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The Reaction of Cationic Cyclopentadienyliron Isocyanide Complexes and Pentafluorophenyllithium

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From the reaction of $C_5H_5Fe(CO)(CNCH_3)_2^+$ and C_6F_5Li we have isolated, in order of chromatographic elution, $C_5H_5Fe(CNCH_3)_2C_6F_5$, $C_5H_5Fe(CO)(CHCH_3)C(C_6F_5){=}NCH_3$ (first isomer), and $C_5H_5Fe(CO)(CNCH_3)C(C_6F_5){=}NCH_3$ (second isomer). The latter two compounds each contain an N-methylpentafluorobenzimido group; these are formally derivatives of acylmetal compounds. Isomer B has a lower stability and converts to isomer A; the latter slowly loses CO to give $C_5H_5Fe(CNCH_3)_2C_6F_5$. From the reaction of $C_5H_5Fe(CO)_2CNCH_3^+$ and C_6F_5Li four direct products are characterized including *exo*-1-$C_6F_5C_5H_5Fe(CO)_2(CNCH_3)$, $[C_5H_5Fe(CO)_2]_2$, $C_5H_5Fe(CO)(CNCH_3)C_6F_5$, and $C_5H_5Fe(CO)_2C(C_6F_5){=}NCH_3$. A secondary product, *exo*-1-$CCl_3C_5H_5Fe(CO)_2(CNCH_3)$, arose unexpectedly when the crude reaction mixture was treated with chloroform; its precursor could not be determined however. We have also characterized the compound $C_5H_5Fe(CO)(CNCH_3)I$, which was believed to arise from reaction of $C_5H_5Fe(CO)_2CNCH_3^+$ and I^-.

We have recently been studying reactions of pentafluorophenyllithium and other nucleophilic reagents with cationic cyclopentadienyliron, -molybdenum, and -tungsten[1] and -nickel[2] complexes. These reactions in some instances have been proven to be useful synthetic routes to new low-valent alkyl or aryl complexes of transition metals. However the facility of these reactions in synthesis is limited by what is perhaps the most striking feature of this type of reaction, its general nonselectivity. Several reaction pathways are often observed to occur, including attack at the metal atom, or at a carbonyl or C_5H_5 ligand, and reduction to a dinuclear species. For example in the reaction of $C_5H_5Fe(CO)_3^+$ with C_6F_5Li three products—$C_5H_5Fe(CO)_2C_6F_5$, $C_5H_5Fe(CO)_2COC_6F_5$, and 1-*exo*-$C_6F_5C_5H_5Fe(CO)_3$—are obtained.[1]

We are continuing our studies of these reactions. Recently our attentions have been focused on cationic isocyanide complexes.[3] We report here the reactions of the cations $C_5H_5Fe(CO)_2CNCH_3^+$ and $C_5H_5Fe(CO)(CNCH_3)_2^+$ with pentafluorophenyllithium. From each reaction several different products are formed. Their isolation and characterization are described in this paper.

Experimental Section

Infrared spectra were recorded on a Beckman IR-10 spectrometer. Proton nmr spectra were recorded on a Varian A-60. (The infrared spectral data are presented in Table I. The ^1H nmr data are given in Table II.) Molecular weights were determined with a Mechrolab osmometer, using benzene solutions of $\sim 10^{-3}$ *m* concentration. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Both $C_5H_5Fe(CO)_2CNCH_3^+PF_6^-$ and $C_5H_5Fe(CO)(CNCH_3)_2^+PF_6^-$ were prepared by addition of an aqueous solution of the corresponding iodide salt, described by Coffey,[4] to a saturated NH_4PF_6 solution. The yellow precipitate was filtered, dried, and recrystallized from acetone–water.

Reaction of C_6F_5Li and $C_5H_5Fe(CO)(CNCH_3)_2^+PF_6^-$.—A 21.2-mmol sample of C_6F_5Li was prepared by treating 5.24 g of C_6F_5Br with 21.2 mmol of *n*-butyllithium in 750 ml of dry, freshly distilled tetrahydrofuran at −78° for about 15 min.[5] To this was added 8.0 g (21.2 mmol) of solid $C_5H_5Fe(CO)(CNCH_3)_2^+PF_6^-$. The mixture was filtered and the solvent was evaporated. The residue was extracted with chloroform, filtered, and evaporated to a volume of about 20 ml. This was chromatographed on a 50 × 4.5 cm alumina column prepared with chloroform. Three yellow bands were observed to develop. Each was eluted with chloroform, giving a yellow solution. This solution was evaporated to dryness and the crystalline residue remaining was purified by crystallization from an ethyl ether–pentane solvent mixture.

