with an average position centered on the sixfold axis of the benzene. The ESR spectrum of the benzene radical anion prepared from finely divided cesium metal was also recorded by another set of workers who subsequently allowed their reaction mixture to warm from -70° to 5°C to afford 10 in good yields [22]. Similar results were realized with Cs/K/Na alloy on both benzene and toluene.

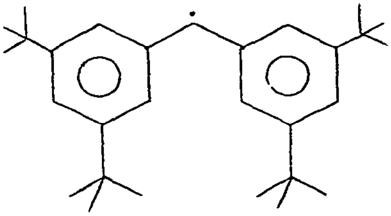


10

ESR spectra have also been obtained on radical anions derived from t-butyl substituted naphthalenes [23], naphthalenes and biphenyls with parallel or crossed triple bonds illustrated by 11 [24], several 2- and 4-nitrostilbenes [25], bisphenyl and fluorenone ion pairs [26], 2,2'-binaphthyl [27], partially deuterated phenylanthracenes [28], quadruple-layered [2.2]paracyclophanes [29], benzo[2.2]-paracyclophane [30], [2.2](2,7)pyrenophane [31], several naphthalenophanes [30, 32], dihydropyridines [33], and certain substituted benzylidenemalononitriles [34]. Radical 12 has been detected by ESR in the reaction of the corresponding alkyl bromide with sodium naphthalene [35]. This work provides direct evidence for the existence of radicals in reductions of alkyl halides by aromatic radical anions. Incidentally, CIDNP has now been observed at high magnetic yields in related reductions of strictly aliphatic halides with sodium naphthalene [36].

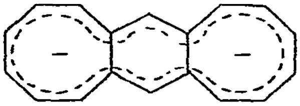


11

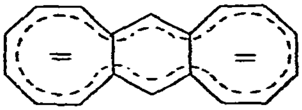


12

Dark green dianion 13 and red tetraanion 14 have been obtained by reduction of the parent hydrocarbon with appropriate amounts of Na/K alloy [37]. The ^{1}H and ^{13}C NMR spectra of 13 were consistent with the 20π electron structure shown, not with an equilibrating restricted 14π electron system. Similar spectra of 14 could not be obtained due to poor solubility.

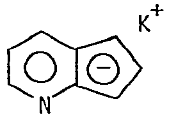


13

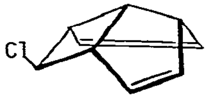


14

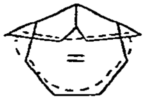
The ^{1}H NMR spectra of 15 [38] and of certain potassioarylacetylenes [39] as well as the ^{13}C NMR spectrum of the anion derived from 16 and Na/K alloy [40] have also been reported. Though 17 has apparently been synthesized from the parent tetraene and potassium in ammonia, its NMR spectra to date has been uncharacterizable [41].



15



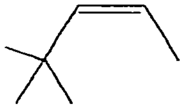
16



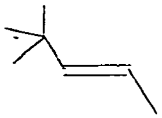
17

In other papers, the disodium and dipotassium salts of cyclooctatetraene dianion display an IR band in the 1300 cm^{-1} region ascribed to a carbon-carbon stretching vibration [42]. The absorption spectrum of KAm(C$_8$H$_8$)$_2$ from 19610 - 7530 cm^{-1} has been reported [43].

Turning to mechanistic aspects, Z-1-alkylated propenes have been found to undergo metalation at an allylic site more rapidly than the corresponding E-isomers regardless of which configuration of the resulting organometallic is thermodynamically more stable [44]. For example, 18 is metalated 15 times faster than 19 by trimethylsilylpotassium.

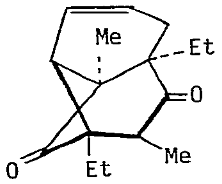


18

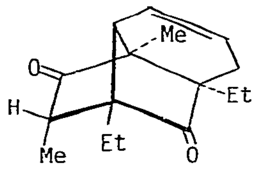


19

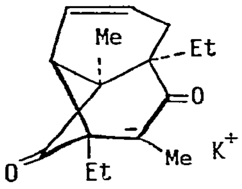
An all-carbon 1,2-anionic rearrangement involving migration of sp^3-hybridized carbon atoms has been observed in the transformation of strained 20 to 21 by potassium hydroxide [45]. Three possible mechanisms are discussed for the reaction where 22 and 23 may be intermediates.



