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CYCLOHEXYLETHYNYL COMPLEXES OF Co^{II} AND Fe^{II}

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Summary

This paper deals with the synthesis of six σ-cyclohexylethynyl complexes of Co^{II} and Fe^{II} and their characterization by chemical analysis, infrared and ^1H NMR spectra, and magnetic measurements. Four of them are six-coordinate complexes, unsubstituted or substituted, namely $K_4[M(C{\equiv}C{-}C_6H_{11})_6] \cdot nNH_3$ ($M = Co, n = 2; M = Fe, n = 0$), $K_2[Co(C{\equiv}C{-}C_6H_{11})_4(NH_3)_2]$ and $K_4[Fe(CN)_4(C{\equiv}C{-}C_6H_{11})_2]$. Two are four-coordinate complexes of formula $[(Ph_3P)_2M(C{\equiv}C{-}C_6H_{11})_2]$ (M = Co, Fe). All are low-spin complexes, the magnetic moment for the six-coordinate Co(II) complexes, measured at various temperatures, being intermediate between low- and high-spin values.

Introduction

Relatively few σ-alkynyl complexes of Co^{II} and Fe^{II} are known. All are six-coordinate low-spin complexes, and most of them have been described by Nast et al. [1—5].

Two series of complexes with hexaalkynylcobaltate(II) anions have been described: the pyrophoric and explosive alkali salts, $M_4^I[Co(C{\equiv}C)_6]$ (M = Na, K; R = H, CH_3) [1], and the somewhat more stable compounds of general formula $[(C_6H_5)_4E]_3 M^I[Co(C{\equiv}CR)_6]$ (M^I = Na, K; R = H, CH_3, C_6H_5; E = P, As) [2]. A series of hexaalkynylferrate(II) complexes is also known [3].

Co^{II} forms six-coordinate alkynyl complexes partially substituted by tertiary phosphine ligands of general formulae $M^1M^2[Co(PR'_3)_2(C{\equiv}CR)_4]$ and $[Co(dppe)_2(C{\equiv}CR)_2]$ (M^1 = Na; M^2 = Na, $(C_6H_5)_4P$; R' = C_2H_5, C_6H_5; R = H, C_6H_5; dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ [4]. Substituted alkynyl complexes of Fe^{II} of the type $M_2^I[Fe(CN)_{5-x}(C{\equiv}C{-}C_6H_5)_x(NO)]$ (M^I = $(C_6H_5)_4P$, $(C_6H_5)_2Tl$;

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$x = 1, 3$) [5] and [η^5-$C_5H_5Fe(CO)_2(C{\equiv}CR)$] ($R = C_6H_5$, n-$C_6H_{13}$) [6] have also been described. The anionic substituted complexes are somewhat more stable than the hexaalkynylmetallate(II) complexes, but they are still pyrophoric, whereas the neutral phosphine-substituted complexes are not.

We describe below attempts to obtain new σ-alkynyl complexes of Co^{II} and Fe^{II} with cyclohexylethynyl (CHE) as ligand, stable enough to be characterized by chemical analysis, infrared spectroscopy and magnetic measurements. Since some alkynyl phosphine complexes of Co^{II} exhibit abnormally low magnetic moments (1.3 B.M) [4], special attention has been paid to the magnetic measurements on the Co^{II} complexes described here.

Results and discussion

Syntheses and properties of the complexes

Table 1 summarizes the analytical data and some properties of the Co^{II} and Fe^{II} cyclohexylethynyl complexes isolated.

The reaction of $Co(NCS)_2 \cdot 2\ NH_3$ with $KC{\equiv}C{-}C_6H_{11}$ in liquid ammonia gives two compounds, $K_4[Co(C{\equiv}C{-}C_6H_{11})_6] \cdot 2\ NH_3$, (light green) (I), and $K_2[Co(C{\equiv}C{-}C_6H_{11})_4(NH_3)_2]$, (light blue) (II); the former belongs to the series of hexaalkynylcobaltates(II) described previously by Nast et al. [1,2]. Whether I or II is formed depends on the molar ratio of reactants and the conditions of the reaction. Thus, compound I is obtained when solutions of the two reactants in liquid ammonia are mixed at a 1/6 molar ratio, whereas II is formed when the ratio is 1/4 and solid $Co(NCS)_2 \cdot 2\ NH_3$ is added to the solution of $KC{\equiv}C{-}C_6H_{11}$ in liquid ammonia. Bluish-green mixtures of both products are formed when the molar ratio of reactants or the reaction conditions are intermediate between those described for the syntheses of I and II in the Experimental sec-

