The resulting complex is nine-coordinate and possesses symmetry no higher than C_{2v} (Figure 9A). This structure exemplifies an appropriate match between a metal ion and the cavity size and charge density of a macrocyclic ligand.

Precise structural predictions about the remaining two metal-ligand complexes are more difficult to make, owing to the multiple species present in solution; however, a number of conclusions can be reached. The results for the binding of K22DA to Eu^{3+} indicate a 1:1 metal-ligand complex with one coordinated water molecule. This ligand, like EGTA, undergoes fluctional processes that result in incomplete binding of the macrocycle. These processes are temperature dependent, as marked changes are observed in the luminescence and NMR spectra with increasing temperature. The complex present at 20 °C appears to be a nine-coordinate species with all the ligating atoms of the macrocyclic ring and two carboxylate oxygens binding along with a single water molecule (Figure 9B). The fluctional processes observed for these ligand-metal complexes are indicative of a poor correlation between the macrocyclic cavity size and ligand charge density with regard to Eu^{3+} and Y^{3+} binding.

Finally, the complex formed by EGTA appears to be in an equilibrium process of wrapping and unwrapping, which places the Eu^{3+} ion in two distinct, but similar, chemical environments. However, these two species are in fast exchange on the Eu^{3+} luminescence ($^5D_0$) lifetime scale. This unwrapping process is also suggested by the NMR bond labilities, which demonstrate that the metal-nitrogen and metal-acetate oxygen bond lifetimes are short on the NMR time scale. These data suggest complete binding of each ligating atom of EGTA with an equilibrium process occurring, possibly between eight- and nine-coordinate species (Figure 9C).

The proposed structures of these complexes are in good agreement with the available X-ray crystallographic data. While no X-ray crystallographic data are available for the lanthanide complexes of these ligands, two relevant structures have recently been reported.[33,34] The first is the Ca^{2+} complex of EGTA.[33] These structural data indicate an eight-coordinate complex with all ligating atoms directly coordinating the Ca^{2+} ion. Three $[CaEGTA]^{2-}$ species exist in the crystal lattice with approximate dodecahedral geometry; however, they are bridged by Ca^{2+} counterions through the EGTA carboxylate arms, forming a polymeric structure. The inner coordination sphere of Ca^{2+} bound to EGTA is similar to the structure proposed here for the Eu^{3+} complex on the basis of NMR and luminescence data. The only difference between these structures is that the Eu^{3+} ion has extended its coordination number to nine by binding a water molecule. The second crystallographic study involves the structure of the Eu^{3+} complex of the 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane macrocycle,[34] which contains no carboxylate groups. Three distinct metal complexes exist in the crystal lattice, one being $[Eu(NO_3)_6]^{3-}$. The remaining two species differ in the way in which the macrocycle coordinates the metal ion. The first species has C_2 symmetry with the Eu-N and Eu-O distances being very similar, while the second complex is best described as elliptical with the Eu-N bond distances being much longer than the Eu-O distances. These structures are in excellent agreement with the NMR and luminescence data, which suggest an uncomfortable fit of this macrocycle to Eu^{3+}. The multiple species present for the Eu^{3+} and Y^{3+} complexes may be due to an equilibrium process involving metal-nitrogen bond breakage and subsequent re-formation.

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Addition of Phosphazenocuprates to Aldehydes and Ketones: A New Route to *gem*-Organo-Substituted Cyclotriphosphazenes

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Novel *gem*-alkyl(hydroxyalkyl)tetrachlorocyclotriphosphazenes (**2**), $(NPCl_2)_2NPR^1C(OH)R^2R^3$ (R^1 = CH_3, *i*-C_3H_7, *t*-C_4H_9; R^2 = H, CH_3; R^3 = CH_3, C_2H_5, C_6H_5, C_6H_4-*o*-NO_2, C_6H_4-*o*-OCH_3, cyclic C_4H_3O, $COOC_2H_5$, CH_2Cl, $CH{=}CHCH_3$, C_6H_4-*p*-$CH{=}CH_2$, η^5-C_5H_4-Fe-η^5-C_5H_5; R^2-R^3 = -$(CH_2)_5$-), have been synthesized in moderate to high yields via the nucleophilic addition of phosphazenocuprates, $[(NPCl_2)_2NPR^1]_2CuMgX{\cdot}(n\text{-}C_4H_9)_3P$, to aldehydes and ketones followed by acid hydrolysis. The proton-decoupled ^{31}P NMR spectra of compounds with $R^2 \neq R^3$ show patterns typical of AXY spin systems, allowing determination of coupling constants between PCl_2 groupings. A proof for the assignment of the spin system was obtained from proton-decoupled homonuclear ^{31}P shift-correlated 2-D NMR spectroscopy. A new structure for the phosphazenocuprate is proposed. In this structure copper is coordinated onto a phosphorus center, whereas magnesium is linked to a ring nitrogen.

Introduction

In the past decade the organic chemistry of phosphazenes has been greatly enlarged. Organophosphazenes are now being applied in medicinal chemistry,[1-3] organometallic chemistry,[4,5] and polymer chemistry.[6-10]

In the field of organometallic and hybrid organic-inorganic polyphosphazenes, the need arose for cyclophosphazenes, derived from the readily available $(NPCl_2)_3$ (**1**), bearing but one reactive

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functional side group. Further substitution of the remaining chlorine atoms then offers the opportunity of directing the solubility (in organic or aqueous media) and the hydrolytic and/or the thermal stability of the compounds.

In the 1970s the syntheses of such organocyclophosphazenes had mostly been accomplished by adding an alkoxide or an amine in stoichiometric quantities to the chlorocyclophosphazene. This led to more or less complicated reaction mixtures, necessitating elaborate workup procedures and thus low yields.

