[Contribution from the Department of Chemistry, Harvard University]

Chemistry of the Metal Carbonyls. IV. Reactions between Certain Metal Carbonyls and Some Condensed Polycyclic Organic Systems[1,2]

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Molybdenum and tungsten hexacarbonyls react with 8,9-dihydroindene to give red solids of composition $C_9H_{10}\cdot M(CO)_3$ [M = Mo, W]. Hydrogenation studies suggest that the molybdenum compound is cyclononatetraene-molybdenum tricarbonyl. An iron compound, an unstable yellow oil $C_9H_{10}\cdot Fe(CO)_3$, has also been prepared from 8,9-dihydroindene, but in this complex the organic moiety appears not to have changed to its monocyclic form. Reactions between chromium carbonyl and anthracene, phenanthrene and pyrene have been investigated. Treatment of thianaphthene with chromium carbonyl or triiron dodecacarbonyl, under the appropriate conditions, affords yellow $C_8H_6S\cdot Cr(CO)_3$ and red-orange $(CO)_3Fe\cdot C_8H_6S\cdot Fe(CO)_3$, respectively. Similarly, acenaphthylene reacts with chromium hexacarbonyl to give purple-black $C_{12}H_8\cdot Cr(CO)_3$, and with triiron dodecacarbonyl to give $(CO)_3Fe\cdot C_{12}H_8\cdot Fe(CO)_3$. The probable structures of the new compounds are discussed.

Recently a variety of metal complexes have been described in which a seven- or eight-membered carbocyclic system is bonded to the metal. Thus direct reactions between molybdenum hexacarbonyl or iron pentacarbonyl and cycloheptatriene yield the cycloheptatriene complexes $C_7H_8\cdot Mo(CO)_3$[4] and $C_7H_8\cdot Fe(CO)_2$,[5] respectively, while $C_7H_8\cdot W(CO)_3$ has been obtained by a displacement reaction between cycloheptatriene and 1,5-cyclooöctadiene-tungsten tetracarbonyl.[6] These complexes are formed from cycloheptatriene without loss of hydrogen. A study of the reaction between cycloheptatriene and the cyclopentadienyl carbonyl $C_5H_5V(CO)_4$ produced the first neutral C_7H_7 sandwich compound $C_5H_5VC_7H_7$.[7] Prior to this work an ionic complex of the tropylium group, $[C_7H_7Mo(CO)_3]^+[BF_4]^-$, had been prepared by abstraction of hydride ion from the neutral compound $C_7H_8\cdot Mo(CO)_3$[8] with trityl fluoborate. In all these seven-membered ring complexes it is likely that metal–ring bonding is of the sandwich type.

Much more varied in nature are several known metal complexes in which the metal is associated with the eight-membered rings of 1,5-cyclooöctadiene, 1,3,5- and 1,3,6-cyclooöctatrienes, and cyclooctatetraene. Thus in $C_5H_5RhC_8H_{12}$[9] and in $C_8H_{12}\cdot W(CO)_4$,[10] cyclooöctadiene functions as a chelating group, and the metal is bonded to the eight-membered ring by two essentially independent coördinate bonds of the σ,π-type[11] with only four of the eight carbon atoms of the ring associated with the metal. Indeed, $C_8H_{12}\cdot W(CO)_4$[10] was prepared for the purpose of enlarging the region in the Periodic Table containing transition metals which form olefin complexes. In contrast to 1,5-cyclooöctadiene, 1,3,5-cyclooöctatriene forms the compounds $C_8H_{10}\cdot M(CO)_3$ [M = Cr, Mo][12] in which six of the eight carbon atoms of the ring are involved in bonding to the metal, and the metal–ring bonding may be somewhat like that proposed[4] for the bonding in cycloheptatriene-molybdenum tricarbonyl, although less electron delocalization must be involved. 1,3,6-Cyclooöctatriene, on the other hand, forms metal complexes, which are very probably of the diolefin chelate type, *e.g.*, $(C_8H_{10})_2W(CO)_2$.[12] Cyclooöctatetraene can also serve as a chelating group as in the compounds $C_8H_8\cdot PtI_2$[13] and $[C_8H_8\cdot RhCl]_2$.[14] In these compounds four of the eight carbon atoms of cyclooöctatetraene are involved in bonding to the metal; two double bonds remain unaffected, as shown by hydrogenation studies in the case of $C_8H_8\cdot PtI_2$.[15] However, in the cyclooöctatetraene complex $C_8H_8\cdot Fe(CO)_3$,[15] and possibly also in the binuclear complex $(CO)_3Fe\cdot C_8H_8\cdot Fe(CO)_3$, evidence has been presented[15] that cyclooöctatetraene has acquired a planar configuration.[16] It thus appears that cyclooöctatetraene can play a dual role, forming olefin complexes, as does 1,5-cyclooöctadiene in, for example, $C_8H_{12}\cdot W(CO)_4$, and forming sandwich compounds, as does benzene in, for example, $C_6H_6\cdot Cr(CO)_3$.

In view of the interesting chemistry associated with metal complexes in which one of the ligands is a seven- or eight-membered cyclic hydrocarbon, it seemed pertinent to consider the possibility of making metal complexes involving a nine-membered ring hydrocarbon. In this connection cyclononatetraene would appear to be the most interesting system. With this hydrocarbon and a suitable metal there is the possibility of forming complexes involving bonding of the metal to two, four, six or eight carbon atoms of the ring; alternatively, there is the possibility of forming cyclononatetraenyl π-complexes derived from the $C_9H_9\cdot$ group, formed by loss of hydrogen from the parent hydro-

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(1) Previous paper in this series, R. B. King and F. G. A. Stone, This Journal, **82**, 3833 (1960); see also, T. A. Manuel and F. G. A. Stone, *Chemistry & Industry*, 231 (1960).