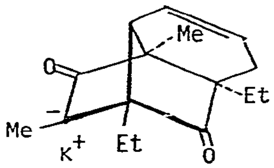
20



21

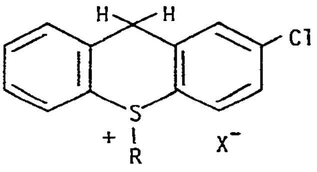


22

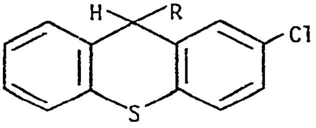


23

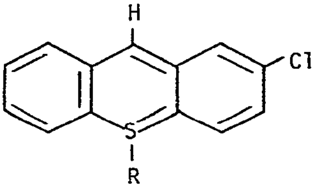
The first example of an asymmetric induction in the transfer of chirality from sulfur to carbon accompanying an intramolecular [1,4] rearrangement has been discovered in the conversion of 24 to 25 via 26 [46]. In these compounds, R = 2,5-xylyl.



24

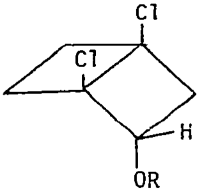


25

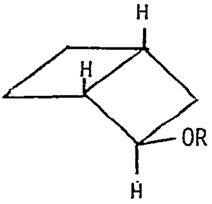


26

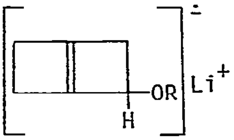
Dichloro-endo-alkoxybicyclics 27 (R = Me, Et) have been converted to exo-bicyclics 28 by lithium/t-butyl alcohol/THF [47]. Based on deuterium quenching experiments, radical anion 29 and dianion 30 are proposed as intermediates in these unique reductions. An unrelated paper discussed the stereochemistry of dissolving metal reductions of ketones in liquid ammonia [48].



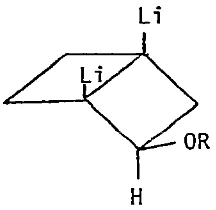
27



28

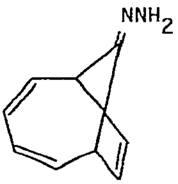


29

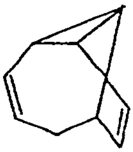


30

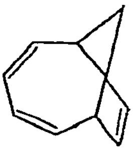
Wolff-Kishner conversions of 31 have been studied as a function of base, solvent and temperature [49]. Thus, 31 with aqueous KOH in diethylene glycol at 210° gives mostly the previously described 32 along with small amounts of 33. In contrast, 31 with t-C_4H_9OK/t-C_4H_9OH/DMSO at 74° affords only 33. Pyrazoline 34 was found to be an isolable intermediate in certain of these reactions Another paper discussed the kinetics and activation parameters of this reaction on benzophenone hydrazone in DMSO in the presence of various basic reagents [50]



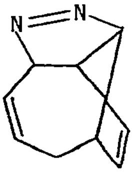
31



32



33



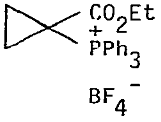
34

Finally, several full papers described certain aspects of substitution reactions of aryl halides. These included discussions about thermally induced aromatic S_{RN1} reactions [51], photostimulated S_{RN1} reactions of halobenzenes with ketone enolates in DMSO [52] and with diethyl phosphite ion [53], photostimulated S_{RN1} reactions of halopyridines with ketone enolates [54], teleaminations of 8-halo-1,7-naphthyridines [55], and arynic and SN_{AR} reactions of polyhalobenzenes [56].

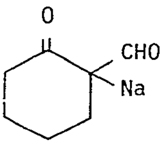
2. SYNTHETIC ASPECTS

The Ramberg-Backlund rearrangement [57] and the chemistry of phosphoryl-stabilized anions [58] have been reviewed.

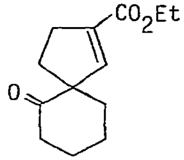
Functionalized spirocycles useful in the synthesis of spirovetivane sesquiterpenes have been synthesized from α-formylcycloalkanones and 35 [59]. The procedure is illustrated by the reaction of 35 and 36 to afford 37 (40%).