TABLE 1

ANALYTICAL DATA AND OTHER PROPERTIES OF CYCLOHEXYLETHYNYL DERIVATIVES OF Co(II) AND Fe(II)

Compound	Analyses (%)					
	C found (calcd.)	H found (calcd.)	N found (calcd.)	Co, Fe found (calcd.)	colour	M.p. (°C) (dec.)
I, $K_4[Co(CHE)_6] \cdot 2\ NH_3$ [a]	64.10	8.40	3.37	6.63	green	—
	(64.65)	(8.08)	(3.14)	(6.61)		
II, $K_2[Co(CHE)_4(NH_3)_2]$	63.90	8.32	4.81	9.77	blue	—
	(64.11)	(8.34)	(4.67)	(9.66)		
III, $[(Ph_3P)_2Co(CHE)_2]$	77.80	6.69	—	7.01	greenish-yellow	158—165
	(78.29)	(6.50)	—	(6.98)		
IV, $K_4[Fe(CHE)_6]$	67.12	7.55	—	6.61	brownish	—
	(67.46)	(7.73)	—	(6.54)		
V, $[(Ph_3P)_2Fe(CHE)_2]$	78.32	6.02	—	7.60	brownish	240—250
	(78.61)	(6.55)	—	(7.03)		
VI, $K_4[Fe(CN)_4(CHE)_2]$	40.13	5.24	18.52	9.57	yellow	—
	(40.06)	(5.71)	(18.69)	(9.31)		

[a] CHE = cyclohexylethinylide, $C_6H_{11}{-}C{\equiv}C^-$.

tion. Both compounds are stable under dry N_2 or NH_3 and under vacuum at room temperature, but they are pyrophoric in air and give off white fumes when treated with water, with partial formation of free cyclohexylethyne, easily recognizable by its smell, and dark brown decomposition products.

It must be emphasized that bis(triphenylphosphine)bis(cyclohexylethynyl) cobalt(II), III, is the first four-coordinate Co^{II} complex of the type $[(R'_3P)_2M(C{\equiv}CR)_2]$ to be synthesized. Chatt and Shaw [7] failed in an attempt to make compounds of this type by treatment of $[(R_3P)_2CoX_2]$ (X = Cl, Br) with phenylethynyl magnesium bromide or phenylethynyl lithium in diethyl ether or with phenylethynyl sodium in liquid ammonia. On the other hand, they succeeded in obtaining square-planar complexes of this type with substituted aryl groups as organic ligands [7]. The only known Co^{II} complexes with both alkynyl and phosphine ligands were described by Nast et al. [4] and they are six-coordinate. The synthesis of III was achieved by a method similar to that described by Chatt and Shaw [8] for analogous Ni^{II} complexes. The reaction in liquid ammonia/ether takes place with initial ammoniation of the $[CoCl_2(PPh_3)_2]$, used as starting material. This fact was demonstrated by the high electrical conductivity ($\Lambda = 22.21\ \Omega^{-1}\ cm^2\ mol^{-1}$ at molar concentration of 5.20×10^{-3} mol/l) and by the colour change observed when the product was dissolved in liquid ammonia. Both effects can be attributed to the presence of ions formed by dissociation of $[Co(NH_3)_6]Cl_2$. The residue after the elimination of the solvent is a mixture of $[Co(NH_3)_6Cl_2$ and free triphenylphosphine. In the ammoniation of the starting compound, the free phosphine goes into the ether, and after addition of $KC{\equiv}C{-}C_6H_{11}$ and stirring the insoluble product III gradually separates.