In addition to the three yellow bands, a faint red band was seen; this disappeared on continued elution and a product could not be isolated. The possible identification of this compound as a dimer, $[C_5H_5Fe(CO)_2]_2$, or a derivative thereof, seems reasonable.

Band A: 0.70 g, identified as $C_5H_5Fe(CNCH_3)_2C_6F_5$ (I), mp 152–153°, 8.9% yield. *Anal.* Calcd for $C_{15}H_{11}N_2F_5Fe$: C, 48.65; H, 2.99; N, 7.60; Fe, 15.08; mol wt, 370. Found: C, 49.45; H, 3.00; N, 7.65; Fe, 15.31; mol wt, 350.

Band B: 1.30 g, identified as $C_5H_5Fe(CO)(CNCH_3)C(C_6F_5){=}NCH_3$ (II), mp 93–94°, 15.4% yield. *Anal.* Calcd for $C_{16}H_{11}N_2F_5FeO$: C, 48.25; H, 2.78; N, 7.06; Fe, 14.02; mol wt, 398. Found: C, 48.17; H, 2.73; N, 7.03; Fe, 14.90; mol wt, 406.

Band C: 1.15 g, shown to have the same molecular formula as II, $C_5H_5Fe(CO)(CNCH_3)C(C_6F_5){=}NCH_3$ (III), mp 90–91°, 13.6% yield. *Anal.* Calcd for $C_{16}H_{11}N_2F_5FeO$: C, 48.25; H, 2.78; N, 7.06; Fe, 14.02; mol wt, 398. Found: C, 48.35; H, 2.69; N, 6.86; Fe, 14.78; mol wt, 402.

Attempted Interconversions of I, II, and III.—In an attempt to interconvert II and III, each compound was refluxed in tetrahydrofuran for 18 hr. The resultant products were then isolated by chromatography as described above and identified by proton nmr and infrared spectra.

From 0.21 g of II (0.53 mmol) a mixture of about 0.03 g of I and 0.13 g of II were recovered. This represents a recovery of about 75% of the material used. From 0.22 g of III, a mixture of 0.05 g of I and 0.12 g of II were formed, giving a total recovery of about the same amount.

An attempted carbonylation of I (60° in hexane, 10 atm carbon monoxide pressure) was unsuccessful.

Reaction of C_6F_5Li and $C_5H_5Fe(CO)_2(CNCH_3)^+PF_6^-$.—A 44-mmol sample of LiC_6F_5 was prepared by treating 10.9 g of C_6F_5Br with 44 mmol of *n*-butyllithium in ~750 ml of dry, freshly distilled tetrahydrofuran at −78° for about 15 min.[5] To this was added 16 g (44 mmol) of solid $C_5H_5Fe(CO)_2(CNCH_3)^+PF_6^-$. The mixture was then warmed to 0° and stirred overnight. A deep yellow-brown solution was formed. The mixture was

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[1] P. M. Treichel and R. L. Shubkin, *Inorg. Chem.*, **6**, 1328 (1967).

[2] P. M. Treichel and R. L. Shubkin, *Inorg. Chim. Acta*, **2**, 485 (1968).

[3] P. M. Treichel and J. P. Stenson, *Chem. Commun.*, 423 (1969).

[4] C. E. Coffey, *J. Inorg. Nucl. Chem.*, **25**, 179 (1963).

[5] P. L. Coe, R. Stephens, and J. Tatlow, *J. Chem. Soc.*, 166 (1959).

