the synthesis of $F_4P_2 \cdot BH_3$ from F_4P_2 and B_2H_6 was reported, but all efforts to produce $F_4P_2 \cdot 2BH_3$ by this reaction were unsuccessful. Since F_4P_2 contains two potential coordination sites, the absence of coordination at the second site was a curious phenomenon which suggested some possible double bonding or other peculiarity in the P–P linkage.

Recently we have shown that $F_4P_2 \cdot 2BH_3$ can be synthesized using $OCBH_3$ as the borane source. The process proceeds by a stepwise base-displacement sequence

$$F_4P_2(g) + OCBH_3(g) \xrightarrow{-78^\circ} F_4P_2 \cdot BH_3(g) + CO(g)$$

$$F_4P_2 \cdot BH_3(g) + OCBH_3(g) \xrightarrow[2.\ \ -196^\circ]{1.\ \ -45^\circ} F_4P_2 \cdot 2BH_3(g) + CO(g)$$

The $F_4P_2 \cdot 2BH_3$ complex was found to be very unstable toward dissociation and decomposition at 0°. The complex reacted, on contact with trimethylamine, to give $(CH_3)_3N \cdot BH_3$, P_2F_4, and PF_3. This reaction served as an analytical reaction for determining the number of borane(3) units coordinated to the ligand.

The ^{11}B nmr spectrum was recorded at 32.1 MHz and at $-40°$ in $CFCl_3$ solvent. The spectrum consisted of a 1:3:3:1 quartet with δ 130.7 ppm relative to $(CH_3)_3B$ and $J_{BH} = 115$ Hz. No further splitting of the ^{11}B signal was observed. The ^{19}F nmr spectrum was recorded at 94.1 and 56.4 MHz at $-40°$. The spectrum in each case was found to be second order, as shown in Figure 1, with δ 10.0 ppm relative to F_3CCOOH. The second-order feature was not unexpected since an earlier study of P_2F_4[3] showed that the ligand exhibited an $X_2AA'X'_2$ type ^{19}F nmr spectrum. On expansion, the inner members of the $F_4P_2 \cdot 2BH_3$ spectrum showed a 1:3:3:1 quartet structure, $J_{FPBH} \cong 25$ Hz. The small, outer members showed no resolvable fine structure.

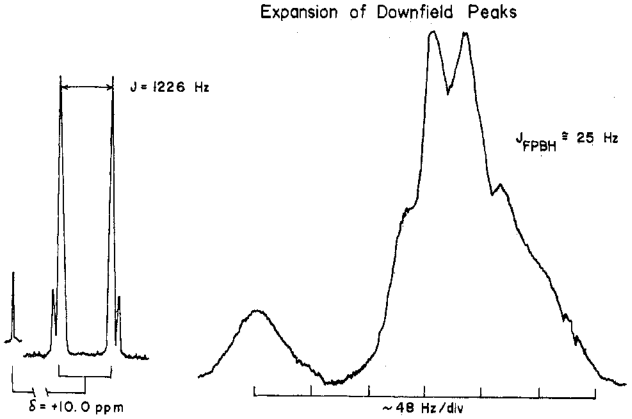

Figure 1.—The ^{19}F nmr spectrum of $F_4P_2 \cdot 2BH_3$ and expansion of the downfield peaks.

In the original paper by Parry[2] it was suggested that the borane group of $F_4P_2 \cdot BH_3$ oscillates between phosphorus sites since no splitting of the ^{11}B nmr signal by phosphorus was detected. This suggestion now appears to be incorrect since the ^{11}B spectrum of $F_4P_2 \cdot 2BH_3$ shows no splitting by phosphorus under the conditions used and oscillation is now clearly impossible. Furthermore Hodges and Rudolph[4] have recently detected the elusive splitting of the ^{11}B signal by phosphorus in $F_4P_2 \cdot BH_3$.

