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π-COORDINATION OF UNSATURATED BONDS CONTAINING A HETEROATOM
I. KETENIMINE COMPLEXES OF IRON CARBONYL

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Reports were made recently on the π-complexes of cumulene hydrocarbons such as allene[1,2,3] and butatriene[1,2,4]. It would be of interest to see if a cumulene system containing a heteroatom forms π-complexes with its carbon–heteroatom unsaturation.

In a ketenimine iron complex, $[C_5H_5Fe(CO)_2(RCH{=}C{=}NH)]^+$ prepared by protonation of a σ-cyano methyl complex[5], $C_5H_5Fe(CO)_2(CRHCN)$(R = H, Me), it was deduced from the presence of ν(C=N) (1554 cm^{-1}) that only the carbon–carbon double bond participates in the coordination bond. By direct substitution of carbonyl ligands with ketenimine of triiron dodecacarbonyl and π-cyclopentadienyl cobalt dicarbonyl we have been able to prepare several π-ketenimine complexes of iron and cobalt. Syntheses and some characteristics of these complexes are given in this paper and the participation of the π-C=N bond in the iron complexes is inferred based on the spectral data.

EXPERIMENTAL

Materials

Triiron dodecacarbonyl[6], π-cyclopentadienylcobalt dicarbonyl[7], dicobalt octacarbonyl, N-phenyldiphenylketenimine[8], and N-methyldiphenylketenimine[8] were prepared by known methods.

Instruments

IR was measured by a Jasco Model DS-402G grating spectrophotometer and NMR by a 100 Mc Model JNM 4H-100 of Japan Electron Optics Lab. Molecular weights were determined in benzene by Mechrolab vapor pressure osmometer. Elemental analyses (C, H, N, and O) were carried out in the Research Laboratory, Japan Synthetic Rubber Co. Ltd, Yokkaichi city.

Preparative procedure

All reactions involving organometallic compounds were carried out under pure nitrogen. Alumina for chromatography was deoxygenated by heating under vacuum at 200–250° and subsequent adsorption of nitrogen until it cooled down.

Reaction of $(C_6H_5)_2C{=}C{=}NC_6H_5$ *with* $Fe_3(CO)_{12}$. A mixture of 2.0 g (7.4 mmole) of N-phenyldiphenylketenimine, 2.0 g (4 mmole) of triiron dodecacarbonyl and 60 ml of toluene was stirred at 70–80° for 4.5 h. The green color of $Fe_3(CO)_{12}$ solution became reddish brown. Dark colored residue left upon removal of toluene was chromatographed on alumina. Elution with n-hexane and subsequent crystallization from n-hexane gave 0.35 g (16%) of deep red N-phenyldiphenylketeniminediiron hexacarbonyl(III), m.p. 97–98° (in air). (Found: C, 56.15; H, 2.53; N, 2.50; O, 18.49; mol.wt., 536. $C_{26}H_{15}Fe_2NO_6$ calcd.: C, 56.71; H, 2.75; N, 2.55; O, 17.48 %; mol.wt., 549.)

Elution with toluene gave 0.16 g of orange-red crystals. These were recrystallized from benzene/heptane to give an organic substance, m.p. 227–228°, of which composition corresponded to $[(C_6H_5)_2C{=}C{=}NC_6H_5]_2CO$. (Found: C, 86,34; H, 5.27; N, 4.66; mol.wt., 575. $C_{41}H_{30}N_2O$ calcd.: C, 86.89; H, 5.34; N, 4.94%; mol.wt., 567.) The IR showed $\nu(CO)$ at 1735 cm^{-1} and $\nu(C{=}C)$ or $\nu(C{=}N)$ at 1635 cm^{-1}. The structure has not been elucidated.

Reaction of $(C_6H_5)_2C{=}C{=}NCH_3$ *with* $Fe_3(CO)_{12}$. A heptane solution (30 ml) of 1.0 g (2 mmole) of triiron dodecacarbonyl and 0.8 g (3.9 mmole) of N-methyldiphenylketenimine was stirred at 75° for 2 h. About 45 ml of carbon monoxide was evolved. From the heptane solution were obtained dark colored solids which gave, upon chromatography on alumina, 0.09 g of dark red N-methyldiphenylketeniminediiron hexacarbonyl (IV), m.p. 109–110° (in nitrogen). (Found: C, 51.00; H, 2.75; N, 2.84; O, 20.05; $C_{21}H_{13}Fe_2NO_6$ calcd.: C, 51.79; H, 2.69; N, 2.88; O, 19.71%.) The chromatography resulted in considerable decomposition of the complex. Thus (IV) is less stable than (III). Elution with benzene gave 0.09 g of red organic crystals, m.p. 219–221.5° (from benzene/n-heptane). The structure is unknown. It has a composition corresponding to $[(C_6H_5)_2C{=}C{=}NCH_3]_2C{=}O$. (Found: C, 84.09; H, 6.11; N, 6.41; mol.wt., 442. $C_{31}H_{26}N_2O$ calcd.: C, 84.13; H, 5.92; N, 6.33%; mol.wt., 416.)