35

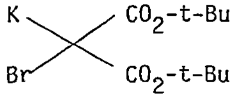


36

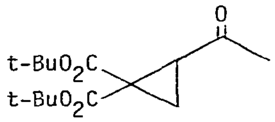


37

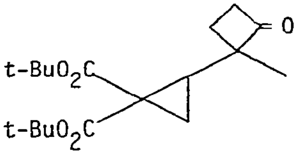
Double chain extensions of α,β-unsaturated ketones have been described in which chemistry is performed at both the carbonyl group and the β-carbon atom [60]. For example, methyl vinyl ketone and 38 give 39 which is converted to 40 by potassium diphenylsulfonium cyclopropylide; subsequent addition of sodium methoxide yields 41.



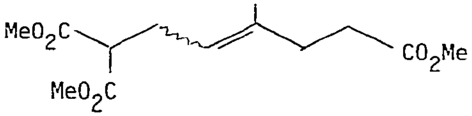
38



39

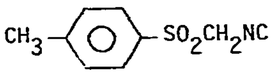


40

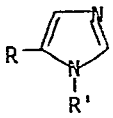


41

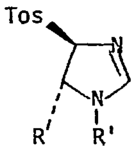
Tosylmethyl isocyanide (42) has been cycloadded to imines by potassium carbonate and sodium hydride to afford imidazoles 43 and 2-imidazolines 44, respectively [61]. Condensations of 42 with ketones R_2CO in the presence of bases has been shown to give cyanides R_2CHCN [62].



42

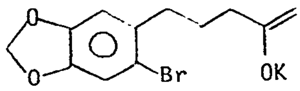


43

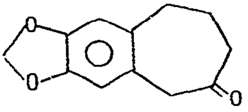


44

A variety of haloaryl enolates have been cyclized to six-, seven-, eight-, and ten-membered rings by photostimulated $S_{RN}1$ reactions [63]. The reactions are illustrated by the conversion of 45 to 46 (42%).



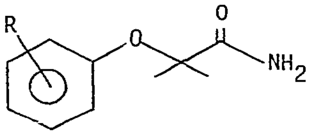
45



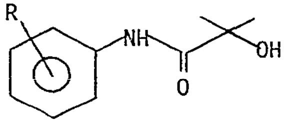
46

Aryl halides have been directly converted to trimethylsilylbenzenes (63 - 92%) accompanied by some reduced product (ArH) (26-4%) by hexamethyldisilazane and bases in HMPA [64]. The authors speculate that the results are consistent with an anionic or a radical process depending upon the halide and the base.

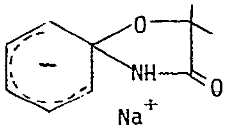
Two papers discussed novel Smiles rearrangements of phenol to aniline derivatives by sodium hydride in HMPA or DMF [65,66]. For example, 47 affords 48 probably via 49 where R has been either electron donating or withdrawing groups.



47

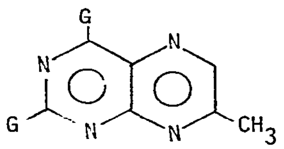


48

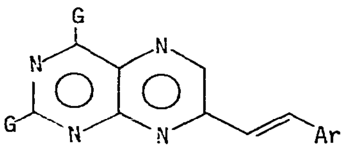


49

7-Methylpteridines 50 (G = OH and/or NH_2) containing an aromatic pyrazine ring have been directly converted to alkylidene derivatives 51 by aldehydes an aqueous/alcoholic sodium hydroxide [67].

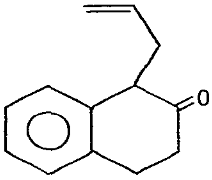


50

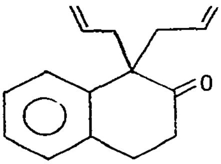


51

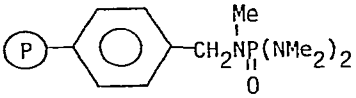
Practically pure monoalkylated derivatives accompanied by only small amounts of dialkylated products have been obtained from nitriles [68], esters [68], and ketones [69] with alkyl halides and C_8K or high surface sodium (HSS) or potassium on charcol, graphite, or alumina. For example, β-tetralone, allyl bromide, and HSS-graphite give 52 and 53 in yields of 90% and 10%, respectively [69]. Other papers disclosing heterogeneous organometallic chemistry were concerned with the conversion of primary and secondary aliphatic nitro compounds to aldehydes and ketones, respectively on dry silica gel impregnated with sodium methoxide [70], and alkylations of certain nitrogen anions effected by "solid HMPA" where P is a polymer of polystyrene-divinylbenzene [71].