Table I

Infrared Spectra of Isocyanide Complexes (cm^{-1})

Compound	ν_{CO}	$\nu_{C\equiv N}$	Other bands
$C_5H_5Fe(CNCH_3)_2C_6F_5$ (I)[a]		2120 s	2950 m, 1495 m, 1425 s, 1045 m, 950 s, 820 m, 540 m, 495 w
$C_5H_5Fe(CO)(CNCH_3)C(C_6F_5){=}NCH_3$ (first isomer) (II)[a]	1955 s	2160 s	2930 m, 1580 s, 1490 s, 1420 mw, 1300 w, 1260 w, 1100 m, 980 s, 830 m, 705 w, 640 vw, 610 m, 580 mw, 555 m
$C_5H_5Fe(CO)(CNCH_3)C(C_6F_5){=}NCH_3$ (second isomer) (III)[a]	1960 s	2160 s	2950 m, 1570 m, 1485 s, 1425 w, 1390 w, 1290 w, 1100 m, 980 s, 830 m, 610 w, 560 mw
exo-1-$C_6F_5C_5H_5Fe(CO)_2CNCH_3$ (IV)[b]	1995 s, 1950 s	2155 s	2945 m, 2888 w, 1650 m, 1520 s, 1490 s, 1300 m, 1200 w, 1100 s, 1075 m, 1050 m, 990 s, 950 m, 895 m, 675 m, 620 m, 595 s, 555 s, 515 w
exo-1-$CCl_3C_5H_5Fe(CO)_2CNCH_3$ (V)[b]	1995 s, 1950 s	2155 s	2940 m, 1415 s, 1320 w, 1210 s, 1050 m, 920 m, 645 s, 625 s, 590 s, 550 s
$C_5H_5Fe(CO)(CNCH_3)C_6F_5$ (VI)[b]	1985 s	2160 s	2950 w, 1630 w, 1615 s, 1500 s, 1450 s, 1435 s, 1055 s, 955 s, 630 w, 580 m, 540 m
$C_5H_5Fe(CO)_2C(C_6F_5){=}NCH_3$ (VII)[b]	2020 s, 1980 s		2960 w, 2920 w, 2860 w, 1520 s, 1490 s, 1330 w, 1300 w, 1130 w, 1100 w, 980 s, 960 m, 705 m, 630 m, 595 m, 560 m
$C_5H_5Fe(CO)(CNCH_3)I$ (VIII)[a]	1995 s	2180 s	2980 w, 1620 vw, 1420 w, 1220 vw, 1005 vw, 580 w, 555 w, 530 w

[a] $CHCl_3$ solution. [b] CCl_4 solution.

Table II

Proton Nmr Data[a,b]

Compound	Chemical shift, τ (intensity)
I	5.62 (5), 6.66 (6)
II	5.30 (5), 6.45 (3), 6.72 (3)
III	5.36 (5), 6.66 (3), 6.95 (3)
IV	4.65 (2), 5.92 (1), 6.62 (3), 7.12 (2)
V	4.60 (2), 6.46, 6.64 (4, unsym), 7.11 (2)
VI	5.35 (5), 6.65 (3)
VII	5.00 (5), 6.42 (3)
VIII	5.25 (5), 6.42 (3)

[a] In $CDCl_3$ *vs.* TMS, internal standard. [b] All singlets.

filtered and the solvent was evaporated. The residue was extracted with benzene, filtered, and evaporated to a volume of about 20 ml. This was chromatographed on a 50 × 4.5 cm alumina column prepared with benzene. Three bands (A, B, and C below; yellow, red, and green-brown) were observed to develop. Each was eluted with benzene giving yellow, red, and yellow-brown solutions, respectively. The solutions were evaporated and the residues were examined.

Band A: The residue from the first band, 3.17 g, was recrystallized from a chloroform-hexane mixture; it was identified as *exo*-1-$C_6F_5C_5H_5Fe(CO)_2(CNCH_3)$ (IV), pale yellow needles, mp 105–106°, 18.7% yield. *Anal.* Calcd for $C_{15}H_8NF_5FeO_2$: C, 46.75; H, 2.08; N, 3.64; mol wt, 385. Found: C, 47.43; H, 2.11; N, 3.57; mol wt, 371.

Band B: 1.09 g, identified as known $[C_5H_5Fe(CO)_2]_2$, 14% yield.

