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CHEMISTRY OF MIXED TRANSITION METAL COMPLEXES III*. PREPARATION AND STRUCTURE OF NEW COMPLEXES OF ACETYLENES COORDINATED ON IRON AND NICKEL

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SUMMARY

Reactions of (tricarbonyliron)-μ-carbonyl-μ-(diphenylphosphido)-π-cyclopentadienylnickel (I) with acetylenes, $C_6H_5C{\equiv}CC_6H_5$, $C_6H_5C{\equiv}CCH_3$, $C_6H_5C{\equiv}CH$, $C_6H_5C{\equiv}CCO_2CH_3$, $CH_3C{\equiv}CCO_2CH_3$, $HC{\equiv}CCO_2CH_3$ and $CH_3OCOC{\equiv}CCO_2CH_3$, have been carried out yielding new mixed transition metal monoacetylene complexes (II). Two isomers were found for complexes involving unsymmetrical acetylenes. IR, NMR and mass data are consistent with vicinal dicarbene coordination of the acetylenes to the iron and the nickel.

INTRODUCTION

The chemistry of mixed metal complexes with metal–metal bonds has engendered much interest[1], and reactions of complexes containing main group elements bonded to transition metals have been studied in some detail. Recently, the insertion reactions of perfluoroacetylenes and -olefins or sulfur dioxide into Group IVB metal–transition metal bonds have been studied[2], but similar reactions involving mixed transition metal complexes have hardly been investigated except for the insertion of mercury into the iron–cobalt bond in (tricarbonylcobalt)-μ-dicarbonyl-carbonyl-π-cyclopentadienyliron which yields another mixed transition metal complex, (tetracarbonylcobalt)(dicarbonyl-π-cyclopentadienyliron)mercury[3]. Of those systems studied, it has been found that reaction of (carbonyl-π-cyclopentadienyl-iron)-μ-dicarbonyl-π-cyclopentadienylnickel with acetylenes does not yield mixed transition metal complexes since dissociation of the complex into the respective diiron and dinickel species occurs[4]. Mixed metal acetylene complexes containing iron and nickel have, however, been prepared by the reaction of $(C_5H_5Ni)_2RC{\equiv}CR$ with iron pentacarbonyl[4].

In previous papers we have reported the preparation of some mixed transition metal μ-diphenylphosphido complexes[5,6]. We now report the reaction of (tricarbonyl-iron)-μ-carbonyl-μ-(diphenylphosphido)-π-cyclopentadienylnickel (I) with acetylenes,

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* For Part II see ref. 6.

TABLE 1

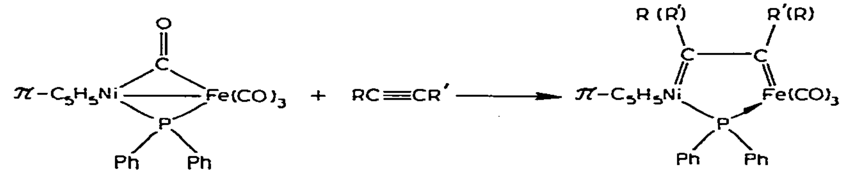
Complex[a]	Acetylene	Yield (%)	M.p.[b] (°C)	Analysis (%) found (calcd.)		Mol. wt.[c] (m/e)	NMR assignment (τ)[d]	
				C	H		π-C_5H_5	Other
(II-1)	PhC≡CPh	85	215–220 d.	65.02 (65.13)	4.19[e] (4.00)	626	4.93	
(II-2a)	PhC≡CCH_3	20	oil			564	5.02	≡CCH_3 6.88 d, J(PFe=CCH) 4.8 Hz
(II-2b)	PhC≡CCH_3	21	169–170	61.67 (61.65)	4.14 (4.11)	564	4.95	≡CCH_3 8.46 d, J(PNi=CCH) 13.2 Hz
(II-3a)	PhC≡CH	20	152–153	61.23 (61.13)	4.19 (3.85)	550	5.06	≡CH 1.90 d, J(PFe=CH) 19.8 Hz
(II-3b)	PhC≡CH	30	138–139	61.02 (61.13)	4.01 (3.85)	550	5.03	≡CH 5.53 d, J(PNi=CH) 6.0 Hz
(II-4a)	CH_3C≡CCO_2CH_3	29	95– 96	55.08 (54.90)	4.09 (3.87)	546	4.96	-CO_2CH_3 6.43 ≡CCH_3 6.85 d, J(PFe=CCH) 4.8 Hz
(II-4b)	CH_3C≡CCO_2CH_3	15	147–149	55.14 (54.90)	4.04 (3.87)	546	4.94	-CO_2CH_3 6.13 ≡CCH_3 8.40 d, J(PNi=CCH) 13.2 Hz
(II-5a)	HC≡CCO_2CH_3	28	141–142	54.43 (54.09)	3.87 (3.59)	532	4.95	-CO_2CH_3 6.42 ≡CH 1.75 d, J(PFe=CH) 19.2 Hz
(II-5b)	HC≡CCO_2CH_3	13	109–110	54.35 (54.09)	3.52 (3.59)	532	4.92	-CO_2CH_3 6.16 ≡CH 5.50 d, J(PNi=CH) 7.2 Hz
(II-6a)	PhC≡CCO_2CH_3	36	178–179	59.09 (59.16)	3.96 (3.81)	608	4.83	-CO_2CH_3 6.59
(II-6b)	PhC≡CCO_2CH_3	24	159–161	59.30 (59.16)	3.89 (3.81)	608	4.93	-CO_2CH_3 6.15
(II-7)	CH_3O_2CC≡CCO_2CH_3	37	128–133 d.	52.76 (52.85)	3.66[e] (3.59)	590	4.86	-CO_2CH_3 6.10, 6.42