52



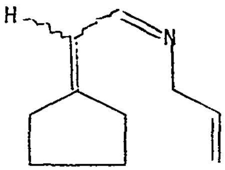
53



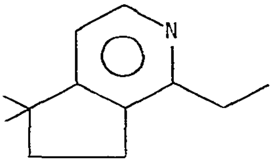
54

Complex reducing agents derived from sodium hydride, sodium alkoxides, and nickel(II) acetate have been found to be capable of reducing enolizable ketones to alcohols and alkenes and alkynes to alkanes [72]. Most of these reductions proceed in excellent yields.

A variety of azatrienes derived from aldehydes have been cyclized to pyridine derivatives by sodium-2,6-dimethyl-2,4-6-octatriene [73]. For example, 55 affords 56. In another paper, sodium has been found to dissovle in N,N-diethylacetamide, N,N-dimethylpropanamide, and tetramethylurea to give blue solutions of varying stability [74]. Similarly, Na-K alloy forms solutions in tetraethylurea, N,N-dipropylacetamide, and N,N-dimethylpropanamide.



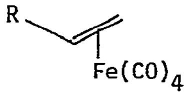
55



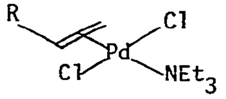
56

3. INORGANIC AND ORGANOMETALLIC COMPOUNDS

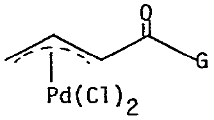
Certain olefins complexed with transition metals have been found to be electrophiles towards carbanions derived from malonate esters. Thus, 57 [75], 58 [76], and 59 (G = OEt, R') [77] combine with such enolates to ultimately afford species such as 60, often in high yields. The condensations of 59 occur stereospecifically at the α-carbon atom.



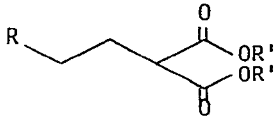
57



58



59



60

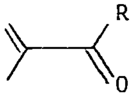
Ethylene complexes 61 (M = W, Mo) have been condensed with alkali metal carbonyl anions to give bridged carbonyl species such as 62 [78]. Combination of disodium tetracarbonylferrate with alkyl halides (RX) and allenes have been shown to yield α,β-unsaturated ketones such as 63 presumably via 64 [79].

$(\pi\text{-}C_5H_5)(CO)_3M(\pi\text{-}C_2H_4)^+$

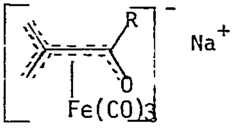
61

$(\pi\text{-}C_5H_5)(CO)_3M(CH_2)_2Re(CO)_5$

62

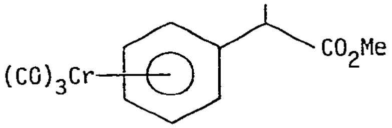


63

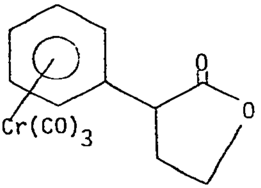


64

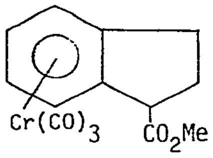
Esters 65 -67 in which the aromatic rings are complexed with $Cr(CO)_3$ are rapidly and quantitatively stereospecifically alkylated by alkyl haides and sodium hydride in DMF or under phase transfer conditions [80].