Now several regioselective routes have become available for the introduction of organofunctional side groups in **1**, involving P–O,[10,11] P–C,[12-15] and P–N[16] bond formation. One of the most versatile methods involves the reaction of copper(I)-assisted Grignard reagents with **1**,[12-15] leading to the formation of intermediate copper(I) cyclophosphazenes. These intermediates are then treated with an alcohol[12,13] to give *gem*-alkylhydrocyclotriphosphazenes or with alkyl halides[14,15] to give *gem*-alkylcyclotriphosphazenes. The formation of dialkyl derivatives is in fact an overall nucleophilic substitution of halide in the organic substrate with the cyclophosphazene being the nucleophile.

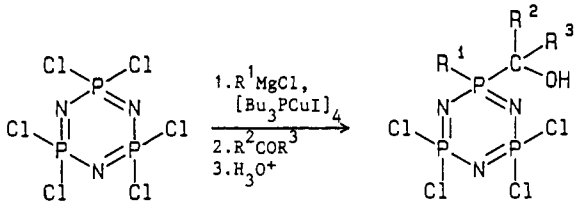
In this paper we describe the regioselective introduction of organofunctional side groups onto chlorocyclophosphazenes, involving the nucleophilic addition of copper(I) phosphazenes to aldehydes and ketones followed by acid hydrolysis to yield *gem*-alkyl(hydroxyalkyl)tetrachlorocyclotriphosphazenes (**2**).[17]

Moreover, a more detailed insight into the formation and the structure of the metallophosphazene intermediate was obtained from ^{31}P NMR measurements of the reaction intermediate, independently synthesized via deprotonation of a *gem*-alkylhydrocyclotriphosphazene.

Experimental Section

General Procedures and Reagents. All experiments were carried out under an atmosphere of dry oxygen-free nitrogen, applying gas-vacuum techniques in combination with Schlenk-type glassware. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone prior to use. All other solvents were dried and distilled according to conventional methods.[18] The Grignard reagents were prepared from the alkyl chlorides and magnesium in tetrahydrofuran according to standard procedures.[19] Polymer grade $(NPCl_2)_3$ was obtained from Shin Nisso Kako Co. and was used without further purification. $[(n\text{-}C_4H_9)_3PCuI]_4$ was synthesized from CuI and $(n\text{-}C_4H_9)_3P$.[20] *p*-Formylstyrene was synthesized according to the method of Wiley and Hobson.[21] $(NPCl_2)_2NP(H)\text{-}i\text{-}C_3H_7$ was synthesized by using the method described in ref 13. All other reagents were commercial grade and obtained from Janssen, Merck, or Aldrich. Benzaldehyde, substituted benzaldehydes, furfural, and acetaldehyde were distilled prior to use. ^1H NMR spectra were recorded on a Bruker WH90 spectrometer, operating at 90 MHz, using TMS as an internal reference. ^{31}P NMR spectra were recorded on a Nicolet NT200 (80.99 MHz) or a Varian VXR300 spectrometer (121.42 MHz), using $(NPCl_2)_3$ (19.9 ppm) in $CDCl_3$ as an external reference. ^{13}C NMR spectra were recorded on the Nicolet and Varian spectrometers, operating at 50.31 and 75.43 MHz, respectively ($CDCl_3$, 76.91 ppm, as internal reference). All spectrometers were operating in the Fourier transform mode using the ^2H resonance of the solvent as field-frequency lock. Chemical shifts (in ppm) are positive in the low-field direction. The proton-decoupled ^{31}P homonuclear shift correlated 2-D NMR spectrum was recorded on the Varian VXR300 instrument by using standard Varian microprograms. Mass spectra were obtained with an AEI MS9 mass spectrometer (A. Kiewiet, Department of Organic Chemistry, University of Groningen). IR spectra were recorded on a Pye-Unicam SP3-300 spectrophotometer. Elemental analyses were carried out at the Microanalytical Department of the University of Groningen under supervision of A. F. Hamminga.

Scheme I



Preparation of $(NPCl_2)_2NP\text{-}i\text{-}C_3H_7CH(OH)C_6H_5$. To a solution of 0.85 g (0.0025 mol) of $(NPCl_2)_3$ (**1**) and 0.50 g (0.00033 mol) of $[(n\text{-}C_4H_9)_3PCuI]_4$ in 25 mL of tetrahydrofuran was added dropwise at −78 °C 8.5 mL of a 1.2 M (0.010 mol) solution of $i\text{-}C_3H_7MgCl$ in tetrahydrofuran. The resulting mixture was stirred for 16 h at ambient temperature. Then 1.05 g (0.0100 mol) of benzaldehyde was added, and stirring was continued for 48 h. The solvent was removed, and 25 mL of a saturated aqueous ammonium chloride solution and 25 mL of diethyl ether were added. The organic layer was separated and the aqueous layer extracted twice with 25 mL of diethyl ether. The combined organic phases were dried with $MgSO_4$, and the solvent was removed. Flash chromatography (silica gel 230–400 mesh, column length 20 cm, internal diameter 3 cm, hexane/tetrahydrofuran (9:1) as eluant) and recrystallization from petroleum ether (bp 60–80 °C) yielded 0.70 g (0.0017 mol, 66%) of $(NPCl_2)_2NP\text{-}i\text{-}C_3H_7C(OH)HC_6H_5$ as a white solid.

All other products were prepared in essentially the same way; only the eluant in the chromatographic separation varied slightly. The products could be obtained in an analytically pure state by either a second recrystallization, a sublimation, or a distillation. Elemental analyses gave satisfactory results (supplementary material).