[a] "a" denotes isomers eluted first during chromatographic separation while "b" denoted isomers eluted later. [b] Measured on a hot-stage apparatus. [c] Molecular ions consisted of ^{58}Ni and ^{56}Fe. [d] Measured in $CDCl_3$ solution. [e] Metal analyses, found (calcd.): for (II-1), Fe 7.9 (8.9), Ni 8.8 (9.4); and for (II-7), Fe 8.6 (9.4), Ni 9.2 (9.9).

which has been found to give new mixed transition metal acetylene complexes in which the acetylenes are coordinated to both iron and nickel forming a structure similar to that proposed by Sternberg *et al.*[7]. A preliminary communication incorporating part of this work has been published[8].

RESULTS AND DISCUSSION

Refluxing of compound (I) with excess acetylenes resulted in good yields of the 1/1 adducts which were separated by column chromatography. With unsymmetrical acetylenes, repeated chromatography led to the isolation of two isomeric products. In each case the products were characterized by chemical analyses, mass spectra, IR and NMR spectra, the complexes prepared, together with analytical data, molecular weights and NMR spectra, being listed in Table 1.



(I) (II)

The IR spectra of these complexes, listed in Table 2, show the existence of three bands in the spectral region 2100–1900 cm^{-1} corresponding to terminal carbonyl groups, with no bands corresponding to a bridged carbonyl.

The NMR spectra of the complexes, in addition to the signals shown in Table 1, exhibit signals of the phenyl protons of the diphenylphosphido group τ 2.0–2.8 as complex multiplets in all of the spectra, overlapping between these signals and those of the phenyl protons of the acetylene groups occurring in complexes (II-2b), (II-3b) and (II-6a). The signals for the phenyl protons of the other isomers of these complexes [(II-2a), (II-3a) and II-6b)] appeared at τ 2.89, 2.99 and 2.94, respectively, and were thus separate from those attributable to the phosphido phenyl protons. One phenyl signal of (II-1) appeared at τ 3.12 and the other was included in the multiplets of the phosphido phenyl group. The protons attached to the acetylenic carbons in (II-3) and

TABLE 2

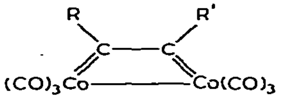
$\nu(C{\equiv}O)$ OF THE COMPLEXES (II)[a]

Complex	Isomer (a)	Isomer (b)
(II-2)	2014, 1965, 1948	2014, 1965, 1947
(II-3)	2015, 1968, 1950	2015, 1965, 1951
(II-1)	2014, 1965, 1950	
(II-4)	2017, 1968, 1954	2024, 1982, 1957
(II-5)	2023, 1975, 1958	2025, 1978, 1958
(II-6)	2020, 1972, 1958	2026, 1982, 1960
(II-7)	2031, 1988, 1965	

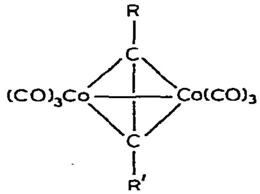
[a] In cm^{-1}; measured in CH_2Cl_2 solution, all bands shown are strong.

(II-5), and also the methyl protons on the acetylenic carbons in (II-2) and (II-4) appeared as doublets, which might be due to long-range coupling with ^{31}P. These data are compatible with the suggestion that the complexes (II) are formed from compound (I) and the various acetylenes by the loss of the bridged carbonyl group.