(2) We are indebted to the Milton Fund of Harvard University for financial support of this work.

(3) National Science Foundation Predoctoral Research Fellow, 1958–1960.

(4) E. W. Abel, M. A. Bennett, R. Burton and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).

(5) R. Burton, M. L. H. Green, E. W. Abel and G. Wilkinson, *Chemistry & Industry*, 1592 (1958).

(6) T. A. Manuel and F. G. A. Stone, *ibid.*, 231 (1960).

(7) R. B. King and F. G. A. Stone, This Journal, **81**, 5263 (1959).

(8) H. J. Dauben and L. P. Honnen, *ibid.*, **80**, 5570 (1958).

(9) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

(10) T. A. Manuel and F. G. A. Stone, *Chemistry & Industry*, 1349 (1959).

(11) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(12) (a) E. O. Fischer, C. Palm and H. P. Fritz, *Ber.*, **92**, 2645 (1959); (b) E. O. Fischer and C. Palm, *Z. Naturforschg.*, **14b**, 598 (1959).

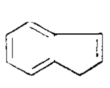
(13) K. A. Jensen, *Acta Chem. Scand.*, **7**, 868 (1953).

(14) E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

(15) T. A. Manuel and F. G. A. Stone, This Journal, **82**, 366 (1960).

(16) For the interesting suggestion that whereas in $C_8H_8\cdot Fe(CO)_3$ the cyclooöctatetraene moiety is probably planar while in $(CO)_3Fe\cdot C_8H_8\cdot Fe(CO)_3$ it may retain its normal tub form, see F. A. Cotton, *J. Chem. Soc.*, 400 (1960).

carbon. The latter eventuality would be analogous to formation of the $C_5H_5\cdot$ group in the preparation of many cyclopentadienyl metal complexes, and to the formation of $C_7H_7VC_5H_5$. Formation of metal complexes from $C_9H_9\cdot$, however, is rather unlikely when the number of electrons involved is considered in conjunction with the effective atomic number rule, the latter not being entirely valueless in this field. It is improbable, therefore, that cyclononatetraene would lose hydrogen in reaction with a metal carbonyl. More likely is the formation of compounds analogous to cycloheptatriene-molybdenum tricarbonyl,[4] and 1,3,5-cyclooctatriene-molybdenum tricarbonyl.[12] Considerations such as these, however, would seem at first sight somewhat hypothetical, since cyclononatetraene (I) has never been reported in the chemical literature. However, the bicyclic compound, 8,9-dihydroindene (bicyclo[4.3.0]nonatriene) has been prepared by Alder and Flock[17] by pyrolysis of 1-dicyclopentadienone. Formally, 8,9-dihydroindene (II) is the bicyclic tautomer of cyclononatetraene (I), although Alder and Flock did not detect its presence in II. Nevertheless, it seemed possible that the reaction between 8,9-dihydroindene and an appropriately chosen metal carbonyl at elevated temperatures might produce a metal derivative of cyclononatetraene. This idea seemed worthwhile since there is already an example in the literature of a reaction between a metal carbonyl and a tautomeric mixture of hydrocarbons in which one tautomer forms a metal complex in preference to the other. It is well known[18] that 1,3,5-cyclooctatriene(III) is in dynamic equilibrium with bicyclo[4.2.0]octa-2,4-diene (IV). When these tautomers, together with isomeric 1,3,6-cyclooctatriene, are heated with iron pentacarbonyl at elevated temperatures, one reaction product is a compound $C_8H_{10}\cdot Fe(CO)_3$.[12a,15] Although Fischer, Palm and Fritz[12a] consider this complex to be 1,3,6-cyclooctatriene-iron tricarbonyl, evidence presented elsewhere[15] strongly suggests that this is incorrect, and that the bicyclo[4.2.0]octa-2,4-diene group (IV) is present in this particular $C_8H_{10}\cdot Fe(CO)_3$ compound, made independently by Fischer, *et al.*,[12a] and in this Laboratory.[15]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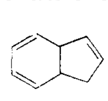
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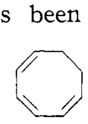
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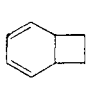
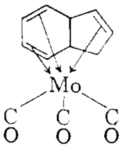
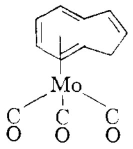

IV

Molybdenum hexacarbonyl and 8,9-dihydroindene react at about 170° to give brick-red crystals of molecular composition $C_9H_{10}\cdot Mo(CO)_3$. From the analytical and molecular weight data two structures (V and VI) are possible.


V


VI

If the compound has structure V, it would be a derivative of the bicyclic 8,9-dihydroindene and all three double bonds would be involved in bonding to the metal. If the compound is cyclononatetraene-molybdenum tricarbonyl (VI), however, one double bond is not involved in bonding to the metal. Therefore, the compound should absorb up to one mole of hydrogen. Hydrogenation studies were carried out and it was found that the complex did indeed absorb close to one mole of hydrogen per mole of complex. This result suggests that $C_9H_{10}\cdot Mo(CO)_3$[19] is very probably a cyclononatetraene derivative, but in order to confirm the structure further evidence is required. A nuclear magnetic resonance study was made, but as is frequently the case when a non-aromatic moiety is bonded to a metal, the proton spectrum was exceedingly complicated.

The compound $C_9H_{10}\cdot Mo(CO)_3$ is soluble in a variety of organic solvents to give slightly air-sensitive solutions. In the solid state when kept in a sealed container the molybdenum complex partially decomposes after storage for several weeks. The infrared spectrum of $C_9H_{10}\cdot Mo(CO)_3$, taken in carbon disulfide, shows carbonyl stretching bands at 1960, 1890 and 1861 cm.$^{-1}$.