65



66



67

Reaction of NaB_5H_8, NaC_5H_5, and iron(II) chloride has afforded 2-(η^5-C_5H_5)FeB_5H_{10}, a compound which is isoelectronic with ferrocene [81]. Similar condensation of KB_5H_8 and K(1-BrB_5H_7) with diphosphine complexes of nickel(II) halides has given [Ni(μ-B_5H_8)X(dppe)] and [Ni(μ-1-BrB_5H_7)X(dppe) where X = Cl, Br, or I and dppe = 1,2-bis(diphenylphosphino)ethane [82]. Carborane $Me_4C_4B_8H_8$ has been reduced by sodium in THF to presumably afford $(Me_4C_4B_8H_8)^{2-}$ $2Na^{+}$; subsequent addition of NaC_5H_5 and iron(II) chloride gives four isomers of $(\eta^5$-$C_5H_5)_2Fe_2Me_4C_4B_8H_8$ and one isomer of $(\eta^5$-$C_5H_5)FeMe_4C_4B_7H_8$ [83].

A quadruple bond between tungsten atoms has been reported in the air-stable $W_2(C_8H_8)_3$, prepared from WCl_4 and $K_2C_8H_8$ [84].

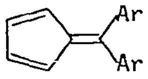
Carbyne complexes 68 (M = Cr, Mo, W) have been combined with sodium pentacarbonylmanganese and -rhenium to afford dinuclear carbyne complexes 69 [85]. Carbyne 68 (M = W) and related compounds have also been condensed with 70 (M' = Mo, W) [85] and with cyclopentadienylsodium [86] to give 71 and 72, respectively Reagent 70 (M" = Cr, Mo, and W) itself has been combined with Me_2BiBr to yield 73 and the related Bi-Br organometallic [87].

$BrM(CO)_4CPh$	$(OC)_5M'$-$M(CO)_4CPh$	$(C_5H_5)(CO)_3M''Na$
68	69	70
$(C_5H_5)(CO)_3M''$-$W(CO)_4CPh$	$(C_5H_5)(CO)_2WCPh_2$	$[(C_5H_5)(CO)_3M'']_2BiMe$
71	72	73

"Super-reduced" carbonyl anions, $M(CO)_4{}^{3-}$ (M = Mn, Re) have been obtained by reduction of $M_2(CO)_{10}$ and $M(CO)_5Na$ with sodium in HMPA [88]. Such anions, which contain Mn and Re in their lowest known oxidation states, have been condensed with chloro derivatives of Group IV elements and of gold reagents to afford organometallics such as 74, 75 (E = Ge, Sn, Ph), and 76. Another paper suggests that reactions of $M(CO)_5Na$ with $XM(CO)_5$ (M = Mn, Re) and related electrophiles to give metal-metal systems may involve radical anion intermediates [89].

$PhCH_2(CO)_2Mn(CO)_4{}^-$	$(R_3E)_2M(CO)_4{}^-$	$(Ph_3PAu)_3M(CO)_4$
74	75	76

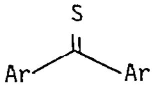
A novel synthesis of fulvenes such as 77 via desulphurization has been realized in condensations of 78 with thioketones 79 [90]. Also in this triad, $Na_2[Fe(CO)_4]$ has been combined with mixed carbonyls 80 (n = 1, m = 2 or n = 2, m = 1) to afford the first examples of clusters 81 and 82 comprised of three different transition metals [91].



77

$(C_5H_5)Fe(CO)_2Na$

78



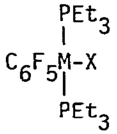
79

$Ru_nOs_m(CO)_{12}$ 80

$H_2FeRuOs_2(CO)_{13}$ 81

$H_2FeRu_2Os(CO)_{13}$ 82

Highly reactive slurries of metallic Ni, Pd, and Pt have been generated by the reduction of their dihalides by potassium metal in the presence of trialkyl- and triphenylphosphines [92]. Such slurries have been employed to insert the above metals into aryl-halide bonds to give species such as 83. Nickel dihalides or halonitroso derivatives all complexed with triphenylphosphine have been reacted with a variety of metal carbonyl systems to afford metal-metal complexes such as 84 and 85 [93].