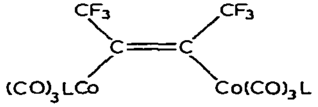
At an early stage of acetylene complex chemistry, structure (III) was proposed as possible for complexes of the type $RC_2R'Co_2(CO)_6$[7]. Later, an X-ray diffraction study[9] showed that the correct structure is as in (IV), a structure which has since been recognized as a general one for the coordination of acetylene in monoacetylene dinuclear complexes. Another structure, (V), of the vinylene type has been suggested[10] for complexes of the type $Co_2(CO)_6C_4F_6L_2$ and $Co_4(CO)_{12}C_8F_{12}$ on the basis of the presence of bands in the IR spectra of the complexes corresponding to carbon–carbon double bonds.



(III)

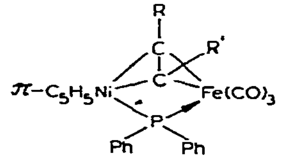


(IV)

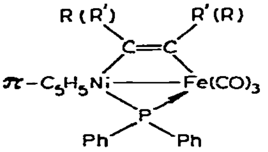


(V)

The existence of isomeric products with unsymmetrical acetylene complexes and the presence of dissimilar methyl signals in the NMR spectrum of (II-7) eliminates the existence of structure (VI) which is based on the general structure (IV). Similarly, structure (VII) may also be eliminated by virtue of the absence of a band corresponding to a carbon–carbon double bond in the IR spectrum, despite the fact that this structure is consistent with the presence of isomers. Indeed, the structure of (II) could be considered as one in which the acetylenes are coordinated to iron and nickel as a vicinal dicarbene.



(VI).



(VII)

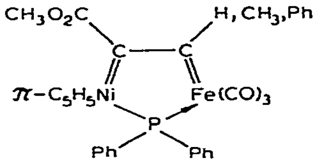
Assignment of the configuration

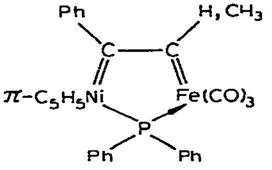
On the basis of the NMR spectra the complexes may be sub-divided into two isomeric series. Thus, in the spectrum of (II-7) the two methyls of the methoxycarbonyl groups are not equivalent and exhibit signals at τ 6.10 and 6.42 respectively. Similar values for the methyl signals in the spectra of complexes (II-4), (II-5) and (II-6) may be attributed to the two isomers which occur in these cases, one at low field being due to one isomer while the signal at high field is due to the second isomer. The isomers of (II-2) and (II-3) may be related to the isomers of (II-4) and (II-5) in a similar fashion by comparison of the respective positions of the signals corresponding to either the methyl groups associated with the acetylenic carbon atom or the acetylenic hydrogens. In this way it is possible to sub-divide the isomers into the series (a) and (b) listed in Table 1; series (a) corresponds to the isomers first eluted during a chromatographic separation while series (b) corresponds to the isomers eluted later.

Table 2 lists the carbonyl stretching bands of the complexes in terms of the electron-withdrawing order of the substituents associated with the acetylenes in the two isomeric series (a) and (b). The positions of the bands increase in both series as the electron-withdrawing ability of the substituents increases, ranging from 2014, 1965 and 1945 cm^{-1} for (II-2a) and (II-2b) to 2031, 1988 and 1965 cm^{-1} for (II-7). It is well known that the carbonyl stretching frequencies of metal carbonyls are affected by the donor–acceptor ability of the ligand[11], a higher acceptor ability leading to decreasing back-donation between the *d* electron associated with the metal and the carbonyl ligand, thus causing higher $\nu(C\equiv O)$ values.

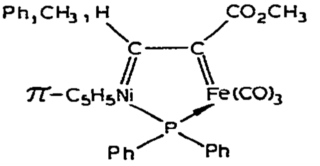
The bands for isomers (b) are apparently higher than those for isomers (a) in complexes (II-4), (II-5) and (II-6), although in the case of (II-2) and (II-3) these differences are not particularly significant. The electron-withdrawing substituent, CO_2CH_3, has a stronger effect on the carbonyl stretching frequency $\nu(C\equiv O)$, associated with the carbonyl groups attached to the iron atom, when it is attached to the iron side of the complex than when it is attached to the nickel side. On this basis the most probable configuration of the acetylene complexes may be written as follows:

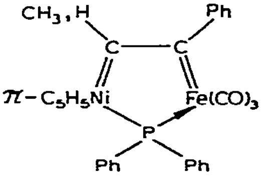
Isomer (a):





Isomer (b):





Isomers (a) have the more electron-withdrawing group associated with the unsymmetrical substituents on the nickel side of the complexes while isomers (b) have this group on the iron side.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin–Elmer model 521 (grating) spectrometer and ^1H NMR spectra were recorded on a Nippon Denshi model C-60 instrument. Mass spectra were recorded on a Nippon Denshi model 1S instrument at 75 eV. Methyl propiolate was prepared from 2-propyn-1-ol by oxidation[12] followed by esterification and methyl tetrolate (2-butynoate) was prepared from ethyl acetoacetate by the method of Feist[13] followed by esterification. Other acetylenes were prepared by conventional methods. (I) was prepared as described previously[5]. Metal analyses were performed colorimetrically. M.p.'s are uncorrected.