Synthesis of Phosphazenocuprate via Deprotonation. To a solution of 0.32 g (0.0010 mol) of $(NPCl_2)_2NP(H)\text{-}i\text{-}C_3H_7$ and 0.20 g (0.00013 mol) of $[(n\text{-}C_4H_9)_3PCuI]_4$ in 10 mL of tetrahydrofuran was added at −78 °C 1.1 mL of a 2.89 M (0.011 mol) solution of $i\text{-}C_3H_7MgCl$ in tetrahydrofuran. Stirring was continued for 16 h at room temperature. A proton-decoupled ^{31}P NMR spectrum of the reaction product was taken of a 3-mL sample from the resulting suspension.

Synthesis of $[NP(OPh)_2]_2NP\text{-}i\text{-}C_3H_7C(OH)HCH_3$ (3). To a stirred suspension of 1.67 g (0.070 mol) of NaH in 45 mL of tetrahydrofuran was added a solution of 5.99 g (0.0636 mol) of phenol in 45 mL of tetrahydrofuran. After decline of the first vigorous reaction, 50 mL of tetrahydrofuran was added and the mixture was heated to 50 °C. The hot solution was transferred through glass wool into a dropping funnel. The sodium phenoxide solution was added dropwise to a solution of 5.51 g (0.015 mol) of $(NPCl_2)_2NP\text{-}i\text{-}C_3H_7C(OH)HCH_3$ in 45 mL of tetrahydrofuran. After the mixture was stirred overnight, the solvent was removed in vacuo. The product was dissolved in diethyl ether, and the solution was washed twice with water. After the mixture was dried over $MgSO_4$, the solvent was removed and the product recrystallized from petroleum ether (bp 60–80 °C) to yield 7.26 g (0.012 mol, 80%) of $(NP(OPh)_2)_2NP\text{-}i\text{-}C_3H_7C(OH)HCH_3$ (**3**) as a white solid (mp 73–74 °C). Exact mass: calculated for $C_{29}H_{32}N_3O_5P_3$, 595.155; found, 595.154. ^1H NMR: δ 0.7–1.6 ppm (m, 11 H); δ 3.5–3.7 ppm (m, 1 H); δ 7.2–7.3 ppm (m, 20 H). ^{31}P NMR: $\delta(P(i\text{-}C_3H_7)C(OH)HCH_3)$ 45.8 ppm; $\delta(P(OPh)_2)$ 8.1 ppm; $^2J_{PP}$ = 16.3 Hz.

Results and Discussion

Synthesis. The metallophosphazenes were synthesized via the reaction of **1** with the appropriate Grignard reagent in the presence of $[(n\text{-}C_4H_9)_3PCuI]_4$.[13] Treatment of the copper(I) phosphazenes with an aldehyde or a ketone and subsequent acid hydrolysis yielded *gem*-alkyl(hydroxyalkyl)tetrachlorocyclotriphosphazenes (Scheme I), $(NPCl_2)_2NPR^1C(OH)R^2R^3$ (**2**) (R^1 = CH_3, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$; R^2 = H, CH_3; R^3 = CH_3, C_2H_5, C_6H_5, $C_6H_4\text{-}o\text{-}NO_2$, $C_6H_4\text{-}o\text{-}OCH_3$, cyclic C_4H_3O, $COOC_2H_5$, CH_2Cl, $CH{=}CHCH_3$, $C_6H_4\text{-}p\text{-}CH{=}CH_2$, $\eta^5\text{-}C_5H_4\text{–Fe–}\eta^5\text{-}C_5H_5$; R^2–R^3 = $-(CH_2)_5-$).

Products **2** were isolated in moderate to high yields (35–75%, Table I) as air- and moisture-stable compounds. In general, products **2** are crystalline solids, except for the compounds with $R^1 = R^2 = R^3 = CH_3$, with $R^1 = i\text{-}C_3H_7$ and $R^2 = R^3 = CH_3$, and with $R^1 = i\text{-}C_3H_7$, $R^2 = CH_3$, and $R^3 = C_2H_5$, which are colorless, distillable liquids.

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Table I. Data for the Compounds $(NPCl_2)_2NPR^1C(OH)R^2R^3$ (**2**)

R^1	R^2	R^3	$^{31}P\{^1H\}$ NMR data[a] δ_A	δ_X	δ_Y	J_{AX}	J_{AY}	J_{XY}	yield, %	$M^+(^{35}Cl)$ *m/e*	mp or bp, °C
CH_3	H	CH_3	39.3	19.3	18.7	*b*	*b*	36.2	63	*c*	53–55
CH_3	H	C_6H_5	37.1	19.0		*b*	*b*	*b*	42	*c*	101–104
CH_3	CH_3	CH_3	43.8	18.5			*b*		58	337	130/0.1 mmHg
i-C_3H_7	H	CH_3	48.8	19.7	19.1	9.5	12.4	34.0	70	365	109–111
i-C_3H_7	H	C_2H_5	47.7	19.4	19.1	8.4	12.4	33.9	70	*c*	103–103.5
i-C_3H_7	H	C_6H_5	47.2	19.3		*b*	*b*	32.6	66	425	135–137
i-C_3H_7	H	C_6H_4-*o*-NO_2	48.1	19.8	18.7	−0.4	12.6	33.4	75	470	131–134
i-C_3H_7	H	C_6H_4-*o*-OCH_3	48.2	19.2		*b*	*b*	*b*	45	455	107.5–110
i-C_3H_7	H	cyclic-C_4H_3O	44.5	19.8		*b*	*b*	*b*	54	415	126–127
i-C_3H_7	H	C_6H_4-*p*-$CH{=}CH_2$	46.8	19.6	19.3	10.9	11.7	32.9	66	451	114–115
i-C_3H_7	H	η^5-C_5H_4–Fe–η^5-C_5H_5	45.2	19.3		*b*	*b*	*b*	60	533	106–107.5
i-C_3H_7	CH_3	CH_3	50.3	18.8		13.1			70	377	120/0.1 mmHg
i-C_3H_7	CH_3	C_2H_5	51.0	18.6		*b*	*b*	*b*	70	*c*	120/0.1 mmHg
i-C_3H_7		$-(CH_2)_5-$	49.8	18.6		14.6			50	417	104–104.5
i-C_3H_7	CH_3	$COOC_2H_5$	46.1	19.2		*b*	*b*	*b*	35	435	93–94
t-C_4H_9	H	CH_3	50.0	19.5	18.1	10.2	14.4	32.4	41	377	108–108.5
t-C_4H_9	H	C_6H_5	49.0	19.5	18.0	12.6	14.9	31.4	52	429	142.5–143.5
t-C_4H_9	H	$CH{=}CHCH_3$	48.9	19.6	18.3	15.2	17.0	31.5	42	403	106–109
t-C_4H_9	CH_3	CH_2Cl	49.5	18.6		*b*	*b*	*b*	37	*c*	140–141.5