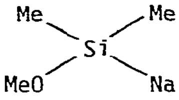
$C_6F_5M(PEt_3)_2X$

83

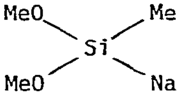
$ON(PPh_3)_2Ni\text{-}Co(CO)_4$ 84

$ON(PPh_3)_2Ni\text{-}Fe(CO)_3NO$ 85

A new class of organosilysodium reagents illustrated by 86 and 87 have been prepared by cleavage of the corresponding disilanes by sodium methoxide [94]. Reagents 86 and 87 undergo alkylation and arylation with appropriate alkyl and aryl halides. Finally, alkylations of phosphide 88 with alkyl, allyl, and benzyl iodides and bromides to give phosphines occur at least in part by a radical process [95]. In contrast, 88 and alkyl chlorides react by an S_N2 mechanism.



86



87

Me_2PK 88

4. REFERENCES

1. E. Weiss and H. Koster, Chem. Ber., 110 (1977) 717.

2. C. Riche, C. Pascard-Billy, C. Cambillau, and G. Bram, J. Chem. Soc., Chem. Comm., (1977) 183.

3. R. Gruning and J.L. Atwood, J. Organomet. Chem., 137 (1977) 101.

4. F.G. Bordwell , Pure & Appl. Chem., 49 (1977) 963.

5. F.G. Bordwell, J.E. Bares, J.E. Bartmess, G.J. McCollum, M. Van Der Puy, N.R. Vanier, and W.S. Matthews, J. Org. Chem., 42 (1977) 321.

6. F.G. Bordwell, J.E. Bares, J.E. Bartmess, G.E. Drucker, J. Gerhold, G.J.

McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, J. Org. Chem., 42 (1977) 326

7. F. G. Bordwell, D. Algrim, and N. R. Vanier, J. Org. Chem., 42 (1977) 1817.

8. F. G. Bordwell and H. E. Fried, Tetrahedron Lett., (1977) 1121.

9. J. Chrisment and J.-J. Delpuech, J. Chem. Soc., Perkin II, (1977) 407.

10. K. P. Ang and T. W. S. Lee, Aust. J. Chem., 30 (1977) 521.

11. E. Buncel and B. Menon, J. Am. Chem. Soc., 99 (1977) 4457.

12. E. Buncel and B. Menon, J. Organomet. Chem., 141 (1977) 1.

13. B. Evans, K. M. Smith, G. N. LaMar, and D. B. Viscio, J. Am. Chem. Soc., 99 (1977) 7070.

14. E. M. Arnett and V. M. DePalma, J. Am. Chem. Soc., 96 (1977) 5828.

15. S. Lillie, S. Slomkowski, G. Levin, and M. Szwarc, J. Am. Chem. Soc., 99 (1977) 4608.

16. H. C. Wang, E. D. Lillie, S. Slomkowski, G. Levin, and M. Szwarc, J. Am. Chem. Soc., 99 (1977) 4612.

17. H. C. Wang, G. Levin, and M. Szwarc, J. Am. Chem. Soc., 99 (1977) 2642.

18. F. Jachimowicz, G. Levin, and M. Szwarc, J. Am. Chem. Soc., 99 (1977) 5977.

19. A. Fischer, M. W. Mogan, and C. Eaborn, J. Organomet. Chem., 136 (1977) 323

20. J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, J. Am. Chem. Soc., 99 (1977) 2515.

21. M. T. Jones and T. C. Kuechler, J. Phys. Chem., 81 (1977) 360.

22. E. Grovenstein, Jr., T. H. Longfield, and D. E. Quest, J. Am. Chem. Soc., 99 (1977) 2800.

23. I. B. Goldberg and B. M. Peake, J. Phys. Chem., 81 (1977) 571.

24. C. Elschenbroich, F. Gerson, H. Ohya-Nishiguchi, C. Wydler, and A. Nissen, Helv. Chim. Acta, 60 (1977) 2530.

25. L. Ciohodaru, V. E. Sahini, and E. Volanschi, Rev. Roum. Chem., 22 (1977) 171.

26. W. Lubitz, R. Biehl, and K. Mobius, J. Magn. Resonance, 27 (1977) 411.

27. S. Konishi, A. H. Reddoch, and D. S. Leniart, J. Magn. Resonance, 28 (1977) 41.

28. R. Biehl, K. Hinrichs, H. Kurreck, W. Lubitz, U. Mennenga, and K. Roth, J. Am. Chem. Soc., 99 (1977) 4278.

29. M. Iwaizumi, S. Kita, T. Isobe, M. Kohno, T. Yamamoto, H. Horita, T. Otsubo, and S. Misumi, Bull. Chem. Soc. Japan, 50 (1977) 2074.