Reaction of $(C_6H_5)_2C{=}C{=}NC_6H_5\cdot Fe_2(CO)_6$ *with* $P(C_6H_5)_3$. A mixture of 0.058 g (0.106 mmole) of N-phenyldiphenylketenimine diiron hexacarbonyl, 0.103 g (0.393 mmole) of triphenylphosphine and 4 ml of heptane was heated at 60° for 2 h. The brown crystals separated were recrystallized from ether/n-hexane to give 0.05 g of brown N-phenyldiphenylketeniminediiron pentacarbonyl mono(triphenylphosphine), m.p. 120–121°. (Found: C, 66.51; H, 4.60; N, 1.67; O, 9.08; mol.wt., 756. $C_{43}H_{30}Fe_2NO_5P$ calcd.: C, 65.94; H, 3.86; N, 1.78; O, 10.21%; mol.wt., 783.)

Reaction of $(C_6H_5)_2C{=}C{=}NCH_3\cdot Fe_2(CO)_6$ *with* $P(C_6H_5)_3$. To a solution of 0.046 g (0.09 mmole) of N-methyldiphenylketenimine diiron hexacarbonyl in 10 ml heptane was added 0.08 g (0.3 mmole) of triphenylphosphine at room temperature. Dark red crystals precipitated out immediately. To complete the reaction the mixture was heated at 70° for 1.5 h. The crystals were recrystallized from benzene/n-heptane to give 0.027 g of dark red N-phenyldiphenylketeniminediiron pentacarbonyl mono(triphenylphosphine), m.p. 131–132° (decomposition). (Found: C, 63.87; H, 4.13; N, 1.87; O, 11.09. $C_{38}H_{28}Fe_2NO_5P$ calcd.: C, 63.28; H, 3.91; N, 1.94; O, 11.09%.)

Reaction of $(C_6H_5)_2C{=}C{=}NC_6H_5$ *with* π-$C_5H_5Co(CO)_2$. An n-heptane solution (15 ml) of 0.45 g (2.51 mmole) of cyclopentadienylcobalt dicarbonyl and 0.54 g (2.00 mmole) of N-phenyldiphenylketenimine was refluxed for 18 h. Purple precipitates were separated and dissolved in benzene. The benzene solution was chromatographed on alumina pretreated for removal of adsorbed oxygen. Elution with benzene and subsequent evaporation gave purple oil which was crystallized by treating with n-hexane. These were recrystallized from benzene/heptane at room temperature to give 0.28 g of purple π-cyclopentadienylcobalt N-phenyldiphenylketenimine, $\pi\text{-}C_5H_5Co(C_6H_5)_2C{=}C{=}NC_6H_5$, m.p. 195–196° (in nitrogen). (Found: C, 76.34; H, 5.13; N, 3.56; mol.wt., 393. $C_{25}H_{20}CoN$ calcd.: C, 76.75; H, 5.39; N, 3.18%; mol.wt., 436.)

Attempted reaction of $(C_6H_5)_2C{=}C{=}NCH_3$ *with* $\pi\text{-}C_5H_5Co(CO)_2$. Reaction of N-methyldiphenylketenimine with π-cyclopentadienylcobalt dicarbonyl was attempted similarly. Polymerization of the ketenimine occurred readily at room temperature preventing formation of π-complexes.

Attempted addition of $P(C_6H_5)_3$ *or* $P(OC_6H_5)_3$ *to* $\pi\text{-}C_5H_5Co(C_6H_5)_2C{=}C{=}NC_6H_5$. A mixture of the ketenimine cobalt complex and triphenylphosphine or triphenylphosphite in a mole ratio of 1 : 2 in n-heptane was refluxed for 15 h to find no reaction. The reaction of the ketenimine cobalt complex with a large excess or triphenylphosphite, refluxed for 15 h resulted in degradation of the complex.

SPECTRA

IR spectra of these ketenimine complexes of iron and cobalt are summarized in Table 1. The Table also contains the NMR of complex (II).