Band C: The residue of this band, 1.46 g, was shown by its infrared and nmr spectra to be a complex mixture. (It should be noted here that this crude mixture was treated with $CHCl_3$ and $CDCl_3$ at this point in order to obtain the preliminary spectra. Because of the low yield, the materials were recovered from the solvents and used in the subsequent chromatographies; as $CHCl_3$ was not used previously or in subsequent operations, the $-CCl_3$ group in compound V, *vide infra*, must have been introduced at this point.) This mixture was rechromatographed on a 40 × 2 cm alumina column prepared with a 50:50 benzene-hexane solvent mixture. Four bands (three yellow and one green-brown—C1, C2, C3, C4 in order of elution) were observed to develop. Each was eluted with the same benzene-hexane solvent mixture, giving a yellow solution. The solution was evaporated to dryness and the residue was crystallized from an appropriate solvent mixture.

Band C1: 0.32 g, crystallized from chloroform-hexane, identified as *exo*-1-$CCl_3C_5H_5Fe(CO)_2(CNCH_3)$ (V), yellow crystals, mp 105–106° dec, 2.2% yield. *Anal.* Calcd for $C_{10}H_8NCl_3FeO_2$: C, 35.8; H, 2.40; N, 4.16; Cl, 31.70; mol wt, 336. Found: C, 36.3; H, 2.49; N, 4.07; Cl, 31.8; mol wt, 341.

Band C2: 0.15 g, crystallized from ethyl ether-pentane, identified as $C_5H_5Fe(CO)(CNCH_3)(C_6F_5)$ (VI), yellow crystals, mp 83–74.5°, 0.95% yield. *Anal.* Calcd for $C_{14}H_8NF_5FeO$: C, 47.00; H, 2.24; N, 3.92. Found: C, 47.04; H, 2.22; N, 3.95. (The nmr of the crude sample of band C2 showed a small amount of $C_5H_5Fe(CNCH_3)_2C_6F_5$, which was separated in the crystallization. Its presence here in such a small amount did not make isolation possible.)

Band C3: 0.19 g, crystallized from ethyl ether-pentane, was identified as $C_5H_5Fe(CO)_2C(C_6F_5){=}NCH_3$ (VII), yellow crystals, mp 108–109°, 1.1% yield. *Anal.* Calcd for $C_{15}H_8NF_5FeO_2$: C, 46.75; H, 2.08; N, 3.64; mol wt, 385. Found: C, 47.77; H, 2.01; N, 3.67; mol wt, 355.

Band C4: 0.06 g, crystallized from benzene-heptane, was identified as $C_5H_5Fe(CO)(CNCH_3)I$ (VIII), green-brown crystals, mp 141–142° dec, 0.43% yield. *Anal.* Calcd for C_8H_8NIFeO: C, 30.30; H, 2.52; N, 4.42; mol wt, 317. Found: C, 30.38; H, 2.53; N, 4.67; mol wt, 319.

Results and Discussion

The reaction of $C_5H_5Fe(CO)_3^+$ and C_6F_5Li had been previously carried out in our group and had been particularly interesting.[1] The observed products in this reaction indicate that the cationic iron complex is rather susceptible to nucleophilic attack, but furthermore, reaction occurs with a lack of selectivity. We turned to the reactions reported here with the expectation that a similar nonselectivity would be found. In addition, the possibility that the isocyanide ligand would be one point of attack by C_6F_5Li was intriguing as such reactions would yield N-methylpentafluorobenzimido derivatives of metal carbonyls. The general class of acylimino complexes, though formally quite similar to well-known acylmetal complexes, has received very little attention, and in fact to date there is only one reference to such complexes being isolated. King and Pannell[6] reported the compound $C_5H_5Fe(CO)(NCCH_3)C(CF_3){=}NH$ arises in the reaction of $C_5H_5Fe(CO)_2CH_3$ and CF_3CN; several complexes arising from substitution of CO by various ligands are noted. Analogous compounds have been proposed as intermediates in protonation of pentacyanocobaltate(II)

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(6) R. B. King and K. H. Pannell, *J. Am. Chem. Soc.*, **90**, 3984 (1968).

reactions[7] and in amination of copper isocyanide compounds, however.[8]

It should be observed that the general area of low-valent isocyanide metal complexes has been studied very little until now. Primarily work to date has been concerned with derivatives of metal carbonyls and metal carbonyl halides.[9] It seems likely to us, however, that this area may be a particularly interesting one. We refer to our recent communication on the complex $C_5H_5Fe(CO)(CNCH_3)_2BH_4$[3] and to the complexes $(C_5H_5)_2Fe_2(CO)_3(CNC_6H_5)$[10] and $[C_5H_5Ni(CNC_6H_5)]_2$[10,11] described by Pauson, Mills, and coworkers which were found to contain bridging isonitrile groups.