[a] Solvent $CDCl_3$, external reference $(NPCl_2)_3$, $\delta(^{31}P)$ = 19.9 ppm; chemical shifts in ppm, coupling constants in Hz. [b] Coupling not resolved. [c] M^+ not observed.

Scope and Limitations. It has been shown that alkyl-substituted copper(I) cyclophosphazenes can be formed from virtually all alkyl Grignard reagents.[13,15] In our studies we therefore restricted ourselves to only three different Grignard reagents, viz. CH_3MgCl, *i*-C_3H_7MgCl, and *t*-C_4H_9MgCl. However, a wide variety of aldehydes and ketones was employed in order to demonstrate the general applicability of the synthetic method described. As shown in Table I, various functional groups (alcohol, ester, double bond, nitro, aromatic, heterocyclic, halide, and organometallic) can be introduced via this procedure. In the proton-decoupled ^{31}P NMR spectra of the crude reaction mixtures, products **2** were in most cases the only phosphazenes observed, proving the regioselectivity of the method described.

A general application of the method seems to be limited to some extent by the bulk of the aldehyde or ketone. For instance, if the copper(I) intermediate with R^1 = *i*-C_3H_7 is stirred together with benzophenone ($R^2 = R^3 = C_6H_5$), no product formation could be detected by ^{31}P NMR spectroscopy, not even after a reaction time of 10 days. On the other hand, reactions with benzaldehyde and ferroceniumcarboxaldehyde gave excellent yields, suggesting that steric hindrance becomes manifest, if both R^2 and R^3 are steric-demanding groups.

Compound **2** with R^1 = *i*-C_3H_7, R^2 = H, and $R^3 = CH_3$ was allowed to react with 4 equiv of sodium phenoxide to form $[NP(OPh_2)]_2NP$-*i*-$C_3H_7C(OH)HCH_3$ (**3**) in 81% yield, demonstrating that the chlorine atoms are still susceptible toward nucleophilic substitution.

Structure Assignment. The structure assignment of compounds **2** is based on IR spectroscopy, mass spectrometry, elemental analysis, ^1H NMR and ^{31}P NMR spectroscopy, and in selected cases ^{13}C NMR spectroscopy.

The IR spectra show absorptions typical of products **2**, an absorption between 3200 and 3500 cm^{-1}, arising from the OH stretch vibration, a strong absorption between 1150 and 1250 cm^{-1}, characteristic of the NP ring skeleton,[22] and two absorptions, one between 500 and 530 cm^{-1} and one between 560 and 600 cm^{-1}, typical of the PCl_2 groupings.[22]

In the 70-eV electron-impact mass spectra the intensity of the parent ion, if present at all, appears to be very low (<2%). In all cases the most abundant fragment occurs at *m/e* = 276, which is typical of the $N_3P_3Cl_4H^+$ ion (all chlorines are ^{35}Cl). This fragment is formed after initial cleavage of the alkyl group, followed by a "McLafferty type" rearrangement[23,24] involving the OH bond. Evidence for this degradation route is provided by the observations that in the mass spectrum a fragment is always observed coinciding with the R^1 radical and that fragments are observed which can be assigned to the degradation of the aldehyde or ketone formed in the rearrangement. For instance, in the 70-eV mass spectrum of the compound with R^1 = *t*-C_4H_9, R^2 = H, and $R^3 = C_6H_5$, the fragments with intact ring skeletons are observed at *m/e* = 439 (M^+), *m/e* = 333 ($N_3P_3Cl_4$-*t*-$C_4H_9H^+$), and *m/e* = 276 ($N_3P_3Cl_4H^+$). The R^1 radical is observed at *m/e* = 57 ($C_4H_9^+$), while at *m/e* = 106, 105, 77, 51, and 50 fragments occur that exactly match the spectrum of benzaldehyde.[25]

The ^{31}P NMR resonance lines of the organo-substituted phosphorus atoms lie between 37 and 52 ppm (Table I). For compounds with a fixed combination of R^2 and R^3, a downfield shift of these signals is observed in going from $R^1 = CH_3$ via R^1 = *i*-C_3H_7 (mean difference in shift ~10 ppm) to R^1 = *t*-C_4H_9 (mean difference in shift ~2 ppm). An analogous trend is observed for the relative ^{31}P NMR chemical shift for organo-substituted phosphorus atoms of *gem*-dialkyltetrachlorocyclotriphosphazenes.[15] The variations of chemical shift cannot completely be attributed to changes in σ-electron-donating ability of the organic side group, as has been proposed by Harris.[26] The chemical shifts of the compounds with R^1 = *i*-C_3H_7, R^2 = H, CH_3, and $R^3 = CH_3$, C_2H_5 suggest that other factors (i.e. steric hindrance and resulting deformation of the molecular geometry) also play an important role. The ^{31}P NMR chemical shifts of the PCl_2 groupings occur between 18 and 19.8 ppm and are shifted somewhat upfield compared to the chemical shift of $(NPCl_2)_3$ (19.9 ppm).