30. J. Bruhin, F. Gerson, W. B. Martin, Jr., and C. Wydler, Helv. Chim. Acta, 60 (1977) 1915.

31. K. Ishizu, Y. Sugimoto, T. Umemoto, Y. Sakata, and S. Misumi, Bull. Chem. Soc. Japan, 50 (1977) 2801.

32. C. Elschenbroich, F. Gerson, and J. A. Reiss, J. Am. Chem. Soc., 99 (1977) 60.

33. L. Grossi, F. Minisci, and G. F. Peduli, J. Chem. Soc., Perkin II, (1977) 943.

34. A. M. Block, R. Concepcion, and G. R. Stevenson, J. Phys. Chem., 81 (1977) 367.

35. K. Schreiner, H. Oehling, H. E. Zieger, and I. Angres, J. Am. Chem. Soc., 99 (1977) 2638.

36. M. A. Kamha, N. M. Katkova, T. V. Leshina, R. Z. Sagdeev, and S. M. Shein, Tetrahedron Lett., (1977) 1313.

37. L. A. Paquette, G. D. Ewing, S. Traynor, and J. M. Gardlik, J. Am. Chem. Soc., 99 (1977) 6115.

38. A. G. Anastassiou, E. Reichmanis, and S. J. Girgenti, J. Am. Chem. Soc., 99 (1977) 7392.

39. N. M. Libman, P. A. Brestkin, S. G. Kuznetsov, Y. A. Ignat'ev, and A. A. Andreev, Zh. Org. Khim., 12 (1976) 2149.

40. L. A. Paquette, H. C. Berk, C. R. Degenhardt, and G. D. Ewing, J. Am. Chem. Soc., 99 (1977) 4764.

41. L. A. Paquette, M. J. Kukla, J. V. Ley, and S. G. Traynor, J. Am. Chem. Soc., 99 (1977) 4756.

42. G. M. Kuzyants, A. O. Baronetsky, T. M. Chernyshova, and Z. V. Todres, J. Organomet. Chem., 142 (1977) 139.

43. D. G. Karraker, J. Inorg. Nucl. Chem., 39 (1977) 87.

44. M. Stahle, J. Hartmann, and M. Schlosser, Helv. Chim. Acta, 60 (1977) 173

45. J. R. Scheffer, R. E. Gayler, T. Zakouras, and A. A. Dzakpasu, J. Am. Chem. Soc., 99 (1977) 7726.

46. C. A. Maryanoff, K. S. Hayes, and K. Mislow, J. Am. Chem. Soc., 99 (1977) 4412.

47. R. N. McDonald and C. A. Curi, J. Am. Chem. Soc., 99 (1977) 7078.

48. A. Rassat, Pure & Appl. Chem., 49 (1977) 1049.

49. T. V. Rajan Babu, D. C. Sanders, and H. Shechter, J. Am. Chem. Soc., 99 (1977) 6449.

50. H. H. Szmant, A. Birke, and M. P. Lau, J. Am. Chem. Soc., 99 (1977) 1863.

51. R. G. Scamehorn and J. F. Bunnett, J. Org. Chem., 42 (1977) 1449.

52. R. G. Scamehorn and J. F. Bunnett, J. Org. Chem., 42 (1977) 1457.

53. S. Hoz and J. F. Bunnett, J. Org. Chem., 42 (1977) 4690.

54. A. P. Komin and J. F. Wolfe, J. Org. Chem., 42 (1977) 2481.

55. H. C. van der Plas, M. Wozniak, and A. van Veldhuizen, Recueil, 96 (1977) 151.

56. M. F. Moreau-Hochu and P. Caubere, Tetrahedron, 33 (1977) 955.

57. L. A. Paquette, Org. Reactions, 25 (1977) 1.

58. W. S. Wadsworth, Jr., Org. Reactions, 25 (1977) 73.

59. W. G. Dauben and D. J. Hart, J. Am. Chem. Soc., 99 (1977) 7307.

60. B. M. Trost and W. J. Frazee, J. Am. Chem. Soc., 99 (1977) 6124.

61. A. M. van Leusen, J. Wildeman, and O. H. Oldenziel, J. Org. Chem., 42 (1977) 1153.