From the reaction between 8,9-dihydroindene and tungsten carbonyl the compound $C_9H_{10}\cdot W(CO)_3$ may be obtained. This complex, like its molybdenum analog, is a red solid sublimable at 150° (0.05 mm.) with carbonyl bands in its infrared spectrum (CS_2 solution) at 1950, 1894 and 1861 cm.$^{-1}$. Unfortunately, although $C_9H_{10}\cdot W(CO)_3$ absorbed some hydrogen the compound proved to be too unstable for accurate hydrogenation studies. However, the nuclear magnetic resonance spectrum of $C_9H_{10}\cdot W(CO)_3$ was very similar to that of $C_9H_{10}\cdot Mo(CO)_3$ so that the two compounds appear to have the same structure. Under conditions similar to those used to make $C_9H_{10}\cdot M(CO)_3$ (M = Mo, W), chromium carbonyl and 8,9-dihydroindene react rapidly with formation of a yellow-black solution. The reaction mixture had an infrared spectrum which showed carbonyl bands at 1958, 1893, 1870 and 1989 cm.$^{-1}$. The band at 1989 cm.$^{-1}$ is due to unreacted chromium carbonyl, but the other three bands could well be due to the presence of the chromium complex $C_9H_{10}\cdot Cr(CO)_3$. However, attempts to isolate a pure chromium compound from this mixture by sublimation at temperatures up to 140° (0.1 mm.) yielded only the merest trace of a green oil which decomposed instantaneously on exposure to air to a red gum. Apparently the chromium complex is much less stable than even the tungsten compound. It is interesting that chromium carbonyl reacts more rapidly with 8,9-dihydroindene than does molybdenum or tungsten hexacarbonyls. This is in contrast to the relative rates of reaction of carbonyls of the Group VI metals with aromatic hydrocarbons, sodium cyclopentadienide and cyclooctatriene. With these substances chromium carbonyl is the least reactive of the three carbonyls.

In view of the reactions which occurred between 8,9-dihydroindene and carbonyls of the Group VI

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[17] K. Alder and F. H. Flock, *Ber.*, **87**, 1916 (1954).

[18] A. C. Cope, A. C. Haven, F. L. Ramp and E. R. Trumbull, THIS JOURNAL, **74**, 4867 (1952).

[19] For a preliminary mention of the compound $C_9H_{10}\cdot Mo(CO)_3$ see R. B. King and F. G. A. Stone, *Chemistry & Industry*, 232 (1960).

metals it was considered worthwhile to determine if triiron dodecacarbonyl would react with 8,9-dihydroindene to afford an iron carbonyl complex.[20] Treatment of $Fe_3(CO)_{12}$ with 8,9-dihydroindene at 80° in benzene gave a very unstable compound $C_9H_{10}\cdot Fe(CO)_3$, as a yellow volatile oil crystallizing to a light yellow solid slightly below room temperature. The iron compound decomposed even when kept below 0° under nitrogen. The infrared spectrum (CS_2 solution) showed strong bands at 2053 and 1989 cm.$^{-1}$ characteristic of an iron tricarbonyl group. Unfortunately, the low stability of the iron compound prevented its detailed investigation. In general, complexes of iron tricarbonyl with conjugated dienes are much more stable than those of non-conjugated dienes.[21] This suggests that in $C_9H_{10}\cdot Fe(CO)_3$ a dihydroindene group is bonded to iron by two dative bonds involving two double bonds which are non-conjugated.

It is interesting to compare the behavior of 8,9-dihydroindene toward metal carbonyls with that of indene itself. Hallam and Pauson[22a] have shown that in an autoclave at elevated temperatures iron pentacarbonyl and indene form $[C_9H_7Fe(CO)_2]_2$, analogous to the cyclopentadienyl derivative $[C_5H_5Fe(CO)_2]_2$.[22b] In this Laboratory reactions between indene and the iron carbonyls $Fe(CO)_5$ and $Fe_3(CO)_{12}$ in both polar and non-polar solvents under mild thermal conditions yielded only Hallam and Pauson's indenyl derivative. No indene complexes such as $C_9H_8\cdot Fe(CO)_3$ or $C_9H_8[Fe(CO)_3]_2$ were isolated.

In an attempt to determine whether an arene derivative of indene of the type $C_9H_8\cdot Mo(CO)_3$, analogous to $C_6H_6\cdot Mo(CO)_3$, or an indenyl derivative of the type $[C_9H_7Mo(CO)_3]_2$, analogous to $[C_5H_5Mo(CO)_3]_2$, would be formed, the reaction between indene and molybdenum hexacarbonyl was investigated. The reaction product was a brown solid sublimable *in vacuo* which proved to be the indenyl derivative $[C_9H_7Mo(CO)_3]_2$ with the molybdenum atom bonded to the five-membered ring of the indene system. As in the corresponding cyclopentadienyl derivative, this new indenyl derivative shows no bridging carbonyl bands in its infrared spectrum and, therefore, the two halves of the molecule must be held together by a molybdenum-molybdenum bond.

In addition to the work described above, involving 8,9-dihydroindene and indene, a number of reactions of aromatic hydrocarbons with chromium carbonyl and the iron carbonyls have been investigated in this Laboratory.