Experimental Section

In a typical preparation, 3.6 mmol of tetrafluorodiphosphine[5] and 4.0 mmol of borane carbonyl[6] were condensed together in a 300-ml bulb attached to a standard high-vacuum line. The bulb was then closed off by a stopcock and held at $-78°$ for 2–3 days. During this reaction period the bulb and contents were periodically frozen at $-196°$ and the liberated carbon monoxide pumped away. This served to drive the reaction to completion. When the carbon monoxide evolution ceased, the reaction was considered complete. The volatile products were passed through -78, -100, and $-196°$ traps. The monoborane(3) complex was retained at $-100°$. A 2.0-mmol sample of pure $F_4P_2 \cdot BH_3$ was then combined with 3.0 mmol of borane carbonyl in a 300-ml flask and closed off from the vacuum line. The flask was then warmed to $-45°$ for 1 min and then cooled to $-196°$, and the evolved carbon monoxide was pumped away. The warming–cooling cycle was repeated until no further carbon monoxide was evolved. The volatile products were passed through -78, -100, and $-196°$ traps. The desired product, $F_4P_2 \cdot 2BH_3$, was retained at $-78°$ in 60% yield based on the amount of $F_4P_2 \cdot BH_3$ used.

The mass spectrum of $F_4P_2 \cdot 2BH_3$ showed a parent peak, $F_4P_2 \cdot 2BH_3^+$ 166 (0.5), and the principal fragments: $F_4P_2 \cdot BH_3^+$, 152 (1.3); $F_4P_2^+$, 138 (11.5); $F_3P \cdot BH_3^+$, 102 (11.4); F_3P^+, 88 (9.4); F_2P^+, 69 (100); and FP^+, 50 (25.6), with the indicated mass numbers and (relative intensities). The overall pattern was consistent with the assigned formula. Infrared absorptions were observed: 2440 (ν_{BH}) (m); 2410 (ν_{BH}) (m, br); 1095 (δ_{BH_3}) (w, br); 1035 (δ_{BH_3}) (m, br); 930 (?) (sh); 915 (ν_{PF}) (vvs); 885 (ν_{PF}) (s); 860 (impurity); 845 (impurity); 660 (?) (m); and 585 (ν_{PB}) (w). (The symbols used above are defined as follows: ν, stretch; δ, deformation.)

Acknowledgments.—We gratefully acknowledge the support of the National Science Foundation and the National Aeronautics and Space Administration who supported a traineeship at the University of Michigan for R. T. P., 1966–1969.

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(4) H. L. Hodges and R. W. Rudolph, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

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(6) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **59**, 780 (1937).

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Studies on Interactions of Isocyanides with Transition Metal Complexes. VIII.[1] Reactions of Alkyl Isocyanide with Dicarbonyl-π-cyclopentadienylalkyliron

BY YASUHIRO YAMAMOTO* AND HIROSHI YAMAZAKI

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Recently we have reported that the treatment of *tert*-butyl and cyclohexyl isocyanides with tricarbonyl-π-cyclopentadienylmethylmolybdenum undergoes readily a carbonyl insertion, affording the corresponding acyl complexes,[2] and that the reactions of cyclohexyl isocyanide with benzyl derivatives take place by an isocyanide insertion to give the iminoacyl complexes.[3] Of particular interest is the fact that only

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(1) Part VII: Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jap.*, **44**, 1873 (1971).

(2) Y. Yamamoto and H. Yamazaki, *ibid.*, **43**, 143 (1970).

(3) Y. Yamamoto and H. Yamazaki, *J. Organometal. Chem.*, **24**, 717 (1970).

the benzyl group migrates ultimately to the entering cyclohexyl isocyanide rather than to a coordinated carbonyl ligand.

It is well-known that dicarbonyl-π-cyclopentadienylalkyliron reacts with carbon monoxide[4] and phosphine[5,6] to give acyl derivatives.

Recently it has been established by Treichel and Stenson that the treatment of cationic π-cyclopentadienyliron isocyanide complexes with pentafluorophenyllithium gave an imino complex.[7]

We studied the direct reactions of isocyanides with dicarbonyl-π-cyclopentadienylalkyliron in order to compare their reactions with those of alkylmolybdenum.

Results and Discussion

No reaction of dicarbonyl-π-cyclopentadienylmethyliron with cyclohexyl isocyanide in THF occurred at room temperature. However, the treatment in refluxing THF for 20 hr gave yellow crystals, identified as π-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_3$. The complex was soluble in most organic solvents and was stable to air in the solid state. The infrared spectrum showed three sharp bands at 2142, 1946, and 1632 cm^{-1}; the first band was assignable to the coordinated isocyanide group, the second to the coordinated carbonyl, and the last to the acyl carbonyl. The proton nmr spectrum in $CDCl_3$ showed two broad signals at τ 8.3 and 6.2 due to the cyclohexyl protons and to the α proton of the cyclohexyl group, respectively, and two sharp singlets at τ 7.50 and 5.37 attributable to the methyl and cyclopentadienyl groups.