The reaction of $C_5H_5Fe(CO)(CNCH_3)_2^+$ and C_6F_5Li was run in tetrahydrofuran at 0°. As the reaction proceeded, the amount of the insoluble cationic complex was observed to diminish, and the resulting reaction products, soluble in the solvent, gave a yellow-brown solution. The solvent was evaporated, and a chloroform solution was chromatographed on alumina to achieve a separation of the three products.

The first compound to elute on chromatography was identified as a new stable pentafluorophenyl complex of the formula $C_5H_5Fe(CNCH_3)_2C_6F_5$. As no isocyanide-substituted arylmetal complexes are known, this complex is of particular interest. Monosubstituted derivatives of $C_5H_5Fe(CO)_2R$ (R = alkyl or aryl) have been reported for several phosphines and phosphites,[12] but no disubstituted $C_5H_5Fe(L)_2R$ compounds are yet known.[13] To our knowledge there has been no effort to study the direct reactions of isocyanides and $C_5H_5Fe(CO)_2R$ compounds. There is one report of a reaction of isocyanides with $CH_3Mn(CO)_5$[14] which resulted in substituted $Mn_2(CO)_{10-x}L_x$ compounds ($L = C_6H_5NC$; $x = 1, 2$).

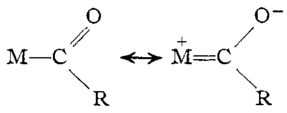
The second and third compounds from this reaction are isomers of the molecular formula $C_5H_5Fe(CO)(CNCH_3)C(C_6F_5){=}NCH_3$. Given the general structure, the most reasonable rationale for the existence of isomers is that the two compounds differ by the orientation of the $=NCH_3$ group. The methyl group could assume either a *cis* or a *trans* orientation to the metal group with respect to the C=N double bond. The isomers would be required not to interconvert appreciably by virtue of their isolation.

The infrared spectral data support this formulation. Both complexes have a single terminal carbonyl band at 1960 cm^{-1}, somewhat higher than the value of ν_{CO} found for $C_5H_5Fe(CO)(L)COCH_3$ derivatives (1920 cm^{-1}).[12] The $\nu_{C\equiv N}$ band is seen as a single sharp absorption at 2160 cm^{-1}. This is at a higher frequency than is seen in $C_5H_5Fe(CNCH_3)_2C_6F_5$ (2120 cm^{-1}); this shift to higher frequency is anticipated as the difference between $-C_6F_5$ and $-C(C_6F_5){=}NCH_3$ groups, and CO and $CNCH_3$ bonded to iron would both be expected to cause the observed variation in frequency.

In addition to the values of ν_{CO} and ν_{CN}, the infrared spectra of compounds II and III both show a strong peak near 1580 cm^{-1}, which is not seen in I. This peak can be assigned to the C=N stretching mode.

The proton nmr spectra of these complexes are simple. Each compound shows a peak near τ 5.5 (relative intensity, 5) associated with the C_5H_5 group. In addition each has a peak near τ 6.70: I, τ 6.66, intensity, 6; II, τ 6.72, intensity, 3; III, τ 6.66, intensity, 3) which we feel is most likely associated with the terminal CH_3NC group protons. Other $CNCH_3$ complexes (described later) also show this feature. Peaks for compounds II and III at τ 6.45 and 6.95, respectively, would then be assigned to the protons in the $=NCH_3$ group.

