761 and 689 cm$^{-1}$ in the recovered ligand and the residual product coupled with the nmr data support substitution of the pyridine ring at the 3 or 6 position in the polymeric organic portion of the residue.

The thermal decomposition of bis-(N-alkylthiopicolinamidato)copper(II) complexes to produce cuprous compounds and protonated ligand appears to be a general reaction though not necessarily one of simple stoichiometry. That this disproportionation is facilitated by the presence of reactive protons on the carbon adjacent to the amide nitrogen is supported by the slow thermal degradation of bis-(N-*t*-butylthiopicolinamidato)copper(II) and the reported stability of the N-phenyl copper(II) chelate.[4] Facile and specific removal of similarly situated protons has been noted for radical reactions with amines,[5] as well as in the reduction of cupric chloride by amines.[6] The particular reactivity of benzylic protons is demonstrated by the reported conversion of toluene to bibenzyl in the presence of cupric chloride.[7] The loss of aromatic protons in reactions involving cupric compounds has recently been reviewed.[8] The present decomposition can also be compared with the thermal decompositions of copper acetylacetonate[9] and copper benzoate.[10] In these examples a principal degradation product is the protonated ligand. In close analogy with the present work cuprous benzoate and aromatic substituted products were reported in the thermal degradation of copper benzoate.[10] In the present systems isolation of the cuprous chelate may be further facilitated by the $\pi$-electron acceptor and the multiple coordination characteristics of the sulfur atom.

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CONTRIBUTION FROM THE
OLIN MATHIESON CHEMICAL CORPORATION,
CHEMICALS DIVISION, NEW HAVEN, CONNECTICUT

## Bis(arylamino)tetrachlorophosphonitriles and Bis(arylamino)tetrakis(polyfluoroalkoxy)phosphonitriles[1]

BY HENRY LEDERLE, GERHARD OTTMANN,
AND EHRENFRIED KOBER

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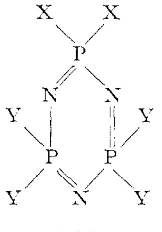
Although arylamino-disubstituted tetrameric phosphonitrilic chlorides, $P_4N_4Cl_6(NHaryl)_2$, have been described,[2] previous attempts to synthesize arylamino-disubstituted trimeric phosphonitrilic chlorides, $P_3N_3Cl_4(NHaryl)_2$, have met with failure.[3] We now wish to report that we have synthesized 2,2-bis(anilino)-4,4,6,6-tetrachlorophosphonitrile (I), mp 207.5–208.5°, in 30% yield from $(PNCl_2)_3$ and 2 moles of aniline in presence of triethylamine and in toluene as solvent. Because of its low solubility in toluene, relative to the other components of the reaction mixture, compound I precipitates together with triethylamine hydrochloride, from which it is separated by extraction with boiling toluene. Phosphorus-31 nuclear resonance spectroscopy confirms structure I. On irradiation of $^1H$ at 47.6 MHz the $^{31}P$ spectrum appears as an $AB_2$ spectrum with a coupling constant of 48 Hz. The doublet of relative intensity 2 at 20.4 ppm is indicative of a phosphorus atom bonded to two chlorine atoms. The triplet of unit relative intensity at 2.3 ppm is consistent with a symmetrical arrangement of the attributed phosphorus atom between two of the other type.