The proton-decoupled ^{31}P NMR spectra of compounds **2** with $R^2 = R^3$ show patterns typical of AX_2 spin systems. The value of $^2J_{PP}$ could only be resolved for the compounds with R^1 = *i*-C_3H_7 and $R^2 = R^3 = CH_3$ and with R^1 = *i*-C_3H_7 and R^2–R^3 = $-(C_2H_5)-$. The proton-decoupled ^{31}P NMR spectra of compounds **2** with $R^2 \neq R^3$, however, show patterns typical of AXY spin systems due to the diastereotopic nature of the PCl_2 groupings. From these spectra δ_X, δ_Y, J_{AX}, and J_{AY} can be calculated by using the method of the *effective Larmor frequencies* (δ_A and J_{XY} can be derived directly from the spectra).[27] A spectral simulation is necessary to establish the correct set of parameters (Table I).

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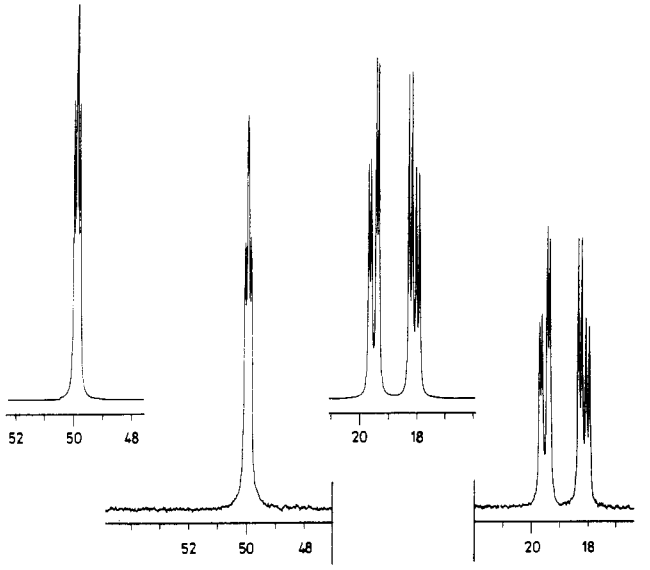

Figure 1. Experimental (lower part) and simulated (upper part) proton-decoupled ^{31}P NMR spectra of $(NPCl_2)_2NP$-*t*-$C_4H_9CH(OH)CH_3$.

The most interesting parameter of the spectra is J_{XY}, which stands for the coupling constant between the PCl_2 groupings. J_{XY} lies between 31 and 37 Hz and can be compared with the $^2J(P(Cl_2)P(Cl_2))$ in some tetrameric systems.[28,29] It is noteworthy that this is the first time that these coupling constants have been measured in the trimeric system.

In Figure 1 the proton-decoupled ^{31}P NMR spectrum of the compound with R^1 = *t*-C_4H_9, R^2 = H, and R^3 = CH_3 is shown together with its simulation (upper part). The A part of the spectrum, the resonances belonging to the organo-substituted phosphorus atom, is deceptively simple; three lines are observed instead of the expected four (apart from the weak outer transitions). The XY part (resonances of the PCl_2 groupings) shows eight lines and allows full determination of all parameters.

A proof for the assignment of the spin system is obtained from the proton-decoupled ^{31}P homonuclear shift-correlated 2-D NMR spectrum (Figure 2) of the same compound. In the lower right- and upper left-hand corners cross peaks are observed, arising from the coupling of the organo-substituted phosphorus atom with the two nonequivalent PCl_2 groupings. The off-diagonal elements around 19 ppm confirm the existence of the coupling between the PCl_2 centers. Furthermore, this 2-D NMR spectrum allows a cross check of the chemical shift assignment.[30]

In most cases the nature of the organic side group was determined by means of ^1H NMR spectroscopy. For the compounds with R^1 = *i*-C_3H_7, R^2 = H, and R^3 = C_2H_5, with R^1 = *i*-C_3H_7, R^2 = CH_3, and R^3 = C_2H_5, with R^1 = *i*-C_3H_7, R^2 = CH_3, and R^3 = $COOC_2H_5$, and with R^1 = *i*-C_3H_7 and R^2–R^3 = $-(CH_2)_5-$, respectively, proton-decoupled ^{13}C NMR spectroscopy was necessary to make an unambiguous structural assignment of the organic moiety. In these spectra the carbon atoms directly connected to the phosphorus center appeared as triplets of doublets. Most of the remaining carbon atoms appeared as doublets. The magnetic nonequivalence of the CH_3 groups of the *i*-C_3H_7 moiety of the compounds with $R^2 \neq R^3$ was observed in some spectra, since these groups appear as two separate doublets.