It is remarkable that the formation of simple imino derivatives of acylmetal compounds through common organic derivatization reactions has not been reported. The acyl carbonyl functional group might be expected to be quite inert to reactions that are common to carbonyls in organic chemistry. Among the possible rationalizations for this is the assumed back-bonding interaction from the metal, which transfers charge to the oxygen group[4,12]



Such an interaction is believed to be important since the ν_{CO} frequency is quite low ($\lesssim$1650 cm^{-1}) in these complexes. Derivatization reactions are generally assumed to proceed by addition of a group (*e.g.*, N–H of NH_2OH) to the carbonyl group, resulting in an intermediate having a coordinately saturated carbon atom which could not back-bond to the metal and thus be of higher energy. This would suggest, in turn, that such a pathway involves a reaction intermediate of somewhat higher energy, and a higher activation energy and lower reaction rate are expected.

It is clear to us that work along these lines is needed, however, to verify this hypothesis. We are continuing to look into this problem.

The structures of acylmetal compounds and the iminometal derivatives would appear to be rather similar, and one might conclude that bonding from the metal to these groups would be analogous. We felt, therefore, that an investigation of the carbonylation–decarbonylation reactions of these systems was appropriate. The information obtainable in an extensive study would find close analogy to the currently inter-

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[7] J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.* (Amsterdam), **3**, 433 (1965).

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[9] Reviewed: L. Malatesta, *Progr. Inorg. Chem.*, **1**, 283 (1959).

[10] K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw, and W. H. Stubbs, *Chem. Commun.*, 181 (1965).

[11] P. L. Pauson and W. H. Stubbs, *Angew. Chem. Intern. Ed. Engl.*, **1**, 333 (1962).

[12] (a) J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, **5**, 889 (1966); (b) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *ibid.*, **5**, 1177 (1966).

[13] Such compounds where $R = R_3Sn$ are reported: R. B. King and K. H. Pannell, *ibid.*, **7**, 1510 (1968). Attempted substitution reactions to give $C_5H_5FeL_2C_6H_5$ gave instead $[C_5H_5FeL_2]_2$: A. N. Nesmeyanov, Yu A. Chapovsky, and Yu. A. Ustynyuk, *J. Organometal. Chem.* (Amster dam) **9**, 345 (1967).

[14] K. K. Joshi, P. L. Pauson, and W. H. Stubbs, *ibid.*, **1**, 51 (1963).

esting carbonylation–decarbonylation studies being carried out with alkylmetal carbonyls.

As it turned out, our preliminary attempts at carbonylation of I were unsuccessful, utilizing moderate temperature and pressure. We would have anticipated migration of the C_6F_5- group to an isocyanide ligand, giving II or III. It will perhaps be possible to carry out this reaction under more severe conditions. However, fluoroalkyl and fluoroaryl groups are noticeably difficult to carbonylate anyway, and this result was not unexpected. Rather more interesting results were obtained when II or III was refluxed in tetrahydrofuran. Compound II was shown to be partially converted to I in several hours. Though in theory the new compound $C_5H_5Fe(CO)(CNCH_3)C_6F_5$ (VI, *vide infra*) could have been formed by expulsion of the terminal $CNCH_3$ ligand accompanied by C_6F_5 migration, this was not observed among the products. The results of the same reaction with III were quite surprising. From this reaction II and I were formed. Apparently isomer III is unstable with respect to II; our former success in isolating it arose from the mild reaction conditions fortunately employed in the synthesis. A slightly smaller conversion to I was noted in this reaction.

The reaction of $C_5H_5Fe(CO)_2CNCH_3{}^+PF_6{}^-$ and C_6F_5Li proved to be a challenge because of the many products that arose. In all, a total of at least seven products (five of which were new) and some starting material were present in the crude reaction mixture; careful and repeated chromatographies eventually led to isolation of each product.

The first compound to elute from alumina was also the one in largest yield. This compound, *exo*-1-$C_6F_5C_5H_5Fe(CO)_2CNCH_3$ (IV), was obtained as yellow crystals, which were quite soluble in organic solvents. Having observed no analogous product from the previous reactions of $C_5H_5Fe(CO)(CNCH_3)_2{}^+$, the isolation of this compound was unexpected; in retrospect, however, its formation complements our earlier results in which analogous products were described from reactions between $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+$ and RLi compounds. The characteristic set of nmr absorptions for IV at τ 4.65, 5.92, 7.12 (intensities 2:1:2) is typical for this type of 1-substituted cyclopentadiene–metal complex. One has to be predisposed to an *exo* disposition of the substituent group, in the face of considerable precedent for such a geometry from these reactions; the lack of a very low ν_{CH} absorption ($\sim$2750 cm^{-1}) is an adequate criterion for this assignment.[15]

Following IV in the chromatographic separation, one obtains a small amount of $[C_5H_5Fe(CO)_2]_2$. Though we looked carefully, no evidence could be obtained for isocyanide-substituted dimers such as that reported by Pauson, Mills, and coworkers.[10] The isolation of $[C_5H_5Fe(CO)_2]_2$ occurs regularly in cyclopentadienyliron carbonyl reactions and is not unexpected here.