When *tert*-butyl isocyanide was treated with methyliron derivative under reflux for 12 hr, the similar carbonyl insertion occurred, affording the corresponding acyl complex.

$$\pi\text{-}C_5H_5Fe(CO)_2R^1 + R^2NC \longrightarrow \pi\text{-}C_5H_5Fe(CO)(CNR^2)COR^1$$

However, the reaction of benzyliron complex with *tert*-butyl isocyanide gave π-$C_5H_5Fe(CO)(CNC(CH_3)_3)CH_2Ph$. The attempt to resolve the route was carried out at present. However, this reaction results probably from an initial formation of the acyl complex, π-$C_5H_5Fe(CO)(CNC(CH_3)_3)COCH_2Ph$, accompanied by the decarbonylation of the acyl one.

The isocyanide ligand behaved as a Lewis base similar to carbon monoxide and phosphine in these reactions.

In the infrared spectra of the acyl complexes, the terminal and acyl carbonyl stretching frequencies increased in the order PPh_3, $(CH_3)_3CNC$, $C_6H_{11}NC$, CO, as shown in Table I. This order was consistent with that of the π-acceptor ability.[8]

The formation of the acyl complexes in the series of these reactions was analogous to that in the reactions of alkylmolybdenum derivatives with isocyanides. Accordingly, the isocyanide insertion may be expected to occur in the reaction of dicarbonyl-π-cyclopentadienylbenzyliron with cyclohexyl isocyanide.

Thus, the reaction in refluxing THF for 20 hr gave brown crystals, formulated as $C_5H_5Fe(CO)(CNC_6H_{11})_3CH_2Ph$ (**1**) on the basis of its elemental analysis and its cryoscopic molecular weight determination in C_6H_6. The complex **1** was soluble in hexane, benzene, and methylene chloride, and was very stable in the solid state.

TABLE I
THE CARBONYL STRETCHING FREQUENCIES (CM^{-1}) OF π-$C_5H_5Fe(CO)(L)COCH_3$

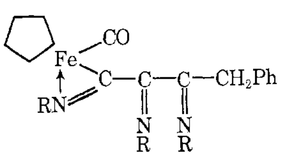
L	$\nu_{C\equiv O}$	$\nu_{C=O}$	Lit.
CO	2018, 1963	1655	*a*
$C_6H_{11}NC$	1940	1632	This paper
tert-BuNC	1933	1620	This paper
PPh_3	1920	1598	*b*

[a] R. B. King, *J. Amer. Chem. Soc.*, **85,** 1918 (1963). [b] J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, **5,** 890 (1966).

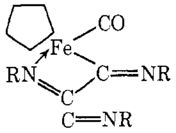
The infrared spectrum showed five characteristic bands, at 1892, 1880, 1606, 1560, and 1503 cm^{-1}. It is well-known that the C–N stretching frequencies of the coordinated isocyanide appear higher than 2100 cm^{-1}. Thus, two peaks at 1892 and 1880 cm^{-1} were attributable to the terminal carbonyl groups and the other three bands were assignable to carbon–nitrogen double bonds, suggesting the multiple insertion of isocyanide into a benzyl–iron σ bond.

The proton nmr spectrum in $CDCl_3$ showed three broad signals at τ 7.4 (1 H), 6.6 (1 H), and 5.7 (1 H) assignable to each α proton[9] of three cyclohexyl groups, and a singlet at τ 5.50 due to the cyclopentadienyl group in addition to three cyclohexyl groups (τ 8.4, 30 H) and a phenyl (τ 2.8, 5 H). Furthermore, it should be noted that the benzylic methylene protons consisted of two relatively broad resonances of equal intensity centered at τ 3.27 separated by 10 Hz, suggesting the magnetic nonequivalence of methylene protons.[10]

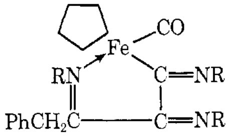
Three possible structures may be considered from the spectroscopic studies and the electronic configuration of iron



a



b



c

It seems reasonable, at present, to assume that the complex **1** has the structure **c** containing a five-membered chelate ring complexed to metal through the lone pair electrons, based on the presence of the similar che-

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[4] T. H. Coffield, J. Kozikowski, and R. D. Closson, *Proc. Int. Conf. Coord. Chem., 3rd, 1959*, 126 (1959).