The spectroscopic data presented above provide unambiguous evidence for the structure of compounds **2**. Further proof was gained from an X-ray structure determination of the compound with R^1 = *i*-C_3H_7, R^2 = H, and R^3 = η^5-C_5H_4–Fe–η^5-C_5H_5, which is published elsewhere.[31]

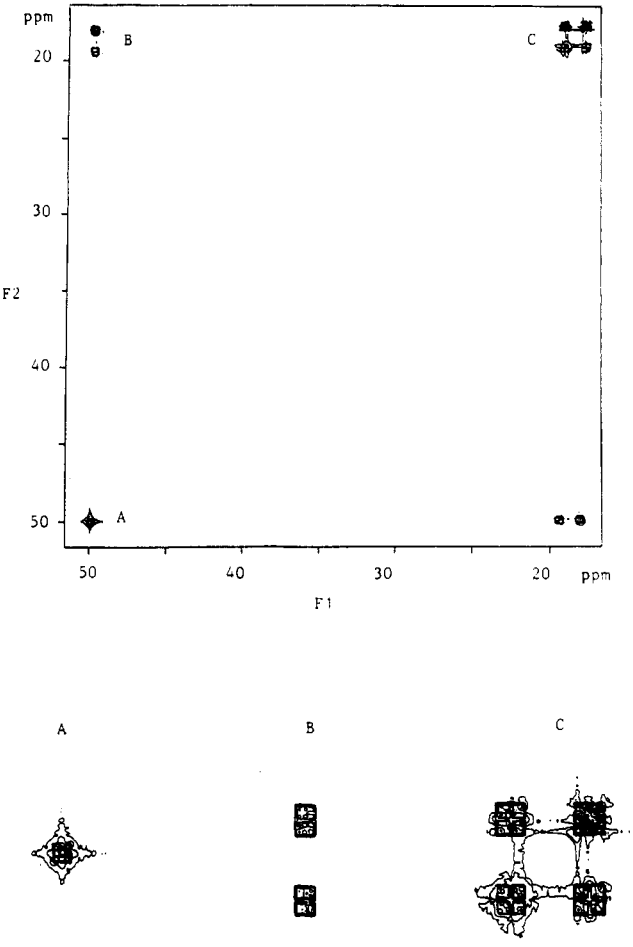

Figure 2. Proton-decoupled ^{31}P homonuclear 2-D NMR spectrum of $(NPCl_2)_2NP$-*t*-$C_4H_9CH(OH)CH_3$, together with expansions of the A, B, and C parts of the spectrum.

Reaction Mechanism. The representation of the copper(I)-containing intermediate, as given by Allcock and Harris,[13] provides insight into the reaction sequence and the products formed. However, some issues remain unclear: Viz. the "soft" copper(I) is associated with the "harder" ring nitrogen, while association with the "softer" trivalent phosphorus atom has to be expected.[32] Secondly, the phosphine is not reflected in the structure, although, in the ^{31}P NMR spectrum of the intermediate metallophosphazene, resonance lines of the phosphine are observed at −20.0 ppm, pointing to a metal coordination (free phosphine would be located at −32.5 ppm, and the phosphine of the $[(n\text{-}C_4H_9)_3PCuI]_4$ complex, at −33.8 ppm, with tetrahydrofuran as solvent).

This prompted us to perform a study in which the metallophosphazene was generated independently via deprotonation of a *gem*-alkylhydrocyclotriphosphazene with a Grignard reagent in the presence of $[(n\text{-}C_4H_9)_3PCuI]_4$. This strategy was chosen because in the formation of the metallophosphazene via metal–halogen exchange the stoichiometry of the reaction is not completely understood.[13] For the formation of the copper(I) phosphazene complex 3 equiv of Grignard reagent/equiv of $(NPCl_2)_3$ (**1**) is required. The first equivalent is consumed in the metal–halogen exchange reaction; the second, in the nucleophilic substitution at phosphorus. The role of the third equivalent of Grignard reagent is not clear. For reactions involving CH_3MgCl it might be consumed in a Posner type of coupling with CH_3Cl, resulting from the metal–halogen exchange reaction. For *i*-C_3H_7MgCl and *t*-C_4H_9MgCl this coupling is highly unlikely, but in these cases 3 equiv of Grignard reagent is necessary as well.

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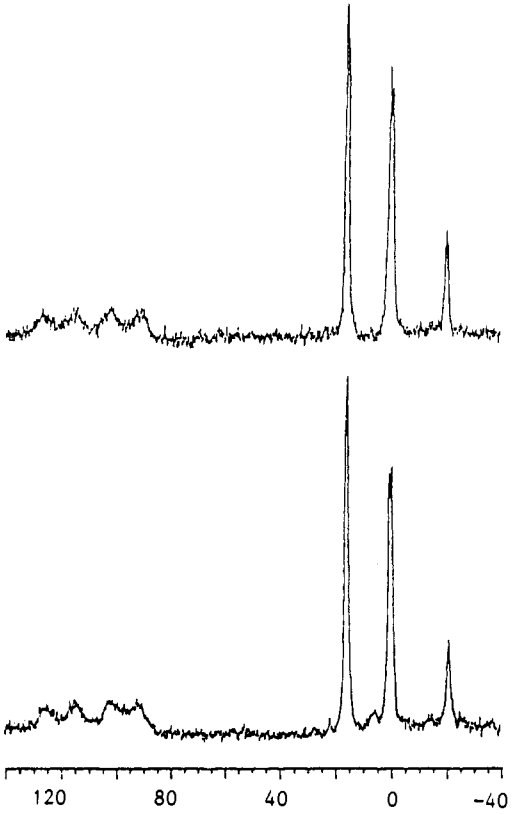


Figure 3. Proton-decoupled ^{31}P NMR spectra of the reaction mixture of i-C_3H_7MgCl with $(NPCl_2)_2NP(H)$-i-C_3H_7 in the presence of $[(n\text{-}C_4H_9)_3PCuI]_4$ (upper part) and of the reaction mixture of i-C_3H_7MgCl with $(NPCl_2)_3$ in the presence of $[(n\text{-}C_4H_9)_3PCuI]_4$ (lower part).