The compound benzene-chromium tricarbonyl is the parent compound of a series of arene-chromium tricarbonyl compounds which have been prepared by the direct reaction between chromium hexacarbonyl and aromatic hydrocarbons.[23] Besides using a great variety of substituted benzene derivatives Fischer, *et al.*,[23b] have extended this reaction to the preparation of naphthalene chromium tricarbonyl, with brief mention of the fact that higher condensed hydrocarbons such as anthracene and phenanthrene give highly colored solutions when heated with chromium hexacarbonyl. Because no chromium carbonyl derivatives of polycyclic benzenoid hydrocarbons other than the naphthalene compound have been isolated, and because it seemed possible that certain polycyclic aromatic compounds might yield either isomeric or polynuclear chromium derivatives, reactions between chromium carbonyl and benzpyrene, chrysene, phenanthrene, anthracene and pyrene were studied. With benzpyrene and chrysene isolation of a pure product was impossible due to the low solubility of the products in organic solvents as well as the low volatility of both the products and the reactant hydrocarbon.[24]

At about 170° phenanthrene and chromium hexacarbonyl form orange crystalline $C_{14}H_{10}\cdot Cr(CO)_3$ in about 27% yield. Phenanthrene-chromium tricarbonyl was too insoluble to permit study of its proton nuclear magnetic resonance spectrum so that it proved impossible by this technique to determine whether the $Cr(CO)_3$ group is bonded to the center ring or one of the outer rings of the phenanthrene molecule. The stability of the phenanthrene derivative is approximately the same as the naphthalene derivative,[23b] fusion of an extra ring to the naphthalene system in an *angular* position apparently not greatly affecting the stability of the chromium-tricarbonyl derivative. Even the hydrocarbon chrysene, produced by fusion of a fourth ring to the phenanthrene system in an angular manner, still gives a chromium derivative of comparable stability; although, because of the difficulties mentioned above, freeing the compound entirely from chrysene proved impossible. In an attempt to prepare anthracene-chromium tricarbonyl from anthracene and chromium hexacarbonyl, using conditions similar to those which led to the isolation of phenanthrene-chromium tricarbonyl, only chromium metal was obtained. If, however, the reaction is carried out at 135° a purple solution is obtained, but the amount of desired chromium compound in this solution, although detectable by its infrared spectrum, is very small.[24] Attempts to isolate a compound in a manner similar to that used successfully for the preparation of the phenanthrene compound or by chromatography yielded negative results. Thus it appears that anthracene-chromium tricarbonyl, unlike the phenanthrene compound, is much less stable than naphthalene-chromium tricarbonyl. Apparently

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(20) Iron pentacarbonyl was not used since it has previously been shown that triiron dodecacarbonyl is a more effective starting material for forming iron complexes; see W. Hübel, E. H. Braye, A. Clauss, E. Weiss, U. Krüerke, D. A. Brown, G. S. D. King and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959).

(21) R B. King, T. A. Manuel and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, in press.

(22) (a) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 646 (1958); (b) 3030 (1956).

(23) (a) B. Nicholls and M. C. Whiting, *ibid.*, 551 (1959); (b) E. O. Fischer, K. Öfele, H. Essler, W. Frölich, J. P. Mortensen and W. Semmlinger, *Ber.*, **91**, 2763 (1958); G. Natta, R. Ercoli and F. Calderazzo, *Chem. e Ind. Milano*, **40**, 287 (1958).

(24) After this paper was submitted, a paper by E. O. Fischer, N. Kriebitzsch and R. D. Fischer, *Ber.*, **92**, 3214 (1959), appeared, which independently described the preparation and properties of phenanthrene-chromium tricarbonyl. However, their yield (4.5%) of this compound was substantially lower than that obtained (27%) in our work. Fischer, *et al.*, also report chrysene-chromium tricarbonyl, and a purple compound (0.1% yield) from the reaction between chromium carbonyl and anthracene which they suggest is anthracene-chromium tricarbonyl on the basis of spectral properties, although they obtained insufficient material for analysis.

fusion of an extra ring to the naphthalene system in a *linear* position leads to a marked reduction in the stability of the chromium derivative. As might be expected, therefore, naphthacene gave no evidence of forming a chromium tricarbonyl derivative.

Pyrene, which has still a different type of arrangement of fused benzene rings, reacts with chromium hexcarbonyl at 135° to give brick-red crystalline $C_{16}H_{10}\cdot Cr(CO)_3$ in 12% yield, which is only sparingly soluble in the usual organic solvents. On standing for several months this compound, unlike the naphthalene and phenanthrene derivatives, decomposed completely.

All the polycyclic aromatic chromium derivatives have similar spectra in the carbonyl region of the infrared, showing just two bands near 1960 and 1890 cm.$^{-1}$ like the simpler arene-chromium tricarbonyl derivatives.[23] It is also interesting to note that the stability of chromium derivatives of those aromatic hydrocarbons which can be regarded as derived by fusion of benzene rings decreases with deepening of their color.

Reactions between the polycyclic compounds acenaphthylene or thianaphthene and chromium hexacarbonyl or iron carbonyls were also studied. Acenaphthylene is of interest as a ligand because it is the simplest stable tricyclic system having twelve π-electrons available for bonding to a transition metal. Thianaphthene is the simplest example of a condensed ring system containing a thiophene nucleus. In the case of thianaphthene it was of interest to determine whether the thiophene ring or the benzene ring would bond preferentially to the transition metal.

Thianaphthene and chromium carbonyl react in an inert solvent at 170° to give yellow crystalline thianaphthene-chromium tricarbonyl, volatile at 100° (0.1 mm.), in yields of about 2%. Since benzene-chromium tricarbonyl is yellow[23] and thiophene-chromium tricarbonyl[25] is red-orange, the yellow color of $C_8H_6S\cdot Cr(CO)_3$ suggests that the chromium atom is bonded to the benzene ring. Treatment of thianaphthene with triiron dodecacarbonyl at 80° affords red-orange air stable crystalline $C_8H_6SFe_2(CO)_5$ in about 6% yield. This interesting binuclear iron complex is similar to the previously reported[5] azulene compound $C_{10}H_8Fe_2(CO)_5$, and the two complexes both show three carbonyl bands in their infrared spectra. Thianaphthene, like azulene, has ten π-electrons available for bonding to transition metal atoms. In terms of the effective atomic number rule six π-electrons may be regarded as being associated with the iron atom of the $Fe(CO)_2$ group and the remaining four π-electrons can be regarded as being associated with the iron atom of the $Fe(CO)_3$ group. The nuclear magnetic resonance spectrum of $C_8H_6SFe_2(CO)_5$, besides showing the compound to be diamagnetic, has a single peak at 981 c.p.s. referred to that of hexamethyldisiloxane at 1258 c.p.s. The existence of a single proton resonance is not surprising since all six hydrogen atoms of the thianaphthene moiety are bonded to carbon atoms sandwich bonded to iron atoms.