Complex III is greenish-yellow, and is much more stable than I and II, but it cannot be isolated completely free of phosphine. The product tends to adhere to the walls of the container and a loose powder cannot be obtained. It is soluble in CCl_4, methanol and acetone, but decomposes slowly in them. The ^1H NMR spectrum shows signals of the phenyl group protons of coordinated triphenylphosphine (δ 7.37 ppm, triplet 1/1/2) and of the protons belonging to the CH_2 and CH groups of the cyclohexyl radical (δ 1.25 ppm). As expected, no signal from the acetylenic group proton at δ 2.27 ppm is observed.

The reaction of $Fe(NCS)_2 \cdot 2\ NH_3$ with $KC{\equiv}C{-}C_6H_{11}$ in liquid ammonia leads to only one hexaalkynyl complex, (IV), similar to that described by Nast et al. [3]. The product is diamagnetic, brownish, and sensitive to air and moisture.

As in the case of Co^{II}, the reaction of $[(SCN)_2Fe(PPh_3)_2]$ with $KC{\equiv}C{-}C_6H_{11}$ in liquid ammonia/ether gives rise to the formation of a tetracoordinate complex, $[(Ph_3P)_2Fe(C{\equiv}C{-}C_6H_{11})_2]$, (V), which is light brown, and more stable in air and moisture than the previous complex. Hitherto no Fe^{II} complexes of this type have been described, although some containing substituted aryl ligands are known [7], and are believed to have a square-planar configuration. The ^1H NMR spectrum is very similar to that of the corresponding Co^{II} complex. The signal of the protons of the triphenylphosphine C_6H_5 groups appears at δ 7.37 ppm (triplet 1/1/2) and that of the CH_2 and CH groups of the cyclohexyl radical, at $\delta = 1.25$ ppm, and no signal from the $C{\equiv}C{-}H$ protons is present at 2.27 ppm.

TABLE 2

PRINCIPAL INFRARED FREQUENCIES OF CYCLOHEXYLETHYNYL DERIVATIVES OF Co(II) AND Fe(II)

Compound	$\nu(C\equiv C)$	$\nu(C\equiv N)$	$\nu(C-P)$	$\delta(NH_3)$	$\delta(MCN)$	$\delta(C\equiv C)$	$\delta(C-P)$	$\nu(M-CN)$	$\delta(\equiv C-C)$	$\nu(M-N)$ (cm^{-1})
H(CHE) [a,b]	2113m					548m 532m			379m 350m	
Rb(CHE) [a]	2000m					553(sh) 530m			385m 356m	
I, $K_4[Co(CHE)_6]\cdot 2NH_3$	2095(sh) 2066s					534s			388m 359m	
II, $K_2[Co(CHE)_4(NH_3)_2]$	2088s			650m		556m			380vw 368vw	315m
III, $[(Ph_3P)_2Co(CHE)_2]$	—		690s 680(sh)			533m	510s		388w	
IV, $K_4[Fe(CHE)_6]$	2048m					559m 538m			369m	
V, $[(Ph_3P)_2Fe(CHE)_2]$	2037m		690w			531m	515w		368w	
VI, $K_4[Fe(CN)_4(CHE)_2]$	2080w	2050vs			568s			394w		
$K_3[Fe(CN)_5NH_3]$ [c]		2055vs		612m	566s			395m		

[a] From ref. 11. [b] CHE = cyclohexylethinylide, $C_6H_{11}-C\equiv C^-$. [c] From ref. 18.
s, strong; m, medium; w, weak; sh, shoulder.

In the first attempts to obtain cyanoalkynyl complexes of Fe^{II}, anhydrous nitroprussate was used as starting material, but the compounds obtained were impure, because of a secondary reaction with traces of moisture in the nitroprussate [9]. It seems that mixtures of $K_4[Fe(CN)_5NO_2]$ and $K_4[Fe(CN)_4(C{\equiv}C{-}C_6H_{11})_2]$ are formed; there are no products analogous to those obtained by Nast et al. [5] from the reaction of anhydrous nitroprussate with potassium phenylacetylide.

Since pure cyanoalkynyl complexes were not obtained by using anhydrous potassium nitroprussate, anhydrous $K_3[Fe(CN)_5(NH_3)]$ was tried as starting material, in spite of its virtual insolubility in liquid ammonia. This approach was tried without success by Nast and Urban [10] for other alkynyl ligands. We were able to obtain potassium tetracyano bis(cyclohexylethynyl)ferrate(II), $K_4[Fe(CN)_4(C{\equiv}C{-}C_6H_{11})_2]$ (VI), which is light yellow and diamagnetic.

