52 g.) and potassium fluoride (11.6 g.) in water (50 ml.) for 3 hr. ($KClO_4$ was removed on a filter first). This preparation and the subsequent ion-exchange extraction have been described by Swaddle and King.[1] The required complex was eluted from the ion-exchange resin with sulfuric acid (0.5 *M*) and precipitated as the sulfate by the method described before. The product contained a considerable amount of potassium sulfate and was purified by extracting the complex with the minimum of ice-cold perchloric acid (1 *M*) and removing the residue of potassium perchlorate on a filter while the solution was cooled below −5°. The fluoro complex was reprecipitated as the sulfate by adding absolute ethanol to the saturated filtrate with vigorous stirring. The product was collected on a filter, washed with ether, and dried by sucking air through it and then in a vacuum desiccator over $CaCl_2$; yield 3 g. A better yield would probably be obtained if hydrofluoric acid was used instead of potassium sulfate. However, Pyrex glassware could not then be used.

Anal. Calcd. for $[Cr(H_2O)_5F]SO_4\cdot H_2O$: Cr, 18.9. Found: Cr, 18.9. Fluoride ion interferes with the sulfate ion analysis.

Preparation of the Complex $[Cr(H_2O)_5NO]SO_4\cdot H_2O$.—The complex was prepared essentially by the method of Ardon and Herman.[3] A solution (50 ml.) of 0.1 *M* $Cr(ClO_4)_2$ was added dropwise, in portions of 10 ml., under nitrogen and with stirring to a saturated solution of nitric oxide in 0.2 *M* $HClO_4$ (500 ml.) cooled in an ice bath (to increase the solubility of the nitric oxide). After each addition of $Cr(ClO_4)_2$ the solution was resaturated with nitric oxide gas. The products were separated by ion exchange and the desired red-brown product precipitated as the sulfate by the methods described for the iodo complex. This method of separation gave a monohydrated product rather than the anhydrous salt isolated by previous workers[3]; yield 0.7 g.

Anal. Calcd. for $[Cr(H_2O)_5NO]SO_4\cdot H_2O$: Cr, 18.2. Found: Cr, 18.0.

Spectra.—A Cary Model 14 spectrophotometer was used. The spectra of all the complexes in 1 *M* $HClO_4$ were obtained to check the molar absorbancy indices and peak positions with the reported values.[1-3] Good agreement was observed in all cases. The observed peak positions (in mμ), shoulders (sh), and corresponding molar absorbancy indices (in parentheses) were: fluoro complex 268 (5.0), 417 (12.4), 594 (12.9), *ca.* 667 (sh, *ca.* 5.1); chloro complex 428 (21.9), 608 (17.4), *ca.* 674 (sh, *ca.* 7.5); bromo complex 432 (23.7), *ca.* 470 (sh, *ca.* 15), 622 (21.3), *ca.* 675 (sh, *ca.* 12); iodo complex 474 (32.8), 649 (unsymmetric peak, 36.5); $[Cr(H_2O)_5NO]^{2+}$ 325 (91.7), *ca.* 399 (sh, *ca.* 90.5), 451 (120.9), 562 (28.5).

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Contribution from the Department of Chemistry,
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Modified Friedel–Crafts Preparation of 2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatriene[1]

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The title compound was first prepared[2] by refluxing a benzene solution of hexachlorocyclotriphosphazatriene with aluminum chloride for 2 days. The yield (40%) is not improved substantially either by increasing the proportion of aluminum chloride or by extending the reaction time.[3,4] The low yields and slow reaction rates are unexpected and have not hitherto been explained satisfactorily.