The aromatic compound acenaphthylene was also found to give complexes with both chromium and iron. The purple-black compound $C_{12}H_8\cdot Cr(CO)_3$, volatile at 100–110° (0.1 mm.), is formed in about 5% yield. This compound is evidently an arene-chromium tricarbonyl complex with a $Cr(CO)_3$ group bonded to one of the six-membered rings of the acenaphthylene system. It is the most intensely colored arene chromium-tricarbonyl derivative isolated in the pure state.

From the reaction between acenaphthylene and triiron dodecarbonyl the compound $C_{12}H_8[Fe(CO)_3]_2$ was obtained in about 15% yield. This binuclear iron complex melts at 158°, and its diamagnetism was shown both by a Gouy balance measurement and a nuclear magnetic resonance study. Since the effective atomic number rule predicts that the two iron atoms of the two $Fe(CO)_3$ groups require a total of eight π-electrons to acquire an inert gas configuration, and since acenaphthylene has twelve π-electrons, this would seem to imply that two double bonds of the acenaphthylene moiety in $C_{12}H_8[Fe(CO)_3]_2$ are not involved in bonding to the iron atoms. Acenaphthylene-diiron hexacarbonyl, however, could not be hydrogenated. This situation is entirely analogous to that existing in cycloöctatetraene-iron tricarbonyl[26] where a $Fe(CO)_3$ group is associated with an eight π-electron system, four more electrons than are necessary for the iron atom to acquire the krypton configuration, yet all eight carbon atoms of cycloöctatetraene are bonded to iron.[15]

Experimental[27]

Infrared spectra were recorded using a model 21 Perkin–Elmer double-beam spectrophotometer with sodium chloride optics. Unless otherwise indicated, carbon disulfide solutions were used for the infrared spectra measurements. Proton magnetic resonance spectra were obtained at 40 megacycles by a Varian model 4300B high resolution spectrometer fitted with a super stabilizer. For n.m.r. work saturated solutions of the compounds to be studied were prepared in carbon disulfide. A Cary model 11M recording spectrophotometer was used to take ultraviolet spectra.

8,9-Dihydroindene[17] was obtained in 23% yield by pyrolysis of 1-dicyclopentadienone.[17,28] The pyrolyzate was collected at −78° and fractionally distilled at 59–62° (25 mm.).

Anal. Calcd. for C_9H_{10}: C, 91.5; H, 8.5. Found: C, 91.2; H, 8.5.

The proton n.m.r. spectrum of 8,9-dihydroindene has three peaks of approximate area 3:1:1 at 1038, 1142 and 1172 c.p.s. (hexamethyldisiloxane internal standard at 1258 c.p.s.). The peak of largest area may be ascribed to the vinylic protons, and the two smaller peaks of approximately equal area ascribed to the methylene protons and to the allylic protons at the 8,9-positions of the dihydroindene. Alder and Flock[17] did not report the ultraviolet spectrum of 8,9-dihydroindene. The compound, in cyclohexane, has maxima at 262 mμ (ε 3500) and 271 mμ (ε 3200).

Reaction between 8,9-Dihydroindene and Molybdenum and Tungsten Hexacarbonyls.—A mixture of 1.32 g. (5 mmoles) of molybdenum hexacarbonyl, 0.65 ml. (0.62 g.,

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[25] E. O. Fischer and K. Öfele, *Ber.*, **91**, 2395 (1958).

[26] Cycloöctatetraene-iron tricarbonyl was apparently prepared independently by several groups of workers. See ref. 15, and M. D. Rausch and G. N. Schrauzer, *Chemistry & Industry*, 957 (1959); also A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

[27] Microanalyses were performed by Dr. Carol Fitz, Needham Heights, Mass., and by W. Manser, Eidg. T. H., Zurich, Switzerland. We are indebted to our colleague Mr. L. Nichols for making the molecular weight determinations by measuring vapor pressures of dichloromethane solutions of the various compounds.

[28] (a) M. Rosenblum, THIS JOURNAL, **79**, 3179 (1957); (b) T. J. Katz, Ph.D. Thesis, Harvard University, June, 1959.

5.26 mmoles) of 8,9-dihydroindene and 30 ml. of Phillips solvent Soltrol 130 (b.p.~170°) was refluxed at the boiling point for 1.5 hr. under nitrogen. The reaction mixture soon became dark red. The reaction flask was cooled to room temperature and then for 2 hr. at −78°. The resultant dark red precipitate was filtered and sucked dry. Sublimation (140° (0.1 mm.)) for 12 hr. afforded 260 mg. (17.5% yield based on $Mo(CO)_6$) of $C_9H_{10}{\cdot}Mo(CO)_3$. This material, as well as that from another preparation, was analyzed.

Anal. Calcd. for $C_{12}H_{10}O_3Mo$: C, 48.3; H, 3.3; Mo, 32.2; mol. wt., 298. Found: C, 48.6, 48.8; H, 3.5, 3.2; Mo, 32.4, 33.3; mol. wt., 285, 319.