[5] R. B. Bibler and A. Wojcicki, *Inorg. Chem.*, **5**, 889 (1966).

[6] P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *ibid.*, **5**, 1177 (1966).

[7] P. M. Treichel and J. P. Stenson, *ibid.*, **8**, 2563 (1969).

[8] W. D. Horrocks, Jr., and R. C. Taylor, *ibid.*, **2**, 723 (1963).

[9] The proton magnetic resonance in the lowest field can be considered to be the α proton of the neighboring cyclohexyl group bonded to the terminal imino nitrogen, because of deshielding arising from the coordination of an imino nitrogen to metal.

[10] The intensity of the benzylic methylene protons appeared to be smaller than the normal value (*ca.* 1.2 H), but the mass spectrum was in complete agreement with the proposed composition. The proton magnetic resonances of methylene group in this case generally display AB-type spectra. Appearance of only two central peaks of the AB quartet may obscure the two outer peaks for a large $J_{AB}/\delta_B - \delta_A$ value and broadness of the peaks.

TABLE II

CHARACTERIZATION OF TRIS-IMINO COMPLEXES, π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})_3R]$

	R	Anal % C Calcd	Anal % C Found	Anal % H Calcd	Anal % H Found	Anal % N Calcd	Anal % N Found	Ir, cm^{-1} [a] $\nu_{C\equiv O}$	Ir, cm^{-1} [a] $\nu_{=CN}$	Nmr (τ) in $CDCl_3$[b]
(1)	$CH_2C_6H_5$	71.95	71.73	7.99	7.68	7.40	7.44	1893	1605	7.9–9.5 (b, C_6H_{10}), 7.2–7.58 (b, C_6H)
								1880	1562	6.46–6.8 (b, C_6H), 5.6–5.9 (b, C_6H),
									1503	5.50 (s, C_5H_5), 3.27[c] (d, CH_2), 2.5–2.97 (c, C_6H_5)
(2)	$CH_2C_6H_4Cl$	67.83	68.30	7.37	7.46	6.98	6.93	1899	1605	7.85–9.45 (b, C_6H_{10}), 7.1–7.65 (b, C_6H)
									1574	6.35–6.85 (b, C_6H), 5.6–5.9 (b, C_6H)
									1506	5.64 (s, C_5H_5), 3.38[c] (d, CH_2), 2.78[d] (q, C_6H_4)

[a] KBr method. [b] b = broad signal. c = complex signal. s = singlet. d = doublet. q = quartet. [c] Only two central peaks of AB quartet, separated by 10 Hz, were observed. This shows the central value of doublet. [d] AB type, J_{AB} = 8 Hz, δ_{AB} 29.7 Hz.

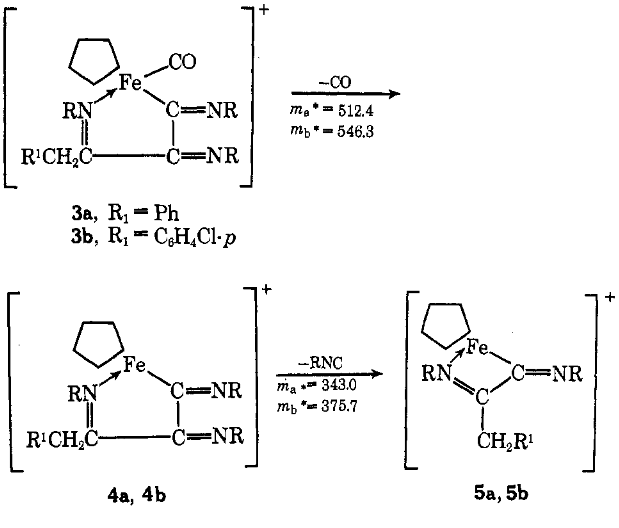
late complexes of palladium[11] and nickel[12] and the isolation of only the triple insertion product in this reaction, and furthermore the fact that the stability of the five-membered chelate structure may be generally considered to be larger than that of the three- or four-membered one.

A similar triple insertion complex π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})_3(CH_2C_6H_4Cl\text{-}p)]$ (2) was isolated from the reaction of cyclohexyl isocyanide with *p*-chlorobenzyliron derivative in refluxing THF for 15 hr.