Preparation of the acetylene complexes

All preparations and purifications were carried out under a nitrogen atmosphere. (I) (0.1 g) and an excess of the acetylenes were allowed to react in 10 ml of refluxing benzene for 6 h. After evaporation of the benzene, the residues were dissolved in a minimum volume of benzene and chromatographed on an alumina column 18 mm in diameter and 15 cm long. A brown band eluted with hexane which contained traces of the unreacted starting materials was discarded. A second brown band eluted with benzene for (II-1) and a red-brown band eluted with methylene chloride

TABLE 3

MASS SPECTRA OF $(RC{\equiv}CR')C_5H_5NiPPh_2Fe(CO)_3$

Assignment	(II-1) $(PhC{\equiv}CPh)$		(II-2a) $(PhC{\equiv}CCH_3)$		(II-3a) $(PhC{\equiv}CH)$	
	m/e	Relative intensity	*m/e*	Relative intensity	*m/e*	Relative intensity
$[M]^+$	626	18.0	564	10.0	550	15.4
$[M-CO]^+$	598	3.2	536	4.0	522	
$[M-2CO]^+$	570	32.0	508	26.0	494	30.8
$[M-3CO]^+$	542	100	480	74.0	466	69.3
$[M-3CO-PhH]^+$					388	15.4
$[M-3CO-RC{\equiv}CR']^+$	364	73.0	364	100	364	100
	515.4[a]	(570→542)	276.0[a]	(480→364)		
	244.4[a]	(542→364)				

Assignment	(II-4a) $(CH_3C{\equiv}CCO_2CH_3)$		(II-5a) $(HC{\equiv}CCO_2CH_3)$		(II-6a) $(PhC{\equiv}CCO_2CH_3)$		(II-7) $(CH_3O_2CC{\equiv}CCO_2CH_3$	
	m/e	Relative intensity	*m/e*	Relative intensity	*m/e*	Relative intensity	*m/e*	Relative intensity
$[M]^+$	546	50.0	532	100	608	13.0	590	33.3
$[M-CO]^+$	518	10.0	504	9.4	580		562	
$[M-2CO]^+$	490	20.0	476	65.7	552	23.4	534	87.5
$[M-3CO]^+$	462	100	448	65.7	524	100	506	100
$[M-4CO]^+$	434	40.0	420	46.7	496	55.4	478	87.5
$[M-4CO-OCH_2]^+$	404	6.6	390	31.2	466	15.0	448	66.6
$[M-4CO-OCH_2-RH]^+$[b]			388	12.5	388	10.6		
$[M-5CO-OCH_2]^+$							420	75.0
$[M-5CO-2OCH_2]^+$							390	33.3
$[M-5CO-2OCH_2-H_2]^+$							388	16.6
$[M-3CO-RC{\equiv}CR']^+$	364	43.3	364	43.7	364	85.7	364	33.3
			393.7[a]	(448–420)	469.5[a]	(524–496)		
			362.1[a]	(420–390)	437.8[a]	(496–466)		

[a] Observed metastable ions corresponding to the transition shown in parentheses.
[b] R = H for the spectrum of (II-5a), R = Ph for the spectrum of (II-6a).

for (II-7) afforded the complexes as brown crystals after concentration of the bands and addition of hexane followed by storage in a refrigerator for one or two days. For (II-6), the brown band eluted with benzene was again chromatographed on an alumina column 18 mm in diameter and 30 cm long using a hexane/methylene chloride mixture as an eluent. Use of the elution mixture in 1/1 proportions gave (II-6a) after concentration followed by storage in a refrigerator, while the use of 1/3 proportions of the elution mixture gave the other isomer (II-6b). The isomers of the other unsymmetrical acetylenes were separated using similar procedures. The acetylene complexes are stable in air and soluble in most organic solvents.

Mass spectra of the complexes

The mass spectra of the complexes of the isomers (a) are shown in Table 3. There was little difference between the spectra of isomers (a) and (b). Some metastable ions were exhibited in the spectra of (II-1), (II-2a), (II-5a) and (II-6a) as is shown in Table 3. Below *m/e* 364, the spectra are similar to the spectrum of complex (I) with respect to nickel and iron ion fragments.

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