The third compound to be eluted from the column was characterized as *exo*-1-$CCl_3C_5H_5Fe(CO)_2CNCH_3$ (V) and was at first a puzzle. The origin of the $-CCl_3$ group was itself unclear; in the first reaction attempted, chloroform had been used indiscriminantly. On repeating the reaction, we found that treatment of the crude reaction mixture with chloroform after a first chromatography but prior to the second led to the formation of this material. We have as yet been unable to learn what the chloroform reacted with in this mixture. We have shown that chloroform and $C_5H_5Fe(CO)_2CNCH_3{}^+PF_6{}^-$ do not react, and of course $C_5H_5Fe(CO)_2CNCH_3{}^+PF_6{}^-$ would not have eluted from the first chromatography anyway. This product (V) is structurally analogous to *exo*-1-$CCl_3C_5H_5CoC_5H_5$, which arises in the reaction of carbon tetrachloride (not chloroform which gives the *exo*-1-$CHCl_2$ compound) and cobaltocene.[15,16]

Compounds VI and VII were the most difficult to obtain from among the products in this reaction, owing to the particularly small quantity of each. Compound VI was identified as $C_5H_5Fe(CO)(CNCH_3)C_6F_5$, the compound which was postulated in the earlier discussion on the decarbonylation reactions. The spectral data left no doubt as to the nature of VI, even prior to obtaining analytical data. The 5:3 ratio of intensities of peaks in the proton nmr spectrum is correct for the $C_5H_5Fe(CO)(CNCH_3)C_6F_5$ formulation; the value of the CH_3 proton resonance was in the position anticipated for a terminal $CNCH_3$ ligand. The infrared spectrum showed the expected ν_{CO}, ν_{CN}, and ν_{CF} peaks. We were somewhat disappointed that the small quantity of material precluded immediate further study of this compound. The carbonylation of VI, which might be facile by analogy to carbonylation reactions of $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$,[12b] could give either VII or the compound $C_5H_5Fe(CO)(CNCH_3)COC_6F_5$, which is as yet unknown in our studies. We are proceeding toward the synthesis of larger quantities of VI by other routes to test this possibility.

Compound VII, $C_5H_5Fe(CO)_2C(C_6F_5){=}NCH_3$, showed two ν_{CO} absorptions at 2020 and 1980 cm^{-1}, similar to peaks at 2035 and 1990 cm^{-1} for the analogous acyl compound $C_5H_5Fe(CO)_2COC_6F_5$.[17] The small difference in these two sets of values is of interest. It suggests that the $C{=}NCH_3$ group is probably not quite as effective as the acyl $C{=}O$ in its capacity to back-bond to the metal. The difference seems small, however.

Finally, from our first attempt to study this reaction, two further products were observed. The first, $C_5H_5Fe(CO)(CNCH_3)I$, a compound analogous to $C_5H_5Fe(CO)(CNC_6H_5)I$,[14] arises from iodide ion attack on $C_5H_5Fe(CO)_2CNCH_3{}^+$. We have concluded that our metathetical reaction of $C_5H_5Fe(CO)_2CNCH_3{}^+I^-$ to the $PF_6{}^-$ salt had not been complete, and this allowed iodide ion to be present in small quantities in these reactions. Qualitative tests quickly verified the pres-

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[15] P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967).

[16] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 5753 (1959). Although these compounds were reported to be the *endo* isomers, sufficient evidence is now available to support the *exo*-substituted geometry.

[17] R. L. Shubkin, Ph.D. Thesis, University of Wisconsin, 1967.

ence of iodide. The same feature was common to some earlier reported reactions.[1] The second product was $C_5H_5Fe(CO)_2CN$, also known.[4] This compound was shown by infrared analysis not to be present as an impurity in the starting material. Hence its origin would appear to be by a demethylation reaction of an unspecified nature.