In all the attempts to isolate the mono- or bis-imino complex which might be considered as an intermediate species, the reaction of dicarbonyl-π-cyclopentadienyl-*p*-chlorobenzyliron with cyclohexyl isocyanide in a 1:1 or 1:2 molar ratio in THF was carried out at 50°. The only isolable product was the tris-imino one (2) in addition to recovery of starting materials.

The mass spectra of the tris-imino derivatives (**1** and **2**) exhibited metastable ions to permit elucidation of part of the fragmentation scheme. It might be depicted as in Scheme I.

SCHEME I



In the mass spectrum of **1**, the initial loss of carbonyl group from the parent ion **3a** (*m/e* 567, relative intensity 14.4) occurred to give the ion $[C_5H_5Fe[(C{=}NC_6H_{11})_3(CH_2Ph)]]^+$ (**4a**) (*m/e* 539, 9.6) and then this ion loses cyclohexyl isocyanide to give the ion $[C_5H_5Fe[(C{=}NC_6H_{11})_2(CH_2Ph)]]^+$ (**5a**) (*m/e* 430, 100) in addition to unidentified peaks (*m/e* 438, 20.8, and *m/e* 351, 16).

Analogous behavior was also observed in complex (2). The spectrum exhibited the successive losses of CO and $C_6H_{11}NC$ from the parent ion **3b**, $[C_5H_5Fe(CO)[(C{=}NC_6H_{11})_3(CH_2C_6H_4Cl\text{-}p)]]^+$, (*m/e* 601).

It has been known that a transfer of the inserted isocyanide to the coordinated one, accompanied by an elimination of the coordinated carbonyl, took place, affording π-$C_5H_5Fe(CNCH_3)_2C_6F_5$ when π-$C_5H_5Fe(CO)(CNCH_3)[C(C_6F_5){=}NCH_3]$ was treated in refluxing THF for 18 hr.[5]

On the other hand, this is the first example of elimination of isocyanide from the imino complexes in the mass spectrometer.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. All the melting points were uncorrected: they were measured by a micro-melting-point apparatus, Yanagimoto Model MP-S2. Infrared spectra were obtained on a Perkin-Elmer 521 spectrometer. Proton nmr spectra were recorded on JEOL C-60 and Varian HA-100B spectrometers and the chemical shifts were measured relative to internal tetramethylsilane. The mass spectra were measured on a Niphondenshi Type JPS-1S mass spectrometer with direct-inlet system. The molecular weights were determined by the vapor pressure osmometer (Mechrolab 501).

Isocyanides were prepared in a manner similar to that described by Ugi and Meyer.[13] Dicarbonyl-π-cyclopentadienylmethyliron was prepared by a literature method.[14]

Preparation of Dicarbonyl-π-cyclopentadienyl-*p*-chlorobenzyliron.—π-$C_5H_5Fe(CO)_2CH_2C_6H_4Cl\text{-}p$ (1.8 g, 59%; mp 65.5–67.5° dec) was prepared by the reaction of $Na[\pi\text{-}C_5H_5Fe(CO)_2]$ (1.95 g, 1.01 mmol) and *p*-$ClC_6H_4CH_2Cl$ (3.5 g). *Anal.* Calcd for $C_{14}H_{11}O_2ClFe$: C, 55.58; H, 3.80. Found: C, 55.73; H, 3.80.

Reaction of Dicarbonyl-π-cyclopentadienylmethyliron with *tert*-Butyl Isocyanide.—π-$C_5H_5Fe(CO)_2CH_3$ (0.35 g, 1.82 mmol) was treated with *tert*-butyl isocyanide (0.6 g, 7.22 mmol) in refluxing THF. After 12 hr, the solvent was evaporated almost to dryness under reduced pressure and the residue was chromatographed on alumina, using benzene–hexane as eluent. Three bands (yellow, orange yellow, and dark violet) were observed and collected. The first band was identified as starting methyliron compound (0.03 g), the second one as π-$C_5H_5Fe(CO)$(*tert*-BuNC)$COCH_3$ (0.25 g, 50%; mp 58–59° dec), and the last one as $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.05 g). *Anal.* Calcd for $C_{13}H_{17}NO_2Fe$: C, 56.75; H, 6.23; N, 5.09. Found: C, 56.32; H, 6.37; N, 5.09.