TABLE 1

SPECTRAL DATA

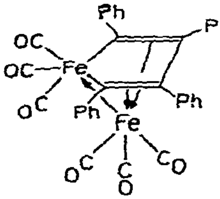
Compound	*IR*[a] *(cm^{-1})*		
	ν(CO)	*ν (C=N)*	*ν (π-C_5H_5)*
$(C_6H_5)_2C{=}C{=}NC_6H_5Fe_2(CO)_6$	2059, 2010, 1990, 1977, 1950		
$(C_6H_5)_2C{=}C{=}NCH_3Fe_2(CO)_6$[b]	2082, 2042, 2018, 1993, 1965		
$(C_6H_5)_2C{=}C{=}NC_6H_5Fe_2(CO)_5P(C_6H_5)_3$	2055, 1977, 1963, 1914		
$(C_6H_5)_2C{=}C{=}NCH_3Fe_2(CO)_5P(C_6H_5)_3$	2045, 1976, 1965, 1916		
$(C_6H_5)_2C{=}C{=}NC_6H_5Co(\pi{-}C_5H_5)$		1565	1416, 1110, 1011, 997, 805
$(C_6H_5)_2C{=}C{=}NCH_3$[c]		1998[d]	

[a] Nujol mull. [b] NMR spectrum measured in C_6D_6 (TMS internal reference): $\tau(CH_3)$, 7.66 (singlet); $\tau(C_6H_5)$, 2.30 (doublet), 2.8 (multiplet), 3.0 ppm (multiplet). [c] NMR spectrum measured in C_6H_6 (TMS internal reference): $\tau(CH_3)$, 7.18 ppm (singlet). [d] ν(C=C=N).

RESULTS AND DISCUSSION

Direct reactions of substituted ketenimines with triiron dodecacarbonyl at 70–80° in toluene gave π-ketenimine complexes. Thus, N-phenyldiphenylketenimine, (I), and N-methyldiphenylketenimine, (II), formed deep red diamagnetic crystalline complexes, (III) and (IV) respectively. They are fairly stable in air and can be purified by alumina chromatography. In contrast to the free ketenimines which are readily hydrolyzed by wet alumina giving 2,2-diphenylacetamide, the complexes (III) and (IV) are rather resistant to hydrolysis.

Based on molecular weight measurements and elemental analysis they are formulated as $R_2C{=}C{=}NR'Fe_2(CO)_6$ (III, $R{=}C_6H_5$, $R'{=}C_6H_5$; IV, $R{=}C_6H_5$, $R'{=}CH_3$). The IR spectra are given in Table 1. It is obvious that the complexes have no bridging carbonyl group. Since $M(CO)_3$ moiety requires two IR active carbonyl bands, provided the C_{3v} local symmetry is not seriously disturbed, the observed IR spectra precludes the possibility for an independent disposition of the two $Fe(CO)_3$ moieties. The band pattern of the carbonyl stretching resembles to that of the binuclear diiron hexacarbonyl complex $A^{*,9}$ suggesting a similar conformation for the carbonyl groups in (III) and (IV) to that of A. Thus B is proposed for the structure of (III) and (IV), in which are assumed participation of both C=C and C=N double bonds in the coordination and presence of an iron–iron bond like in A.



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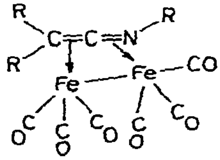

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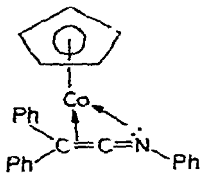

III

The NMR of the complex (IV) appears to support this structure. Downfield shift (0.3–0.8 ppm) of N- or S-methyl proton has been observed in $(CH_3)_3N \cdot B(C_2H_5)_3$[10] or $CH_3SCH_2CH_2COFe(C_5H_5)(CO)$, $CH_3SCH_2CH_2COMn(CO)_4$[11], and $(CH_3)_2NCH_2CH_2COMn(CO)_4$[12] in which the ligands are coordinated by the lone pair on nitrogen or sulfur. Accordingly coordination by the lone pair on nitrogen of a C=N double bond is expected to exert deshielding inductive effect on a proton near to the nitrogen. On the contrary the τ value (7.66) of methyl proton of (IV) is slightly higher than that (7.18) of the free ligand. The upfield shift can be understood as a consequence of reduction of the anisotropic deshielding in the C=N double bond due to its π-coordination. This is somewhat analogous to the upfield shift observed for similarly situated protons in π-complexed olefins (see *e.g.* refs. 13–16). Similar upfield shift has been observed in the aldehyde proton of acrolein π-coordinated by its C=O double bond to molybdenum carbonyl[17] or in the methylene proton (α-position to N) of (crotonylidenebutylamineiron tricarbonyl, $(CH_3CH{=}CHCH{=}NC_4H_9)Fe(CO)_3$ in which the conjugated double bonds participate in the π-coordination[18]. Therefore, the observed upfield shift in (IV) seems not to be due to the shielding effect of $Fe(CO)_3$. Thus the proposed structure B accords with available information. X-ray crystallographical studies of the complex (IV) have been undertaken.