We noted that hydrogen chloride, formed as a coproduct, could protonate $P_3N_3Cl_6$, thereby obstructing the formation of the quasi-phosphonium ion, $P_3N_3Cl_5^+$, which is the probable species[4] attacking benzene. The liberated chloride (as $AlCl_4^-$) could also react with this electrophile, stabilize the protonated species in the form of a complex, and, to a lesser extent, decrease the effective concentration of aluminum chloride.

$$P_3N_3Cl_6 + C_6H_6 \xrightarrow{AlCl_3} P_3N_3Cl_4(C_6H_5)_2 + 2HCl$$

$$HCl + P_3N_3R_6 + AlCl_3 \longrightarrow P_3N_3R_6\cdot H^+\ AlCl_4^-$$

$$(R = Cl_6,\ Cl_4(C_6H_5)_2,\ \text{etc.})$$

The original Friedel-Crafts reaction was modified in the three following ways: (A) Repetition of the reaction using fresh catalyst after decomposition of the complex (no. 3 and 4). (B) Addition of aluminum[5] to the reaction mixture (no. 5 and 6). (C) Addition of amines to the reaction mixture (no. 7, 8, and 9). The results are given in Table I together with those (no. 1 and 2) obtained for unmodified conditions.

All three methods are designed to reduce the effect of hydrogen chloride. Since each gives high yields of phenylated product, the contention that this coproduct is responsible for adversely influencing the reaction is confirmed. When the removal of hydrogen chloride is particularly efficient, as in methods (A) and (B) or when the reaction is doubly modified (no. 10), tetraphenylation is more prevalent, especially when compared with the result for the unmodified reaction. Hence, the possibility that the rate of phenylation of the 2,2,4,4-tetrachloro-6,6-diphenyl compound is greater than that of hexachlorocyclotriphosphazatriene cannot be ignored.

Since some amines are known to complex with aluminum chloride,[6] an excess of the latter is required in method (C). Nonetheless, using triethylamine or pyridine, high yields (up to 77%) of the diphenyl derivative are obtained. Although advantageous, the yields of 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene are unexpectedly small. Possibly, the major product though not the starting material competes successfully with these amines for the protons of hydrogen chloride.

Experimental

Aluminum chloride (anhydrous, granular), a product of Baker Chemical Co., and technical benzene were used without further purification or drying. Separation of the products was generally carried out by chromatography on acid-washed alumina (Merck).

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[1] This paper is based on a portion of the thesis submitted by Kunio Okuhara to the Graduate School of Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] H. Bode and H. Bach, *Ber.*, **75**, 215 (1942).

[3] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **3**, 177 (1964).

[4] K. G. Acock, R. A. Shaw, and F. B. G. Wells, *J. Chem. Soc.*, 121 (1964).

[5] This modification has been reported by E. L. Muetterties [*J. Am. Chem. Soc.*, **81**, 2597 (1959); *ibid.*, **82**, 4163, (1960)] for the phenylation of boron trichloride.

[6] D. D. Eley and H. Watts, *J. Chem. Soc.*, 1914 (1952).

TABLE I

FRIEDEL–CRAFTS PHENYLATION OF $P_3N_3Cl_6$[a]

Expt. no.	$AlCl_3$, moles[e]	Al, g.-atoms[e,f]	$(C_2H_5)_3N$, moles[e]	Yield, %			
				$P_3N_3Cl_6$[g]	$P_3N_3Cl_4(C_6H_5)_2$	$P_3N_3Cl_2(C_6H_5)_4$	$P_3N_3(C_6H_5)_6$
1	4.00			36.7	29.2	(0.3)	
2	2.54			39.9	32.9	(0.4)	
3[b]	2.54			17.3	59.4	4.9	
4[c]	2.54				30.2	24.2	
5	2.54	0.49		7.8	52.8	9.5	
6[d]	2.54	1.29			5.9	31.5	(0.6)
7	6.75		2.00	12.5	69.6	1.3	
8	7.64		3.00	12.8	76.5	2.2	
9	7.64		3.00	8.4	74.8	2.1	
			(pyridine)				
10	7.64	0.72	3.00		1.6	32.0	0.8

[a] The product yields were calculated with the assumption that all the $P_3N_3Cl_6$ reacted. Unless otherwise mentioned, 48-hr. reaction time. [b] The reaction repeated twice (48-hr. each time). [c] The reaction repeated three times (40, 40, and 30 hr., respectively). [d] 96-hr. reaction time. [e] Per mole of $P_3N_3Cl_6$ (0.100 mole of $P_3N_3Cl_6$ was used in each run). [f] Unrecovered aluminum, 1.85 g.-atoms added initially. [g] Recovered starting material.