The proton mmr spectrum in $CDCl_3$ consisted of three singlets at τ 5.35 (C_5H_5), 7.52 (CH_3CO), and 8.55 ($(CH_3)_3$).

Reaction of Dicarbonyl-π-cyclopentadienylmethyliron with Cyclohexyl Isocyanide.—By the procedures similar to those described above, π-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_3$ (0.59 g, 45%; mp 48–50° dec) was obtained from the reaction of π-$C_5H_5Fe(CO)_2CH_3$ (0.87 g, 4.5 mmol) with cyclohexyl isocyanide (1.1 g, 10 mmol) in benzene–THF (10 ml:10 ml) at 80° for 17 hr. *Anal.* Calcd for $C_{15}H_{19}NO_2Fe$: C, 59.82; H, 6.36; N, 4.65. Found: C, 59.77; H, 6.21; N, 4.60.

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(12) S. Otsuka, A. Nakamura, and T. Yoshida, *J. Amer. Chem. Soc.*, **91**, 7196 (1969).

(13) I. Ugi and R. Meyer, *Chem. Ber.*, **93**, 239 (1960).

(14) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, Inc., New York, N. Y., 1965, p 151.

The proton nmr spectrum in $CDCl_3$ consisted of two singlets at τ 5.37 (C_5H_5) and 5.50 (CH_3CO), and two broad signals at τ 7.8–8.85 (C_6H_{10}) and 6.0–6.4 (C_6H).

Reaction of Dicarbonyl-π-cyclopentadienylbenzyliron with *tert*-Butyl Isocyanide.—By the procedures similar to those described above, π-$C_5H_5Fe(CO)(CNC(CH_3)_3)CH_2Ph$ (0.43 g, 39%; mp 55–57° dec) was prepared from the treatment of π-$C_5H_5Fe(CO)_2$-$CH_2C_6H_5$ (0.95 g, 3.6 mmol) with cyclohexyl isocyanide (0.4 g, 4.8 mmol) in refluxing THF for 12 hr. *Anal.* Calcd for $C_{18}H_{21}$-NOFe: C, 66.89; H, 6.55; N, 4.33. Found: C, 66.57; H, H, 6.41; N, 4.16.

Reaction of Dicarbonyl-π-cyclopentadienylbenzyliron with Cyclohexyl Isocyanide in a 1:4 Molar Ratio.—π-$C_5H_5Fe(CO)_2$-CH_2Ph (0.6 g, 2.24 mmol) was treated with cyclohexyl isocyanide (0.98 g, 9.0 mmol) in refluxing THF for 20 hr. The solvent was removed almost to dryness under reduced pressure. The residue was chromatographed on alumina, using hexane–benzene, benzene, and benzene–THF as eluents. The yellow hexane–benzene layer gave unconverted starting material (0.05 g), the benzene one gave $[\pi$-$C_5H_5Fe(CO)_2]$ (0.03 g), and the reddish-brown layer gave π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})_3(CH_2Ph)]$ (0.64 g, 51%).

Reaction of Dicarbonyl-π-cyclopentadienyl-*p*-chlorobenzyliron with Cyclohexyl Isocyanide in a 1:1 Molar Ratio.—π-C_5H_5Fe-$(CO)_2CH_2C_6H_4Cl$-*p* (0.52 g, 1.72 mmol) and cyclohexyl isocyanide (0.22 g, 2.0 mmol) in THF (2 ml) and benzene (3 ml) was charged in a sealed tube and kept in a water bath at 50° for 20 hr. By the procedures similar to those described above, π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})_3(CH_2C_6H_4Cl$-*p*$)]$ (0.057 g, 5.5%) was obtained.

Reaction of Dicarbonyl-π-cyclopentadienyl-*p*-chlorobenzyliron with Cyclohexyl Isocyanide in a 1:2 Molar Ratio.—π-C_5H_5Fe-$(CO)[(C{=}NC_6H_{11})_3(CH_2C_6H_4Cl$-*p*$)]$ (0.23 g, 22%) was obtained from the reaction of π-$C_5H_5Fe(CO)_2CH_2C_6H_4Cl$-*p* (0.52 g, 1.72 mmol) and cyclohexyl isocyanide (0.4 g, 3.68 mmol) in 2 ml of THF and 3 ml of benzene.