I–V

I: X = $C_6H_5NH$
Y = Cl

II: X = $C_6H_5NH$
Y = $CF_3CH_2O$

III: X = $C_6H_5NH$
Y = $CHF_2CF_2CH_2O$

IV: X = *m*-$ClC_6H_4NH$
Y = Cl

V: X = *m*-$ClC_6H_4NH$
Y = $CF_3CH_2O$

Structure I confirms a geminal substitution pattern for the replacement of the chlorine atoms of $(PNCl_2)_3$ by aromatic amino groups.[3] The isolation of compound I gives some support to a possible structure of the transition state of this reaction suggested on the basis of kinetic measurements.[4] In this connection, it should be noted that substitution of two chlorine atoms by anilino groups in the tetrameric series apparently does not proceed by a geminal pattern but yields 2,6-bis(anilino)-2,4,4,6,8,8-hexachlorophosphonitrile.[2]

Reactions of compound I with sodium trifluoroethoxide and sodium tetrafluoropropoxide afforded 2,2-bis(anilino)-4,4,6,6-tetrakis(2,2,2-trifluoroethoxy)phosphonitrile (II) and 2,2-bis(anilino)-4,4,6,6-tetrakis(2,2,3,3-tetrafluoropropoxy)phosphonitrile (III), respectively. Confirmation of these structures by nmr spectroscopy was sought in case of II. The $^1H$ spectrum, which shows an aromatic resonance of relative intensity 5 centered at 7.11 ppm, an N–H resonance of relative intensity 1 at 5.20 ppm, and a third multiplet of relative intensity 4 at 4.14 ppm, indicates a 2:1 ratio of fluoroalkoxy groups to anilino groups. The decoupled $^{31}P$ spectrum[5] shows an $AB_2$ pattern

(1) This work was supported by the Bureau of Ships, U. S. Navy, under Contract NObs 90092.

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with the "A" portion at −6.37 ppm and the "B" portion at −16.38 ppm relative to external phosphoric acid. The coupling constant is 72 Hz. Using normal heteronuclear decoupling procedures, the frequency required for optimum decoupling of the "A" portion of the spectrum is 12.4 ppm greater than that required for optimum decoupling of the "B" portion. This indicates that the center of resonance of the protons coupled to "A" is 2.4 ppm to lower field than that of the protons coupled to "B."

2,2-Bis(*m*-chloroanilino)-4,4,6,6-tetrachlorophosphonitrile (IV) and bis(*m*-toluidino)tetrachlorophosphonitrile (VI) from $(PNCl_2)_3$ and 2 moles of *m*-chloroaniline and *m*-toluidine, respectively, did not precipitate together with triethylamine hydrochloride as was the case for I. No attempts were made to isolate the pure compounds from the complex reaction mixture. The presence of substantial amounts of IV and VI in the reaction mixture, however, was indicated by reactions of the crude mixtures with sodium 2,2,2-trifluoroethoxide to give pure 2,2-bis(*m*-chloroanilino)-4,4,6,6-tetrakis(2,2,2-trifluoroethoxy)phosphonitrile (V) and bis(*m*-toluidino)tetrakis(2,2,2-trifluoroethoxy)phosphonitrile (VII) in yields of 15 and 35%, respectively.

Structure V is verified by the results of nmr spectroscopy (Table I). The proton-irradiated $^{31}P$ spectrum of V is of the $AB_2$ type and closely resembles that of II. The frequency for optimum decoupling of the "A" portion of the spectrum is 10.3 ppm greater than that required for optimum decoupling of the "B" portion. The center of resonance of the protons coupled to "A" is about 1.0 ppm to lower field than that of the protons coupled to "B."

From the established structure V and in analogy to the conversion of I to II, one may conclude that the geminal substitution pattern established for the disubstitution of trimeric phosphonitrilic chloride by aniline also exists in case of *m*-chloroaniline and, probably, for other aromatic primary amines such as *m*-toluidine.

## Experimental Section

Melting points were determined on a Fisher-Johns block. The $^{31}P$ spectra were obtained at 19.3 MHz with a Varian Type HR nmr spectrometer. Irradiation of hydrogen was accomplished with an NMR Specialties HD-60 spin decoupler.[5] All chemical shifts were measured by the side-band technique relative to external 85% phosphoric acid.