As has been so often the case in these reactions, the total yield of low-valent complexes is small. This is a disappointment, of course, but it suggests that an adequate explanation should be sought. We are inclined to consider the possibility that many neutral complexes formed in these reactions are themselves susceptible to attack by (fairly brutal) reagents such as organolithium compounds; in turn the anionic complexes would be lost in subsequent work-up either by air oxidation or by failure to elute from alumina on chromatography. This result does preclude an estimation of the reactivities of various positions in the molecule and its correlation with bonding theory, which ultimately is one goal in this study.

In summary, we have succeeded in further substantiating the nonselectivity of this kind of reaction. The isocyanide ligand, like carbonyls, is clearly susceptible to attack by a nucleophilic reagent. We find most intriguing, at this time, the potential isocyanide–carbonyl analogies which appear to be possible; we are especially interested in carbonylation–decarbonylation reaction analogies. Some of our present efforts are being directed in this area.

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The Relationship between Chelate Ring Size and the Stereochemistry of Some Cobalt(III) Complexes Containing Quadridentate Ligands

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The three homologous open-chain quadridentate ligands 1,8-diamino-3,6-dithiaoctane (EEE), 1,9-diamino-3,7-dithianonane (ETE), and 1,10-diamino-4,7-dithiadecane (TET) have been used to prepare a number of isomeric dichlorocobalt(III) complexes. It was found that the EEE ligand gave only the blue *cis*-α-$CoEEECl_2^+$ isomer and the ETE ligand gave the green *trans*-$CoETECl_2^+$ and the red-violet *cis*-β-$CoETECl_2^+$ isomers while the TET ligand gave the red-violet *cis*-β-$CoTETCl_2^+$ and the blue *cis*-α-$CoTETCl_2^+$ isomers. In addition, a series of cobalt(III) complexes of the type $CoEEEX_2^{n+}$ (where $X^- = Br^-, N_3^-, NCS^-, NO_2^-$, oxalate, and 2,2'-bipyridyl) has been prepared and investigated. These latter complexes all appear to have the *cis*-α configuration. The equilibria *trans*-$CoETECl_2^+ \rightleftharpoons$ *cis*-β-$CoETECl_2^+$ and *cis*-β-$CoTETCl_2^+ \rightleftharpoons$ *cis*-α-$CoTETCl_2^+$ have been studied and the relationship between chain length and stereochemistry is discussed in terms of the conformations of the chelate rings.

It is well known that[1] five-membered chelate rings formed by bidentate ligands containing only single bonds are the most stable and that, with the saturated ligands, these five-membered rings adopt the stable staggered (*gauche*) conformation.[2] In multidentate ligand systems a new problem arises by the circumstance that the ligand may adopt a number of arrangements about an octahedral metal ion. Thus, for example, the terdentate ligand diethylenetriamine may coordinate either in a planar or vicinal arrangement about an octahedral atom and the question arises as to which of the two arrangements is the most stable. It seems probable that two of the important considerations in deciding the outcome are the size of the individual chelate rings and the conformations which can be adopted. We have discussed this problem recently in relation to the quadridentate ligands triethylenetetramine and 1,4,8,11-tetraazaundecane (the latter contains an extra methylene group between the two secondary nitrogen atoms).[3] It was found that the former ligand tended to give *cis*-octahedral complexes[4] whereas the latter tended to give *trans* isomers. In this paper we wish to pursue this problem further and for this purpose we describe the results of our investigation of the stereochemistries adopted by the three homologous quadridentate ligands 1,8-diamino-3,6-dithiaoctane (EEE), 1,9-diamino-3,7-dithianonane (ETE), and 1,10-diamino-4,7-dithiadecane (TET) (Figure 1) about a cobalt(III) atom.

1. General Considerations

Octahedral metal complexes formed by the ligands EEE, ETE, and TET can be envisaged as existing in potentially three isomeric forms: the *cis*-α, *cis*-β, and *trans* isomers (Figure 2). In deciding which geometries will be the most stable for the quadridentate EEE ligand we shall consider only two factors: (a) that each che-

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