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Nitrogen-15 Chemical Shifts in Cobalt(III)–Pentaammine Complexes

BY JOHN W. LEHMAN[1] AND B. M. FUNG*

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Among diamagnetic transition metal complexes, cobalt(III) complexes have some unique features in their nuclear magnetic resonance (nmr) spectra. For example, the ^{59}Co chemical shifts are unusually large.[2–4] The ^{14}N shifts in the ligands are also quite appreciable.[5] In cobalt(III)–pentaammine complexes, $Co(NH_3)_5X^{n+}$, the trans amine protons have a chemical shift different from that of the cis amine protons,[6,7] a phenomenon which is not observed in rhodium(III) and iridium(III) pentaammine complexes.[8] The origin of the chemical shifts of ^{59}Co and the ligand nuclei is the presence of low-lying paramagnetic states in the cobalt(III) complexes.[2–5,8]

In view of the difference in the trans and cis amine protons in cobalt(III)–pentaammine complexes, one may expect that the trans and cis nitrogens would also have different chemical shifts. However, the ^{14}N resonance absorption is broad and the different absorption signals would be difficult to resolve. Cobalt(III) complexes with $^{15}NH_3$ as ligand can be prepared and the proton nmr shows clearly resolved ^{15}N coupling.[9] By irradiating at the ^{15}N resonance frequency and observing the proton spectrum, namely, performing $\{^{15}N\}$–^1H double resonance, it is possible to determine the ^{15}N chemical shift.

The proton nmr spectra of $[Co(^{15}NH_3)_5X]^{n+}$ complexes showed well-resolved sharp lines. The ^{15}N–H coupling constants are 70 ± 1 Hz for both cis and trans groups and do not vary with the trans ligand X. The ^{59}Co–H coupling did not show up in the spectra because of rapid ^{59}Co quadrupole relaxation. A typical spectrum is shown in Figure 1. In contrast to the pentaammine complexes, $[Co(^{15}NH_3)_6]^{3+}$ showed two broad proton peaks, because the quadrupole relaxation is slow in this highly symmetrical species and the ^{59}Co–H coupling is not completely averaged out. Consequently, the ^{15}N resonance frequencies obtained from the $\{^{15}N\}$–^1H double-resonance experiments were more accurate and reproducible for the pentaammine complexes than for the hexaammine complex. In the latter case, the result was taken from the average of a large number of data.

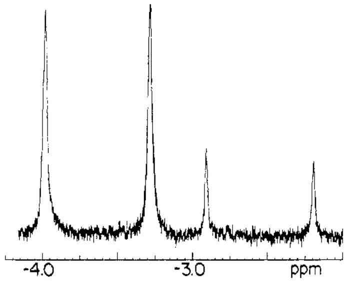

Figure 1.—Proton nmr spectrum of $[Co(^{15}NH_3)_5(H_2O)](ClO_4)_3$ in 20% H_2SO_4–D_2O solution at 100 MHz and 30°.

The ^{15}N and ^1H chemical shifts of the $[Co(^{15}NH_3)_5X]^{n+}$ complexes with respect to $[Co(^{15}NH_3)_6]^{3+}$ are listed in Table I. The proton shifts are slightly different from those listed in ref 8 because of the difference in the solvent composition.

TABLE I

CHEMICAL SHIFTS (PPM) OF COBALT(III)–PENTAAMMINE COMPLEXES FROM HEXAAMMINECOBALT(III) IN SOLUTIONS OF 20% H_2SO_4 IN D_2O

	^{15}N		^1H	
	Cis	Trans	Cis	Trans
$[Co(^{15}NH_3)_5H_2O]^{3+}$	3.4	30.9	0.40	−0.69
$[Co(^{15}NH_3)_5NO_3]^{2+}$	2.8	30.4	0.41	−0.79
$[Co(^{15}NH_3)_5HSO_4]^{2+}$	3.3	31.0	0.32	−0.77
$[Co(^{15}NH_3)_5Cl]^{2+}$	3.2	18.0	0.01	−0.60
$[Co(^{15}NH_3)_5Br]^{2+}$	5.2	10.6	−0.06	−0.64

The data in Table I show that the ^{15}N chemical shifts for both the cis and the trans nitrogens in the pentaammine complexes are both upfield (lower in frequency) from the hexaammine complex, in contrast to the proton

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