**2,2-Bis(anilino)-4,4,6,6-tetrachlorophosphonitrile** (I).—To a stirred solution of 173.8 g (0.5 mole) of $(PNCl_2)_3$ in 800 ml of dry toluene was added a mixture of 100.6 g (1.08 moles) of aniline and 101.2 g (1.0 mole) of triethylamine over a 40-min period at a temperature of 80°. The mixture was then refluxed for 3 hr. After cooling, the precipitate was removed by suction filtration and extracted twice with 250 ml each of boiling toluene. The toluene solutions were combined and concentrated to one-third of its original volume. Upon cooling, compound I precipitated in the form of white crystals, mp 206–208° (68.0 g, 30% yield). Recrystallization from petroleum ether (bp 65–110°) raised the melting point to 207.5–208.5°. *Anal.* Calcd for $C_{12}H_{12}Cl_4N_5P_3$: Cl, 30.78; N, 15.18; P, 20.16. Found: Cl, 30.50; N, 15.20; P, 19.54.

TABLE I

$^1H$ AND $^{31}P$ CHEMICAL SHIFTS OF 2,2-BIS(*m*-CHLOROANILINO)-4,4,6,6-TETRAKIS(2,2,2-TRIFLUOROETHOXY)PHOSPHONITRILE (V) AND BIS(*m*-TOLUIDINO)TETRAKIS(2,2,2-TRIFLUOROETHOXY)PHOSPHONITRILE (VII) IN PPM

| | V | | VII[a] | |
|---|---|---|---|---|
| Proton spectra | Ppm | Rel intens | Ppm | Rel intens |
| $^1H_{C_6H_4}$ | 7.02 | 4 | 6.89 | 4 |
| $^1H_{N-H}$ | 5.41 | 1 | 5.29 | 1 |
| $^1H_{CH_2}$ | 4.24 | 4 | 4.08 | 4 |
| $^1H_{CH_3}$ | . . . | . . . | 2.19 | 3 |
| Phosphorus spectra | | | | |
| $^{31}P_{\text{"A"}}$ | −6.94 | . . . | . . . | . . . |
| $^{31}P_{\text{"B"}}$ | −16.2 | . . . | . . . | . . . |

[a] A decoupled $^{31}P$ spectrum is not available.

**2,2-Bis(anilino)-4,4,6,6-tetrakis(2,2,2-trifluoroethoxy)phosphonitrile (II).**—To a stirred slurry of 36.5 g of sodium trifluoroethoxide (freshly prepared from trifluoroethanol and sodium hydride in ether) in 300 ml of dry toluene was added a solution of 30.0 g of I in 300 ml of dry toluene over a 30-min period. The reaction mixture was refluxed for 20 hr and then cooled and extracted several times with water. The dried organic layer was freed from solvent and the residue (51.0 g) was distilled *in vacuo*. The fraction distilling between 187 and 193° at 0.1–0.3 mm solidified upon standing. Recrystallization from petroleum ether (bp 65–110°) afforded 19.9 g (42.7%) of II, mp 100–101°. *Anal.* Calcd for $C_{20}H_{20}F_{12}N_5O_4P_3$: C, 33.58; H, 2.82; N, 9.79; P, 12.99. Found: C, 33.89; H, 2.89; N, 10.16; P, 13.04.

**2,2-Bis(anilino)-4,4,6,6-tetrakis(2,2,3,3-tetrafluoropropoxy)-phosphonitrile (III).**—This compound was prepared from 153.6 g of I and 256.0 g of sodium 2,2,3,3-tetrafluoropropoxide by the procedure used for the preparation of compound II. Vacuum distillation of the crude reaction product (224.0 g, 80% yield) was accompanied by extensive polymerization and afforded 64.9 g of crude III, bp 209–214° (0.2–0.7 mm), which, after recrystallization from petroleum ether (bp 65–110°), melted at 98–100°. *Anal.* Calcd for $C_{24}H_{24}F_{16}N_5O_4P_3$: C, 34.17; H, 2.87; N, 8.30; P, 11.02. Found: C, 33.88; H, 2.97; N, 8.37; P, 11.35.