The yields given in Table I are based on the amount of product obtained with reasonable purity after recrystallization. Small yields (given in parentheses in the table) were calculated for the crude product obtained from the chromatographic fractions.

Preparation of 2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatriene (No. 8 of Table I).—Triethylamine (30.4 g., 0.300 mole) was added carefully to a mixture of aluminum chloride (102 g., 0.764 mole) and benzene (150 ml.), and the mixture was refluxed for about 30 min. Solid hexachlorocyclotriphosphazatriene (34.8 g., 0.100 mole; m.p. 112–114°) was added, and the mixture was refluxed (83°) with stirring for 48 hr. The resulting homogeneous solution was poured onto a mixture of ice and concentrated hydrochloric acid (100 ml.), more benzene was added to the mixture, and the benzene layer was separated. The aqueous layer was extracted once with benzene. The combined benzene extracts were washed with water and dried with calcium chloride, and the solvent was removed (rotary film evaporator). The resulting syrup, containing a small amount of benzene, deposited 10.60 g. (0.0246 mole, 24.6%) of fairly pure (m.p. 93.5–96°) 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene, which was collected by filtration and washing with hexane. From this syrup, approximately 25 g. (58%) of the diphenyl compound was found to be isolable in purity of m.p. 93–95.5° by careful crystallization (from a minimum amount of benzene) followed by filtration and washing with ethanol. In this particular run the remaining material was dissolved in hot hexane (100 ml.) and poured into a column packed with acid-washed alumina (370 g.) in hexane. A compressed air pressure was carefully applied to lower the level of the hexane solution to the upper level of the alumina quickly, the pressure was released, more hexane (cold) was added, and elution was continued. After the unchanged starting material (4.43 g., 12.8%) had been eluted, the solvent was changed to 3:7 benzene–hexane to elute the tetrachlorodiphenyl compound. When this compound had been eluted, 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene was eluted quickly with benzene. The yield of 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene was 22.36 g. (0.0519 mole, 51.9%; mostly m.p. 94–95.5°) after recrystallization from hexane, increasing the total yield to 76.5%, and that of 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene was 1.13 g. (0.0033 mole, 2.2%; mostly m.p. 141.5–143°) after recrystallization from benzene–hexane.

Correspondence

The π-Accepting Ability of CO in the Group VI-B Metal Carbonyls

Sir:

Semiquantitative estimates of differences among CO (and MC) bond orders for the group VI-B metal carbonyls and their simple substitution products [$M(CO)_{6-x}D_x$; M = Cr, Mo, W] have recently been made on the basis of the essentially linear relationship between force constants and bond orders for simple molecules containing C–O bonds[1,2] and the assumed applicability of this relationship to metal carbonyl derivatives. The force constants employed were determined through use of the secular equations of Cotton and Kraihanzel.[1,3] In this treatment it was necessary to the determination of "absolute"[4] bond orders to assume a value for the π-accepting ability of CO in $M(CO)_6$. It was therefore proposed[1] that in $M(CO)_6$ the six available (t_{2g}) metallic dπ electrons "tend to be fully used," that the six CO's thus each received one dπ electron (0.5 electron pair), and that the CO bond order in $M(CO)_6$ is thus 0.5 less than in free CO. An extension of this argument leads to the accurate prediction of the observed 0.5 drop in CO bond order from $Mo(CO)_6$ to $Mo(CO)_3$(dien),[5] and this agreement has been taken as a demonstration of the essential correctness of the proposal cited. The evidence given below supports a considerably smaller (*ca.* 0.2 electron pair) π-accepting ability for CO in $M(CO)_6$, and thus correspondingly

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(1) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(2) F. A. Cotton and R. M. Wing, *ibid.*, **4**, 314 (1965).

(3) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(4) "Absolute" in the sense that approximate numerical values may be assigned as bond orders for particular M–C and C–O bonds. The M–C and C–O bond orders neglecting dπ → π^*_{CO} back bonding were assumed to be 1 and 3; the probable bond orders in CO and CO^+ have been estimated by Moffitt [*Proc. Roy. Soc.* (London), **A196**, 524 (1949)] to be 2.55 and 2.84. See discussion below.

(5) dien = diethylenetriamine.