Infrared spectra and magnetic properties

Table 2 shows the most relevant infrared frequencies of the complexes obtained and their assignments. The absence of bands corresponding to the characteristic stretching and bending frequencies of the $\equiv C{-}H$ group, and the presence of the remaining cyclohexylacetylene bands, more or less modified, indicate the presence of the cyclohexylethynylide ligand. The $\nu(C{\equiv}C)$ stretching frequency appears at values between that of free cyclohexylacetylene and those of its alkali salts [11]. The remaining infrared bands of the complexes I, II and IV correspond to those of the free cyclohexylacetylene, slightly modified in intensity and frequency. The most altered bands are those corresponding to the $\delta(C{\equiv}C)$ and $\delta(\equiv C{-}C)$ bending vibrations, as was observed in the case of the alkali salts of cyclohexylacetylene [11]. The resemblance of the infrared spectrum of the compound I to the spectra of the rubidium and caesium salts of cyclohexylacetylene in the 800—200 cm^{-1} region is especially noteworthy. The infrared spectra of I, II and VI clearly show bands corresponding to the stretching and asymmetrical bending frequencies, $\nu(NH)$ and $\delta_{as}(HNH)$, respectively, of NH_3.

The infrared spectrum of II shows also a strong band at 650 cm^{-1} and a medium intensity band at 315 cm^{-1}, assigned to a coordinated NH_3 rocking vibration and to a $\nu(Co{-}N)$ vibration, respectively. The infrared spectra of III and V become still more complicated because of the numerous and strong triphenylphosphine bands, some of them modified by the coordination to metal [12]. VI gives an infrared spectrum showing the characteristic bands of the CN groups, some of which appear in the low-frequency region where stretching and bending frequencies of the $M{-}C{\equiv}C$ group would be expected, so that assignment cannot be made for the metal—alkynyl ligand bands in the 800—200 cm^{-1} region.

All the cyclohexylethynyl derivatives of Fe^{II} described here are diamagnetic confirming the relatively strong-field character of the alkynyl ligands. In the case of the Co^{II} complexes, I and II, which are necessarily paramagnetic, magnetic susceptibility measurements were made by the Gouy method, at various temperatures in the range 296 to 77 K, with freshly prepared samples.

A single measurement was made on complex III at room temperature, but the results are unreliable since the sample could not be satisfactorily packed in the Gouy tube.

TABLE 3

GRAM-SUSCEPTIBILITY, χ_g, AND MAGNETIC MOMENT, μ_{eff}, AT VARIOUS TEMPERATURES AND WEISS CONSTANTS, Θ, FOR CYCLOHEXYLETHYNYL Co(II) DERIVATIVES

T(K)	I $K_4[Co(CHE)_6]$ [a] $\cdot$ 2 NH_3		II $K_2[Co(CHE)_4(NH_3)_2]$	
	χ_g ($\times 10^6$) ($cm^3\ g^{-1}$)	μ_{eff} (B.M.)	χ_g ($\times 10^6$) ($cm^3\ g^{-1}$)	μ_{eff} (B.M.)
296	3.63	3.32	10.71	4.01
206	6.54	3.01	13.55	3.76
127	8.92	2.96	20.81	3.63
77	13.63	2.81	31.00	3.43
Θ	—22		—40	

[a] CHE = C_6H_{11}—C≡C$^-$.

σ_n varies between ±0.02 and ±0.03 for the χ_g values of the complex I, and between ±0.04 and ±0.08, for the χ_g values of the complex II. For the plotting of $1/\chi'_M$ versus T seven points were used. Except for the points at 296 K, the values in the Table correspond to points lying exactly on the straight line plots of $1/\chi'_M$ versus T.