The reaction of π-cyclopentadienylcobalt dicarbonyl with (I) gave a purple crystalline complex (VII) in a small yield. The complex is much more unstable in solution than is the corresponding iron carbonyl complex (III) and the chromatography on alumina resulted in its decomposition to a considerable extent. The elemental analysis and the molecular weight measurement indicated that it is a mononuclear cobalt

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* The pattern was referred to the unpublished chart by A. Nakamura and N. Hagihara.

complex having a composition of π-$C_5H_5Co\cdot(C_6H_5)_2C{=}C{=}NC_6H_5$. Consistently the IR spectra showed absence of carbonyl group. An absorption of medium intensity appeared at 1565 cm^{-1} as a shoulder of an intense absorption due to phenyl group (1590 cm^{-1}). In any of the binuclear iron ketenimine complexes, in which both C=C and C=N double bonds are postulated to participate in the coordination to iron, there is no absorption in this region except the phenyl band (1590 cm^{-1}). Moreover, since the cobalt complex is monomeric, the composition requires either C=C or C=N double bond to be left free. Thus the 1565 cm^{-1} band may be assigned to an absorption due to the free C=C or C=N double bond of the ligand. Although there is a deficiency of conclusive evidence, the structure C may be postulated for the cobalt complex in which the C=C double bond and the nitrogen lone pair participate in the coordination attaining an inert gas configuration or the maximum coordination. The failure of addition of triphenyl phosphine or triphenyl phosphite to the complex seems not to be incompatible with the above view.

An attempt synthesis of a corresponding cobalt complex of N-alkyldiphenylketenimine was not successful. The ligand readily polymerized at room temperature upon contact with π-cyclopentadienylcobalt dicarbonyl. Characteristics of the polymerizate are to be studied.

Triphenylphosphine substituted one mole of carbonyl ligand in (III) and (IV), giving corresponding diiron pentacarbonyl triphenylphosphine complexes, (V) and (VI). This was so even when a large excess of triphenylphosphine was used. In contrast, the phosphine or the phosphite did not add to the cobalt complex (VII) at 60–80° in benzene as already mentioned.

SUMMARY

N-Phenyldiphenylketenimine (I) and N-methyldiphenylketenimine (II) were treated with triiron dodecacarbonyl to form binuclear iron complexes; $(C_6H_5)_2$-$C{=}C{=}NC_6H_5\cdot Fe_2(CO)_6$ (III) and $(C_6H_5)_2C{=}C{=}NCH_3\cdot Fe_2(CO)_6$ (IV), and (I) with π-cyclopentadienylcobalt dicarbonyl to form $(C_6H_5)_2C{=}C{=}NC_6H_5\cdot CoC_5H_5$ (V). Spectral data of the iron complexes (III) and (IV) suggested that both carbon–carbon and carbon–nitrogen double bonds of the ketenimines participate in the coordination.

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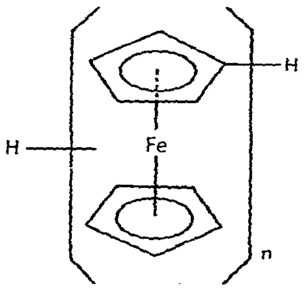
SHORT COMMUNICATIONS

Metallocene polymers
XIX. Polyferrocenylenes

The synthesis of polymers exclusively composed of ferrocenylene recurring units (I) has been the goal of many research efforts in recent years. Korshak and Nesmeyanov with co-workers[1-3] were the first to report a polyrecombination reaction involving the action of tert-butyl peroxide on ferrocene, in which polyferrocenylenes I with number-average molecular weights ($\bar{M}_n$) up to 7000 were claimed as products. However, the inconsistency with structure (I) of the elemental compositional data given by Korshak[2] prompted other workers[4] to re-examine this synthesis, and it was found that the recombination products, rather than constituting pure (I), consisted of small polyferrocenylene segments interlinked by methylene and aliphatic ether groups, these linking groups having arisen *via* methyl and tert-butoxy radicals stemming from thermal decomposition of the peroxide reactant. Spilners and Pellegrini[5] as well as Hata and co-workers[6] obtained polyferrocenylenes, some of these painstakingly isolated as individual compounds, by a radical coupling reaction from lithioferrocenes; yet in both instances the molecular weights reported



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