A 25.9-mg. sample of $C_9H_{10}{\cdot}Mo(CO)_3$ (m.p., apparently with decomp., 128°) was subjected to a microhydrogenation[29] study using glacial acetic acid as solvent. The catalyst was PtO_2 reduced with hydrogen before the determination. Hydrogen (1.55 cc. at 23° (730 mm.)) was absorbed equivalent to 70% of that expected for the presence of one free double bond in $C_9H_{10}{\cdot}Mo(CO)_3$. In repeat hydrogenation studies, using samples of $C_9H_{10}{\cdot}Mo(CO)_3$ obtained from different preparations, hydrogen absorption as a percentage expected for one double bond was 99% (acetic acid as solvent) and 67% (ethanol as solvent).

The compound $C_9H_{10}{\cdot}W(CO)_3$ was prepared (11% yield) in a manner similar to the molybdenum compound. The reaction mixture turned black rather than red, and sublimation was carried out at 150–165° (0.1 mm.).

Anal. Calcd. for $C_{12}H_{10}O_3W$: C, 37.3; H, 2.6. Found: C, 37.0; H, 2.9.

Reaction between 8,9-Dihydroindene and Triiron Dodecacarbonyl.—A mixture of 1.8 g. (3.6 mmoles) of $Fe_3(CO)_{12}$,[30] 0.65 ml. (0.62 g., 5.26 mmoles) of 8,9-dihydroindene and 40 ml. of thiophene-free benzene was refluxed under nitrogen for 6 hr. Filtration under nitrogen gave a red-orange air-sensitive filtrate. Benzene was removed at 30 mm. to give a reddish oil. The latter was shaken with 5 ml. of isohexane, and filtered under nitrogen pressure. On cooling the filtrate to −78° for 6 hr. pale orange crystals were obtained. Supernatant liquid was decanted and the crystals warmed to room temperature, melting in the process. The red liquid thus obtained was transferred to a sublimer, dried at 25° (0.1 mm.) for 0.5 hr., and then sublimed (70°(0.1 mm.)) with the probe of the sublimer at −78°. This gave pale yellow crystals which were resublimed giving 260 mg. (19% yield) of $C_9H_{10}{\cdot}Fe(CO)_3$. The yellow crystals melted near room temperature to an air-sensitive yellow oil.

Anal. Calcd. for $C_{12}H_{10}O_3Fe$: C, 55.8; H, 3.9. Found: C, 55.9; H, 4.0.

Phenanthrene-Chromium Tricarbonyl.—Chromium hexacarbonyl (1.1 g., 5 mmoles), phenanthrene (1.8 g., 10 mmoles) and 40 ml. of Soltrol 130 were boiled (~170°) under nitrogen for 2.25 hr., the reaction mixture developing an orange color. After cooling to room temperature, white and orange crystals were removed by filtration and transferred to a sublimer. Excess of phenanthrene was removed by sublimation (70–90°(0.1 mm.)) for 4 hr., leaving 430 mg. (27% yield) of crude phenanthrene-chromium tricarbonyl. Further purification was accomplished by dissolving the product in 15 ml. of dichloromethane and adding isohexane until the compound just began to precipitate. Filtration was followed by concentration of the filtrate to about half its volume. This gave orange crystals which were separated and recrystallized a second time in the same manner to give 220 mg. of bright orange $C_{14}H_{10}{\cdot}Cr(CO)_3$, which in a melting point tube darkens at 140° and melts at 158–160° to a red-orange liquid. In chloroform solution phenanthrene-chromium tricarbonyl showed carbonyl bands at 1980 and 1900 cm.$^{-1}$. Its ultraviolet spectrum in cyclohexane showed a maximum at 219 mμ (ε 37,500) and a minimum at 317 mμ (ε 3200).

Anal. Calcd. for $C_{17}H_{10}O_3Cr$: C, 65.0; H, 3.2. Found: C, 64.8; H, 3.0.

Pyrene-Chromium Tricarbonyl.—Chromium hexacarbonyl (1.2 g., 5.45 mmoles), pyrene (0.5 g., 2.5 mmoles) and ethylcyclohexane (40 ml.) were refluxed under nitrogen for 24 hr. The bright red reaction mixture was cooled to 0° and the resulting reddish precipitate filtered and washed with three 10-ml. portions of 30–60° petroleum ether. The crude product was then partially dissolved in 15 ml. of dichloromethane and filtered. The filtrate was treated with 30 ml. of petroleum ether and cooled to −78°. Red crystals of $C_{16}H_{10}{\cdot}Cr(CO)_3$ (100 mg., 12% yield based on pyrene taken for reaction) thus obtained were dried at 35° (0.1 mm) for 60 hr. to remove traces of chromium carbonyl. Pyrene-chromium tricarbonyl in chloroform solution showed carbonyl bands at 1960 and 1890 cm.$^{-1}$. On exposure to air over a period of weeks the pyrene-chromium complex turned brown.

Anal. Calcd. for $C_{19}H_{10}O_3Cr$: C, 67.4; H, 2.95; Cr, 15.4. Found: C, 66.3; H, 3.0; Cr, 14.7.

Indenyl-Molybdenum Tricarbonyl Dimer.—Molybdenum hexacarbonyl (1.3 g., 5 mmoles), indene (2 ml.,~17.25 mmoles) and Soltrol 130 (40 ml.) were refluxed for 2 hr. under nitrogen. The mixture was cooled to room temperature and filtered. Sublimation (165–170°(0.1 mm.)) of the residue for 14 hr. afforded 150 mg. (10% yield) of brown crystalline $[C_9H_7Mo(CO)_3]_2$, m.p. 195–197° dec. Indenyl-molybdenum tricarbonyl dimer has in its infrared spectrum carbonyl bands at 2045 (rel. weak), 1965 and 1910 cm.$^{-1}$. For the sake of comparison $[C_5H_5Mo(CO)_3]_2$ has carbonyl bands at 2045 (rel. weak), 1970 and 1920 cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{14}O_6Mo_2$: C, 48.8; H, 2.4; Mo, 32.5; mol. wt., 590. Found: C, 49.0; H, 2.7; Mo, 32.3; mol. wt., 628.