62. O. H. Oldenziel, D. van Leusen, and A. M. van Leusen, J. Org. Chem., 42 (1977) 3114.

63. M. F. Semmelhack and T. M. Bargar, J. Org. Chem., 42 (1977) 1481.

64. M. A. Shippey and P. B. Dervan, J. Org. Chem., 42 (1977) 2654.

65. R. Bayles, M. C. Johnson, R. F. Maisey, and R. W. Turner, Synthesis, (1977) 31.

66. R. Bayles, M. C. Johnson, R. F. Maisey, and R. W. Turner, Synthesis, (1977) 33.

67. E. M. Kaiser and S. L. Hartzell, J. Org. Chem., 42 (1977) 2951.

68. D. Savoia, C. Trombini, and A. Umani-Ronchi, Tetrahedron Lett., (1977) 653

69. H. Hart, B.-L. Chen, and C. Peng, Tetrahedron Lett., (1977) 3121.

70. E. Keinan and Y. Mazur, J. Am. Chem. Soc., 99 (1977) 3861.

71. Y. Leroux and H. Normant, C. R. Acad. Sci. Paris, C, 285 (1977) 241.

72. J. J. Brunet, L. Mordenti, B. Loubinoux, and P. Caubere, Tetrahedron Lett., (1977) 1069.

73. G. Dauphin, B. Jamilloux, A. Kergomard, and D. Planat, Tetrahedron, 33 (1977) 1129.

74. C. A. Young and R. R. Dewald, J. Chem. Soc., Chem. Comm., (1977) 188.

75. B. W. Roberts and J. Wong, J. Chem. Soc., Chem. Comm., (1975) 20.

76. T. Hayashi and L. S. Hegedus, J. Am. Chem. Soc., 99 (1977) 7093.

77. W. R. Jackson and J. U. Strauss, Aust. J. Chem., 30 (1977) 553.

78. W. Beck and B. Olgemoller, J. Organomet. Chem., 127 (1977) C45.

79. A. Guinot, P. Cadiot, and J. L. Roustan, J. Organomet. Chem., 128 (1977) C35.

80. H. des Abbayes and M.-A. Boudeville, J. Org. Chem., 42 (1977) 4104.

81. R. Weiss and R. N. Grimes, J. Am. Chem. Soc., 99 (1977) 8087.

82. N. N. Greenwood and J. Staves, J. Chem. Soc., Dalton, (1977) 1788.

83. W. M. Maxwell, R. F. Bryan, and R. N. Grimes, J. Am. Chem. Soc., 99 (1977) 4008.

84. F. A. Cotton and S. A. Koch, J. Am. Chem. Soc., 99 (1977) 7371.

85. E. O. Fischer, T. L. Lindner, F. R. Kreissl, and P. Braunstein, Chem. Ber.,110 (1977) 3139.

86. E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl, and J. O. Besenhard, Chem. Ber., 110 (1977) 3397.

87. P. Panster and W. Malisch, J. Organomet. Chem., 134 (1977) C32.

88. J. E. Ellis and R. A. Faltynek, J. Am. Chem. Soc., 99 (1977) 1801.

89. D. L. Morse and M. S. Wrighton, J. Organomet. Chem., 125 (1977) 71.

90. H. Alper and H. N. Paik, J. Chem. Soc., Chem. Comm., (1977) 126.

91. G. L. Geoffroy and W. L. Gladfelter, J. Am. Chem. Soc., 99 (1977) 304.

92. R. D. Rieke, W. J. Wolf, N. Kujundzic, and A. V. Kavaliunas, J. Am. Chem. Soc., 99 (1977) 4159.

93. P. Braunstein, J. Dehand, and B. Munchenbach, J. Organomet. Chem., 124 (1977) 71.

94. H. Watanabe, K. Higuchi, M. Kobayashi, M. Hara, Y. Koike, T. Kitahara, and Y. Nagai, J. Chem. Soc., Chem. Comm., (1977) 534.

95. B. W. Bangerter, R. P. Beatty, J. K. Kouba, and S. S. Wreford, J. Org. Chem., 42 (1977) 3247.