The stoichiometry of the deprotonation route, on the other hand, leaves no questions. In the deprotonation route complexation with copper is supposed to take place after initial metalation with magnesium.

$$(NPCl_2)_2NP(H)\text{-}i\text{-}C_3H_7 + i\text{-}C_3H_7MgCl \xrightarrow[-C_3H_8]{} (NPCl_2)_2NP(MgCl)\text{-}i\text{-}C_3H_7 \xrightarrow[+[(n\text{-}C_4H_9)_3PCuI]_4]{} [(NPCl_2)_2NP\text{-}i\text{-}C_3H_7]_2MgCuX\cdot(n\text{-}C_4H_9)_3P$$

X represents a mixture of Cl and I

In Figure 3 the proton-decoupled ^{31}P NMR spectrum of the reaction mixture of 1 equiv of i-C_3H_7MgCl with 1 equiv of $(NPCl_2)_2NP(H)$-i-C_3H_7 in the presence of 0.5 equiv of $[(n\text{-}C_4H_9)_3PCuI]_4$ in tetrahydrofuran is shown (upper part), together with the spectrum of the reaction mixture of 1 equiv of $(NPCl_2)_3$ with 3 equiv of i-C_3H_7MgCl in the presence of 0.5 equiv of $[(n\text{-}C_4H_9)_3PCuI]_4$ (lower part). The striking resemblance indicates that in both cases the same copper(I)-containing species are formed.

We propose, on the basis of the stoichiometry of the deprotonation reaction and the HSAB theory,[32] where soft Cu(I) prefers phosphorus, a structure for the intermediate as shown in Figure 4. Evidence for the intermediate to have such a *phosphazenocuprate*[38] structure is derived from the proton-decoupled ^{31}P NMR spectra shown in Figure 3. Resonances occur in four regions. A broad 1:1:1:1 quartet is observed at 108 ppm. Such a relatively large downfield shift is typical of metal-coordinated phosphorus atoms in phosphazenes.[33,34] The marked broadening and the large coupling constant (920 Hz) indicate a direct coupling between

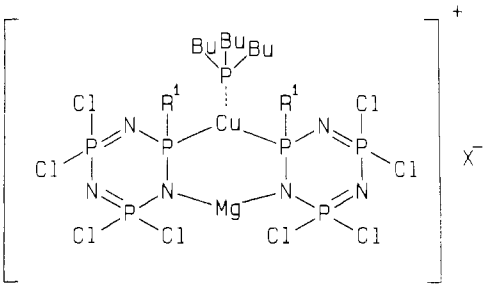
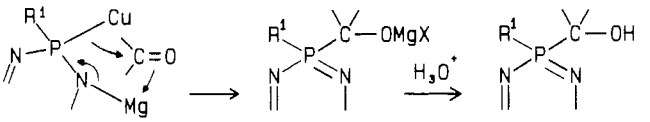


Figure 4. Structure of the intermediate copper(I) phosphazene.

Scheme II



the phosphorus and copper nuclei. The two isotopes of copper are ^{63}Cu (69%) and ^{65}Cu (31%), both having a nuclear spin momentum of $^3/_2$; both also possess a nuclear quadrupole momentum,[35] causing the broadening of the signals observed. At 15.7 ppm a resonance is observed for a PCl_2 grouping. This resonance is shifted upfield compared to the chemical shift of $(NPCl_2)_3$. At 0.2 ppm the resonances of another PCl_2 grouping are observed. The relatively large upfield shift indicates that negative charge is concentrated in the segment to which this PCl_2 center belongs, causing a large shielding. Finally, at −20.0 ppm the resonance of tri-*n*-butylphosphine appears. The chemical shift shows that the phosphine is present neither as a free compound nor as a copper complex. When equimolar amounts of $(NPCl_2)_2NP(H)$-i-C_3H_7, i-C_3H_7MgCl, and $[(n\text{-}C_4H_9)_3PCuI]_4$ were reacted (thus increasing the relative amount of the copper complex), the proton-decoupled ^{31}P NMR spectrum showed virtually no changes, apart from an increase of the intensity of the phosphine resonance at −20.0 ppm. The absence of resonances arising from free $[(n\text{-}C_4H_9)_3PCuI]_4$ implies that the $(n\text{-}C_4H_9)_3P$ ligands are exchanging rapidly. All items discussed in this paragraph are reflected in the structure shown in Figure 4. Although omitted in this figure, it is most likely that the metal atoms are solvated by tetrahydrofuran molecules. In addition, it should be mentioned that in this representation copper merely serves to stabilize the phosphazenium anion, which normally decomposes rapidly at room temperature.[36] Recently the crystal structure of a phosphazene anion is described in which Li^+ (solvated by THF) acts as a counterion.[37] In accordance with the concept used for the structure proposed above, the lithium in the latter compound is coordinated to nitrogen (hard acid–hard base interaction).

Upon addition of a second equivalent of Grignard reagent in the deprotonation reaction, the proton-decoupled ^{31}P NMR spectrum did not change. It is possible that the third equivalent of Grignard reagent in the reaction of $(NPCl_2)_3$ with $[(n\text{-}C_4H_9)_3PCuI]_4/RMgCl$ is involved in the metal–hydrogen exchange reaction, but not consumed.