**2,2-Bis(*m*-chloroanilino)-4,4,6,6-tetrakis(2,2,2-trifluoroethoxy)phosphonitrile (V).**—To a stirred solution of 86.6 g (0.25 mole) of $(PNCl_2)_3$ in 1000 ml of toluene at 80° was added a mixture of 63.8 g (0.5 mole) of *m*-chloroaniline and 50.5 g (0.5 mole) of triethylamine over a period of 1 hr. The mixture was refluxed for 8 hr and then filtered from 70.0 g of $(C_2H_5)_3NHCl$. The filtrate was concentrated to a volume of 500 ml and then added to a vigorously stirred and boiling suspension of 146.6 g (1.2 moles) of sodium trifluoroethoxide in 750 ml of toluene. After a reflux period of 20 hr, the mixture was cooled and then extracted several times with water. The organic phase was stripped from the solvent to yield 155.5 g (79.3%) of a crude, oily reaction product which was distilled to give 59.0 g of product, bp 172–185° (0.2–0.9 mm). Most of the distillate solidified upon standing, liquid contaminants were removed by suction filtration, and the filter cake was recrystallized from petroleum ether (bp 65–110°) to yield 30 g (15.3%) of VI, mp 102–104°. *Anal.* Calcd for $C_{20}H_{18}Cl_2F_{12}N_5O_4P_3$: P, 11.84; N, 8.93; Cl, 9.05. Found: P, 11.61; N, 8.99; Cl, 9.03.

**Bis(*m*-toluidino)tetrakis(2,2,2-trifluoroethoxy)phosphonitrile (VII).**—Amounts of 86.6 g (0.25 mole) of $(PNCl_2)_3$, 1000 ml of toluene, 53.5 g (0.5 mole) of *m*-toluidine, 50.5 g (0.5 mole) of triethylamine, and 146.6 g (1.2 moles) of sodium trifluoroethoxide were allowed to react as described for the preparation of V to give 140 g (75.5%) of crude reaction product. Vacuum distillation afforded 64.3 g (34.6% yield) of VII, bp 186–191° (0.08–0.1 mm), which, after one recrystallization from petroleum ether (bp 65–110°), melted at 102.5–104°. *Anal.* Calcd

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(5) The total irradiation of all three types of hydrogen was done by a technique to be discussed in detail in a forthcoming paper by G. D. Vickers and M. J. Nadel.

for $C_{22}H_{24}F_{12}N_5O_4P_3$: C, 35.55; H, 3.25; N, 9.42; P, 12.50. Found: C, 35.75; H, 3.25; N, 9.49; P, 12.10.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF DELAWARE, NEWARK, DELAWARE

## Transmission of Electronic Effects in Metallocenes

BY S. A. BUTTER AND H. C. BEACHELL[1]

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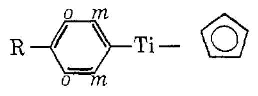
In a recent paper we have shown that nmr chemical shifts of phenyl and cyclopentadienyl protons in aryltitanocenes could be correlated with Hammett $\sigma_p$ values.[2] The slope or $\rho$ value in the correlation of average *ortho* and *meta* proton shifts *vs.* $\sigma_p$ was equal to $-0.75$ unit. Our analysis of the data of other investigators for chemical shifts in *para*-substituted benzenes revealed similar $\rho$ values of 0.70,[3] 0.75,[4] and 0.76.[5] Although the $\rho$ values for the substituent effect of R on proton shielding values cannot be compared with the effect of R on ionization of *para*-substituted benzoic acids (where by definition $\rho = 1$) since they are of a different nature and origin, it is evident that the susceptibility of the shielding values to the substituent effect of R parallels the effect of R in the benzoic acid series.