Thianaphthene-Chromium Tricarbonyl.—Chromium hexacarbonyl (1.15 g., 5.2 mmoles), thianaphthene (0.67 g., 5 mmoles) and 30 ml. of Soltrol 130 were refluxed for 3 hr. under nitrogen. After cooling to room temperature the yellow mixture was filtered, and the filtrate cooled to −78°, giving a bulky yellow precipitate. The latter was filtered, and excess of thianaphthene removed by 2-hr. sublimation (50–60°(0.1 mm.)). After cleaning the probe of the sublimer, sublimation was continued at 90–100°(0.1 mm.) to give 25 mg. (2% yield) of yellow crystals of $C_8H_6S{\cdot}Cr(CO)_3$. The compound turns black at 115°, and has carbonyl bands at 1980 and 1909 cm.$^{-1}$ in its infrared spectrum.

Anal. Calcd. for $C_{11}H_6O_3SCr$: C, 48.9; H, 2.2; Cr, 19.2. Found: C, 49.1; H, 2.3; Cr, 19.0.

Thianaphthene-Diiron Pentacarbonyl.—Triiron dodecacarbonyl (1.8 g., 3.6 mmoles), thianaphthene (0.67 g., 5 mmoles) and 40 ml. of thiophene-free benzene were refluxed for 9 hr. under nitrogen. The reaction mixture was cooled, filtered under nitrogen, and the filtrate evaporated at 30 mm. to give a red-orange oil. The latter was treated with 20 ml. of isohexane and the solution cooled to −78°. An orange crystalline solid separated which was filtered after one hour. Excess of thianaphthene was removed by sublimation at 50–60°(0.1 mm.). After removal of thianaphthene from the probe of the sublimer, sublimation was continued at 80–90°(0.1 mm.) to give 120 mg. (6% yield) of thianaphthene-diiron pentacarbonyl, a red-orange air-stable solid, m.p. 100–101°.

Anal. Calcd. for $C_{13}H_6O_5SFe_2$: C, 40.4; H, 1.5; S, 8.3; Fe, 29.0; mol. wt., 386. Found: C, 40.6; H, 1.5; S, 8.3; Fe, 28.7; mol. wt., 366.

Thianaphthene-diiron pentacarbonyl has maxima in its ultraviolet spectrum (cyclohexane solution) at 210 mμ (ε 45,300) and 309 mμ (ε 7900). The infrared spectrum of the compound shows carbonyl stretching bands at 2087, 2052 and 2010 cm.$^{-1}$. The azulene compound $C_{10}H_8Fe_2(CO)_5$, first reported by Wilkinson, *et al.*,[5] has also been made in this Laboratory and has carbonyl bands at 2045, 2000 and 1973 cm.$^{-1}$.

Acenaphthylene-Chromium Tricarbonyl.—Chromium hexacarbonyl (1.2 g., 5.5 mmoles), acenaphthylene (0.38 g., 2.5 mmoles) and 37 ml. of ethylcyclohexane were refluxed under nitrogen for 15 hr. The yellow reaction mixture soon became a deep violet. After the reaction period the mixture was cooled to room temperature, filtered, and the purple filtrate evaporated to dryness at 25° (0.1 mm.). The purple solid residue was sublimed (105° (0.1 mm.)), after 15 minutes an oily material was removed from the probe, and the sublimation continued for 12 hr. This af-

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(29) We are indebted to Professor R. B. Woodward for making this equipment, described by N. Clauson-Kaas and F. Limborg, *Acta Chem. Scand.*, **1**, 884 (1947), available for our use.

(30) W. Hieber, *Z. anorg. Chem.*, **204**, 165 (1932); W. Hieber and G. Brendel, *ibid.*, **289**, 324 (1957).

forded 40 mg. (5.5% yield based on acenaphthylene) of acenaphthylene-chromium tricarbonyl, a purple-black solid, decomposing near 175°, which gives intense violet solutions in organic solvents which are completely decolorized when exposed to air for several days. The acenaphthylene-chromium complex has carbonyl bands at 1970 and 1892 cm.$^{-1}$ in its infrared spectrum, and maxima in its ultraviolet spectrum (taken in cyclohexane) at 215 mμ (ε 38,500) and 349 mμ (ε 7420), with a minimum at 308 mμ (ε 3220).

Anal. Calcd. for $C_{15}H_{18}O_3Cr$: C, 62.5; H, 2.8. Found: C, 63.0; H, 3.1.

Acenaphthylene-Diiron Hexacarbonyl.—A mixture of triiron dodecacarbonyl (18.0 g., 35.6 mmoles), acenaphthylene (7.6 g., 50 mmoles) and 250 ml. of thiophene-free benzene was refluxed for 10 hr. under nitrogen. After cooling to room temperature, filtration gave a maroon filtrate which was evaporated to dryness. Sublimation at 60–70° (0.1 mm.) for 4 hr. led to the recovery of 4.2 g. (55%) of the acenaphthylene. The red-purple residue, 3.09 g. (32% yield based on acenaphthylene used), was fairly pure $C_{12}H_8Fe_2(CO)_6$. Part of this material (1.0 g.) was treated with a mixture of 25 ml. of petroleum ether and 20 ml. of diethyl ether and the resulting dark red solution filtered. The filtrate was evaporated to 10 ml. and cooled to −78°. The resulting purple crystals were filtered, recrystallized, and dried for 10 hr. at 25° (0.2 mm.). The acenaphthylene-diiron hexacarbonyl thus obtained melted sharply at 158°, and is a red-violet crystalline solid. The compound is stable in air for several months, but its solutions in organic solvents decompose in a few hours.