The most plausible pathway for the addition of phosphazenocuprates to aldehydes and ketones is shown in Scheme II. The phosphorus center adds in a nucleophilic way to the CO double bond, resulting in a magnesium alcoholate. Apparently, the al-

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(38) Organic magnesium cuprates have the overall formula $R_2CuMgCl$, resembling the overall formula of our intermediate copper(I) phosphazene. We therefore propose the term *phosphazenocuprate* for the intermediate species.

coholate is not sufficiently reactive to substitute for the chlorine in PCl_2 centers of other molecules. Mild acid hydrolysis finally yields products **2**.

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Supplementary Material Available: Table SI, compiling the eluants used in flash chromatographic separations, Table SII, giving microanalytical data, Table SIII, giving IR spectroscopic data, and Table SIV, compiling ^1H NMR and proton-decoupled ^{13}C NMR data (9 pages). Ordering information is given on any current masthead page.

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Cytochrome *c* Oxidase Models: Iron(III) Porphyrin–Copper(II) Complexes with Sulfur Bridges

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Three compounds involving sulfur-bridged Fe(porphyrin)–Cu linkages have been synthesized as models for the active site of cytochrome *c* oxidase: (TBA){[Fe(*p*-Cl_4TPP)]$_2$[Cu(MNT)$_2$]$_2$}·C_6H_6 (**1**), (TBA){[Fe(*p*-Cl_4TPP)]$_2$[Cu(MNT)$_2$]$_2$}·$2C_6H_6$ (**2**), and (TBA){[Fe(*p*-Cl_4TPP)]$_2$[Cu(MNT)$_2$]$_2$}·$3C_6H_6$ (**3**) (TBA$^+$ = tetra-*n*-butylammonium, *p*-Cl_4TPP^{2-} = 5,10,15,20-tetrakis(*p*-chlorophenyl)porphyrinate, MNT^{2-} = *cis*-1,2-dicyanoethylenedithiolate). The structures of **1** (monoclinic, a = 17.222 (4) Å, b = 26.818 (5) Å, c = 27.497 (8) Å, β = 103.84 (2)°, Z = 4, space group $C2/c$, T = 20 °C), of **2** (monoclinic, a = 17.489 (5) Å, b = 26.515 (7) Å, c = 27.006 (11) Å, β = 101.39 (3)°, Z = 4, space group $C2/c$, T = −130 °C), and of **3** (triclinic, a = 13.378 (3) Å, b = 17.356 (2) Å, c = 28.918 (7) Å, α = 104.05 (2)°, β = 99.62 (2)°, γ = 98.38 (2)°, Z = 2, space group $P\bar{1}$, T = −130 °C) have been determined by single-crystal X-ray diffraction. **1** contains a pair of [Fe^{III}(*p*-Cl_4TPP)]$^+$ units that sandwich a [Cu^{II}(MNT)$_2$]$^{2-}$ anion; the Fe^{III} atoms are linked to the Cu^{II} atom by sulfur bridges (Fe–S = 2.482 (3) Å). A [Cu^{III}(MNT)$_2$]$^-$ anion interacts weakly with the iron atoms (Fe–S = 3.286 (4) Å). **2** also contains a pair of [Fe^{III}(*p*-Cl_4TPP)]$^+$ units sandwiching a [Cu^{II}(MNT)$_2$]$^{2-}$ anion (Fe–S = 2.472 (2) Å) and a weakly interacting [Cu^{III}(MNT)$_2$]$^-$ anion (Fe–S = 3.176 (3) Å). In both **1** and **2**, the Cu^{II} atom occupies a site of 2-fold symmetry, making the iron porphyrins structurally identical. The structure of **3** is less symmetric but also contains a pair of [Fe^{III}(*p*-Cl_4TPP)]$^+$ units sandwiching a [Cu^{II}(MNT)$_2$]$^{2-}$ anion (Fe–S = 2.444 (2), 2.549 (2) Å). In **3** the [Cu^{III}(MNT)$_2$]$^-$ anion interacts more strongly with one iron atom (Fe–S = 2.956 (2) Å) than with the other (Fe–S = 3.641 (2) Å). The metric parameters are consistent with admixed-spin (S = $^3/_2$, $^5/_2$) assignments for the iron atoms in all three compounds, as are the Mössbauer results for a mixture of **1** and **2** (δ = 0.38 mm s^{-1}, ΔE = 3.09 mm s^{-1}). The magnetic susceptibility of this mixture indicates that the iron atoms are in an intermediate spin (S = $^3/_2$) or a spin-admixed (S = $^3/_2$, $^5/_2$) state.

Introduction

The enzyme cytochrome *c* oxidase (CcO), which catalyzes the reduction of O_2 to H_2O, contains two Fe hemes and at least two Cu sites.[2] The O_2 binding site is thought to contain an Fe atom and a Cu atom in close proximity.[3] The origin of the unusual magnetic and spectroscopic properties exhibited by the resting oxidized form of the active site remains a matter of much interest. The reason(s) for the absence of an EPR signal from this Fe_{a3}–Cu_B site has been the subject of considerable speculation. In one widely accepted model, the EPR silence is thought to result from very strong ligand-mediated antiferromagnetic coupling ($-J$ > 200 cm^{-1}) between the Cu(II) and the Fe(III) heme unit.[4] Another possible model involves a ligand-mediated spin-relaxation broadening between these metal centers.[5] The latter mechanism does not demand a high degree of exchange coupling between the metal centers.

Many putative model complexes for the resting, oxidized active site have been prepared. These complexes have contained various bridging ligands, including imidazolate,[6] oxygen,[7] halogens or pseudohalogens,[8] and bipyrimidyl.[9] None of these "model" complexes have exhibited antiferromagnetic coupling between the metal centers strong enough to produce EPR silence. The largest

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