It is of interest to compare the transmission of the substituent effect through the phenyl ring to the unsubstituted cyclopentadienyl ring in the above-mentioned titanocene system schematically represented as

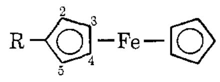


I

and the $\rho$ values may be used for this purpose. The $\rho$ ratio obtained from the slopes of the regression lines for (1) unsubstituted cyclopentadienyl proton shifts *vs.* $\sigma_p$ and (2) average *ortho* and *meta* phenyl proton shifts *vs.* $\sigma_p$ is 0.16/0.75 or 0.21. This value infers that 21% of the substituent effect of R is transmitted through the titanocene bonding system and relayed to the $C_5H_5$ protons.

Since recent studies have confirmed the presence of interannular electronic effects in the ferrocene system, it seemed desirable to look for indications of the transmission of substituent effects by the nmr technique. Linear relationships have been reported between Hammett $\sigma$ constants and $pK_a$ values for substituted ferrocene carboxylic acids[6] and rate constants for esterification of these acids,[7] and in chronopotentiometric studies quarter-wave potentials have been correlated with Hammett $\sigma$ values.[8] Further indication of the transmission of the electronic effect was noted in the spectra of heteroannular ferrocene carboxylic acids in which carbonyl stretch frequencies were shifted as expected from a consideration of the electronic effect of the substituent group.[9]

We have observed correlations of nmr proton shifts with $\sigma_p$ constants in monosubstituted ferrocenes further confirming the transmission of electronic effects, and a quantitative estimate of the transmissivity of the substituent effect in the following system was noted.



II

The data in Table I were taken from work by Nagai, Hooz, and Benkeser[10] with the exception of benzoylferrocene which was examined by Mark and Rausch.[11] Since the latter compound was determined in deuteriochloroform while all others were in carbon tetrachloride, all shifts were converted to shielding values.[12] Figure 1 (line b) shows a plot of $\sigma_p$ *vs.* the shielding value for the substituent R at the substituted ring protons 2,5 and

TABLE I

$^1H$ CHEMICAL SHIFTS FOR MONOSUBSTITUTED FERROCENES[a]

| R | $\delta$ | $\delta_{3,4}$ | $\delta_{2,5}$ | $\sigma_p$[c] |
|---|---|---|---|---|
| $CH_3$ | 3.99 | 3.94 | 3.94 | −0.17 |
| $C_2H_5$ | 4.01 | 3.97 | 3.97 | −0.15 |
| $i$-$C_3H_7$ | 4.02 | 3.96 | 3.96 | −0.15 |
| $t$-$C_4H_9$ | 4.02 | 3.92 | 3.92 | −0.197 |
| H | 4.06 | 4.06 | 4.06 | 0 |
| $CH_3CO$ | 4.12 | 4.36 | 4.67 | +0.50 |
| $C_6H_5CO$[b] | 4.13 | 4.44 | 4.80 | +0.46 |
| $COOCH_3$ | 4.13 | 4.27 | 4.72 | +0.45 |

[a] All values are in ppm downfield from internal tetramethylsilane. Chemical shifts determined by Nagai, *et al.* (ref 10), at 60 Mc in $CCl_4$. $\delta_{Cp}$ is the chemical shift of the unsubstituted $C_5H_5$ ring. [b] From Mark and Rausch (ref 11); corrected for change of solvent ($CDCl_3$) by noting shifts for acetylferrocene determined in both $CDCl_3$ and $CCl_4$. [c] *para*-Substituent constants based on ionization of benzoic acids. From D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23,** 420 (1958).

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(1) To whom inquiries should be addressed.

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(12) For example, the chemical shift of ferrocene is 4.06 ppm while the substituted ring protons of methylferrocene are found at 3.94 ppm. The methyl group therefore shields the 2,5 and 3,4 protons by 0.12 ppm. Since the unsubstituted or Cp protons of methylferrocene are at 3.99 ppm, the methyl group shielding value for the unsubstituted ring protons is 0.07 ppm.