Table 3 gives the values obtained for gram-susceptibility, χ_g, and magnetic moment, μ_{eff}, at various temperatures, together with the Weiss constants, Θ, of complexes I and II. χ_g is field independent, which excludes the presence of ferromagnetic compounds. The plot of $1/\chi'_M$ (χ'_M = mol-susceptibility corrected for diamagnetism) versus temperature gives a straight line for each complex, from which the Weiss constants, Θ, were deduced. Only the points at room temperature lie away from the straight lines defined by the remaining points and lie slightly below the lines.

From the μ_{eff} values (Table 3) we deduce that $K_4[Co(CHE)_6] \cdot 2\ NH_3$ is a low-spin complex, since the μ_{eff} values are always lower than the spin-only magnetic moment of the $(t_{2g})^5(e_g)^2$ configuration (3.87 B.M.). In the case of $K_2[Co(CHE)_4(NH_3)_2]$ μ_{eff} is higher than 3.87 B.M. only at room temperature.

In both complexes the magnetic moment increases with temperature, the values being intermediate between the low-spin and the high-spin values and higher than the μ_{eff} values reported by Nast et al. [1,2,4] for other Co^{II} alkynyl complexes. In the case of I, considered as an anionic six-coordinate complex of formula $K_4[Co(C{\equiv}C{-}C_6H_{11})_6] \cdot 2\ NH_3$, this may be due to a mixture of low- and high-spin states, in concentrations determined by their energy difference. Since a regular octahedral complex cannot possess a ground state of intermediate spin [13], the symmetry of this complex is probably below octahedral, and a tetragonal pyramidal configuration is likely. Solid-state effects and Jahn-Teller distortion may be partly responsible for this effect.

Complex II is probably the six-coordinate complex $K_2[Co(CHE)_4(NH_3)_2]$, since this is consistent with the empirical formula, and since I and II show different ν(C≡C) frequencies and the infrared spectrum of II shows bands characteristic of coordinated ammonia. Furthermore, for the complex II only one ν(C≡C) band is observed, whereas for the complex I two ν(C≡C) bands are present. This can be attributed to the trans-configuration of II. The presence of the NH_3 molecules in this complex may bring closer the low-spin and high-spin energy states and contribute to a larger electron population in the high-spin state at room temperature. These high μ_{eff} values cannot be attributed to a high orbital contribution, since the few known low-spin octahedral complexes show relatively low orbital contribution, and the μ_{eff} values are only slightly larger than 1.73 B.M. [14,15].

The fact that the points of the plots of $1/\chi'_M$ versus T at room temperature lie slightly below the corresponding straight lines (an effect more noticeable for complex I) suggest the possibility of an anomaly case, similar to examples described by Stoufer et al. [15].

The magnetic moment values measured on the partially decomposed complex II (bluish grey, and with lower NH_3 content) are much lower. This suggests a transition to square-planar geometry with a possible metal—metal interaction.

Complex III, $[(Ph_3P)_2Co(CHE)_2]$ probably has a square-planar configuration, since the compound appears to have a low-spin magnetic moment. The unreliability of the μ_{eff} value obtained (1.6 B.M.), lower than the spin-only magnetic moment for an odd electron (1.73 B.M.) does not allow us to make any comment about it nor about the orbital contribution in this complex. However, even lower values of μ_{eff} have been found in six-coordinate complexes of the type $M^I{}_2[Co(PR_3)_2(C{\equiv}CR)_4]$, described by Nast et al. [4].

Experimental

All the reactions and manipulations of products were carried out under dry oxygen free nitrogen.

C and H contents were determined in a Coleman Model 33 microanalyzer, K by flame photometry, Co and Fe by atomic absorption, and N by microkjeldahl. Infrared spectra were recorded on a Perkin-Elmer 325 spectrophotometer (4000—200 cm^{-1}) in KBr or CsI disks and Nujol or polychlorotrifluoroethylene oil mulls. The ^1H NMR spectra were recorded on a Perkin-Elmer R-10 spectrometer with tetramethylsilane as reference.

The Gouy method was used to measure magnetic susceptibilities; freshly prepared samples were used, and measurements made at several temperatures, between at 77—300 K. The magnetic field, which was calibrated with solid $[Ni(en)_3]S_2O_3$, was provided by a Bruker B-M-4 electromagnet. The magnetic forces were measured with a Sartorius electron microbalance, Type 4411. A Leybold-Heraeus cryostat VNK-3-300 was used for the control, regulation and maintenance of temperature. Twenty measurements at each temperature were taken in an increasing magnetic field (0.6—9.0 gauss).