Anal. Calcd. for $C_{18}H_8O_6Fe_2$: C, 50.0; H, 1.85; mol. wt., 432. Found: C, 50.1, 50.4; H, 2.2, 2.2; mol. wt., 433.

The infrared spectrum of acenaphthylene-diiron hexacarbonyl shows carbonyl bands at 2047 and 1985 cm.$^{-1}$, and its ultraviolet spectrum (cyclohexane solution) has maxima at 227 mμ (ε 35,500) and 330 mμ (ε 10,500) with a minimum at 308 mμ.

Acknowledgment.—We are indebted to the Union Carbide Metals Co. for a gift of chromium hexacarbonyl, and to the Climax Molybdenum Co. for a gift of molybdenum and tungsten hexacarbonyls.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

Reactions of Silyl- and Germyllithium Compounds with Azoxybenzene

BY M. V. GEORGE, PURNENDU B. TALUKDAR, CLARE W. GEROW AND HENRY GILMAN

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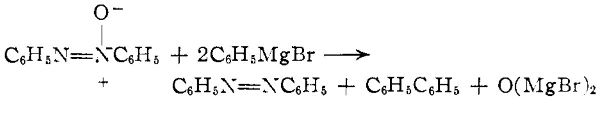
Reaction of triphenylsilyllithium with azoxybenzene gives N,N'-diphenyl-N-triphenylsilylhydrazine, a compound previously prepared by the direct addition of triphenylsilyllithium to azobenzene. Similarly, diphenylmethylsilyllithium and triphenylgermyllithium give N,N'-diphenyl-N-diphenylmethylsilylhydrazine and N,N'-diphenyl-N-triphenylgermylhydrazine, respectively. In these reactions it has been observed that azoxybenzene is first reduced to azobenzene which then reacts with the silyl- or germyllithium compound to give the corresponding addition products.

A number of studies concerned with the preparation and some of the reactions of silyl- and germylmetallic compounds have been reported in recent years.[1,2] The object of the present investigation was to study the reactions of silyl- and germyllithium compounds with azoxybenzene.

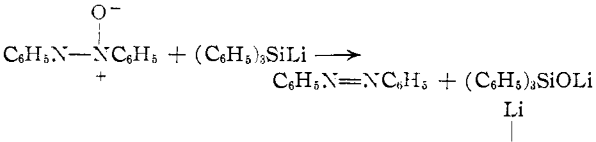
Kursanov, Kursanova and Blokhina[3] have reported the reaction of a number of azoxy compounds with Grignard reagents and have observed that these compounds were reduced to the corresponding azo compounds. Azoxybenzene, for example, on treatment with phenylmagnesium bromide, gave a 95.8% yield of azobenzene and also a 64.4% yield of biphenyl. A similar type of reduction of azoxy compounds was observed on treatment of these compounds with a mixture of magnesium and magnesium iodide.[4,5]



$$C_6H_5\overset{+}{N}{=}\overset{O^-}{N}C_6H_5 + 2C_6H_5MgBr \longrightarrow C_6H_5N{=}NC_6H_5 + C_6H_5C_6H_5 + O(MgBr)_2$$

It seemed of interest to study the reaction of silyl- and germyllithium compounds with azoxybenzene under conditions analogous to those of the reaction of Grignard reagents.

The reaction of a 2:1 mole ratio of triphenylsilyllithium with azoxybenzene gave a 52.9% yield of N,N'-diphenyl-N-triphenylsilylhydrazine.[6] In addition, an 11.0% yield of azobenzene and a 90.9% yield of triphenylsilanol were obtained. The first step in this reaction appears to be the reduction of azoxybenzene to azobenzene, which is immediately followed by the addition of triphenylsilyllithium across the nitrogen-nitrogen double bond in azobenzene giving N,N'-diphenyl-N-triphenylsilyl-N'-lithiohydrazine. The formation of a nearly quantitative yield of triphenylsilanol and the absence of any hexaphenyldisilane may be attributed to the great ease with which compounds containing silicon-oxygen bond are formed under these conditions.



$$C_6H_5N{-}\underset{+}{\overset{O^-}{N}}C_6H_5 + (C_6H_5)_3SiLi \longrightarrow C_6H_5N{=}NC_6H_5 + (C_6H_5)_3SiOLi$$

$$C_6H_5N{=}NC_6H_5 + (C_6H_5)_3SiLi \longrightarrow C_6H_5\underset{(C_6H_5)_3Si}{N}\overset{Li}{N}C_6H_5$$

When azoxybenzene and triphenylsilyllithium were allowed to react in a 1:1 mole ratio, the products isolated were N,N'-diphenyl-N-triphenylsilylhydrazine (26.8%), triphenylsilanol (14.5%) and

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(1) For a recent review on silylmetallic compounds, see, D. Wittenberg and H. Gilman, *Quart. Revs.*, **13**, 116 (1959).

(2) For an account of the preparation and some studies of germylmetallic compounds, see H. Gilman and C. W. Gerow, THIS JOURNAL, **77**, 4675, 5740 (1955); **78**, 5435 (1956); **79**, 342 (1957); *J. Org. Chem.*, **23**, 1582 (1958).

(3) D. N. Kursanov, A. S. Kursanova and A. N. Blokhina, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1786 (1938).

(4) H. Gilman and L. L. Heck, *Rec. trav. chim.*, **50**, 522 (1931).

(5) W. A. Bachmann, THIS JOURNAL, **53**, 1524 (1931).

(6) D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles and H. Gilman, *ibid.*, **80**, 4532 (1958).