Starting materials

Cyclohexylethynyl potassium was prepared from cyclohexylethyne (Merck) and potassium amide or acetylide in liquid ammonia [11].

$Co(NCS)_2 \cdot 4\ NH_3$ was prepared by reaction of $Ba(SCN)_2$ with $CoSO_4$, dehydration of the $Co(NCS)_2 \cdot nH_2O$ obtained, and subsequent crystallisation in liquid NH_3, as a pink, microcrystalline product. It was unstable in air, becoming blue.

$Fe(NCS)_2 \cdot 2\ NH_3$ was obtained as an easily oxidizable grey-green powder by a procedure similar to that described above under oxygen-free conditions.

$K_3[Fe(CN)_5(NH_3)]$ was made as described by Hölzl et al. [16]. The hydrate

obtained, with 2.5 H_2O molecules, was converted into the yellow anhydrous compound by washing with liquid NH_3.

[(Ph$_3$P)$_2$CoCl$_2$] and [(Ph$_3$P)$_2$CoBr$_2$] were made as described by Venanzi et al. [17]. The ^{1}H NMR spectra of these compounds show a doublet at δ values of 7.28 and 7.32 ppm, corresponding to the phosphine phenyl protons.

[(Ph$_3$P)$_2$Fe(NCS)$_2$] was made as described by Venanzi [17]. After refluxing for 6 h in dry butanol, the solution was filtered while still hot and crystallized on cooling. The dark-green crystals were dried in high vacuum. They are diamagnetic and stable in air. Yield 30%. M.p. (dec.) 360°C. The ^{1}H NMR spectrum shows a doublet at δ 7.25—7.30 ppm, corresponding to protons of the phosphine phenyl groups. Found: C, 64.85; H, 4.82; Fe, 7.85. $C_{38}H_{30}FeN_2P_2S_2$ Calcd.: C, 65.53; H, 4.31; Fe, 8.01%.

Preparation of the complexes

K$_4$[Co(C≡C—C$_6$H$_{11}$)$_6$] · 2 NH$_3$, (I). A solution of 0.33 g (1.35 mmol) of Co(NCS)$_2$ · 4 NH_3 in 50 cm^3 of liquid ammonia was mixed with a solution of 1.19 g (8.15 mmol) of KC≡C—C_6H_{11} in 50 cm^3 of liquid ammonia. A blue-green precipitate appeared immediately. This was filtered off on a fritted-glass disk (G-3), washed 3 times with 30 cm^3 of liquid ammonia, and freed of solvent by evaporation at room temperature. The dried product (0.84 g, 70%) was a light-green powder, it is stable in N_2, NH_3 or vacuum at room temperature, pyrophoric in air, sensitive to moisture and insoluble in the usual organic solvents. Found: C, 64.10; H, 8.40; Co, 6.63; K, 17.54; N, 3.37. $C_{48}H_{72}CoK_4N_2$ calcd.: C, 64.65; H, 8.08; Co, 6.61; K, 17.51; N, 3.14%.

K$_2$[Co(C≡C—C$_6$H$_{11}$)$_4$(NH$_3$)$_2$], (II). 0.43 g (1.7 mmol) of solid Co(NCS)$_2$ · 4 NH_3 was added to 1.03 g (6.8 mmol) of KC≡C—C_6H_{11} dissolved in 70 cm^3 of liquid ammonia. A voluminous deep blue precipitate appeared, and this was filtered off on a fritted-glass disk (G-3), washed 3 times with 30 cm^3 of liquid ammonia, and freed of solvent by evaporation at room temperature. The dry precipitate (0.66 g, 65%) was a light blue powder, stable in N_2, NH_3 or vacuum, pyrophoric in air, sensitive to moisture and insoluble in the usual organic solvents. Found: C, 63.90; H, 8.32; Co, 9.77; K, 12.8; N, 4.81. $C_{32}H_{50}CoK_2N_2$ Calcd.: C, 64.11; H, 8.34; Co, 9.66; K, 13.02; N, 4.67%.

[(Ph$_3$P)$_2$Co(C≡C—C$_6$H$_{11}$)$_2$], (III). A solution of 3 mmol of $(Ph_3P)_2CoCl_2$ (1.96 g) or $(Ph_3P)_2CoBr_2$ (2.23 g) in absolute ether was added dropwise to a solution of KC≡C—C_6H_{11} (0.78 g, 6 mmol) in liquid ammonia (60 cm^3), which was stirred from time to time during 10 h. After addition of NH_4Cl (1 g) and evaporation of NH_3, a volume of water equal to that of the ether solution was added. A greenish-yellow solid formed at the interface. This can be recrystallized from methanol/acetone but with partial decomposition, and the isolated product, (1.38 g, 60%), contains traces of free phosphine and never gives a loose powder. M.p. 158—165°C (dec.). It decomposes slowly in contact with moisture, is soluble in CCl_4 and is hydrolyzed by H_2O. μ_{eff} (20°C) = 1.6 B.M. Found: C, 77.20; H, 6.69; Co, 7.01. $C_{52}H_{52}CoP_2$ Calcd.: C, 78.29; H, 6.50; Co, 6.98%.

K$_4$[Fe(C≡C—C$_6$H$_{11}$)$_6$], (IV). A solution of 1.02 g (6.9 mmol) of KC≡C—C_6H_{11} in 50 cm^3 of liquid ammonia was added to a solution of 0.20 g (1.16 mmol) of Fe(NCS)$_2$ · 2 NH_3 in 50 cm^3 of liquid ammonia. After stirring for

10 h at —50°C, a brownish product was formed, and this was filtered off on a glass disk (G-3), washed 3 times with 30 cm^3 of liquid ammonia and dried in a high vacuum. The brownish product (0.5 g, 50%) is stable at room temperature under N_2 or NH_3 and in vacuum, but decomposes in air. It is insoluble in the usual organic solvents and is diamagnetic. Found: C, 67.12; H, 7.55; Fe, 6.61; K, 18.89. $C_{48}H_{66}FeK_4$ Calcd.: C, 67.46; H, 7.73; Fe, 6.54; K, 18.27%.

$[(Ph_3P)_2Fe(C{\equiv}C{-}C_6H_{11})_2]$, (V). A solution of $[(Ph_3P)_2Fe(NCS)_2]$ (1.5 g, 2.5 mmol) in 30 cm^3 of cold absolute diethyl ether was added dropwise with stirring to a solution of $KC{\equiv}C{-}C_6H_{11}$ (0.36 g, 5 mmol) in 100 cm^3 of liquid ammonia at —50°. After 10 h at —50°C with occasional stirring, 1 g of NH_4Cl was added, the liquid NH_3 evaporated and an equal volume of water added. A light-brownish product was isolated from the ether phase. This compound is stable under N_2, is partly soluble in CCl_4, decomposes in air, and is diamagnetically. M.p. 240—260°C (dec.). (Found: C, 78.32; H, 6.02; Fe, 7.60. $C_{52}H_{52}FeP_2$ Calcd.: C, 78.61; H, 6.55; Fe, 7.03%.

$K_4[Fe(CN)_4(C{\equiv}C{-}C_6H_{11})_2]$, (VI). A solution of 0.1 g (0.6 mmol) of $KC{\equiv}C{-}C_6H_{11}$ in liquid NH_3 (50 cm^3) was added to a suspension of $K_3[Fe(CN)_5(NH_3)]$ (0.1 g, 0.3 mmol) in 20 cm^3 of liquid NH_3. After 30 h stirring at —60°C, the product was filtered off, washed 3 times with 30 cm^3 of liquid NH_3, and dried in a high vacuum. The yellow product is stable in dry N_2 at room temperature, decomposes in air, is insoluble in the usual organic solvents and is diamagnetic. Found: C, 40.13; H, 5.24; Fe, 9.57; K, 25.92; N, 18.52. $C_{20}H_{34}FeK_4N_8$ Calcd.: C, 40.06; H, 5.71; Fe, 9.31; K, 26.04; N, 18.69%.

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