Organometallics 1991, *10*, 1865–1874

Synthesis and Structure of Phosphazene–(η^6-Arene)chromium Tricarbonyl Derivatives

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Received November 9, 1990

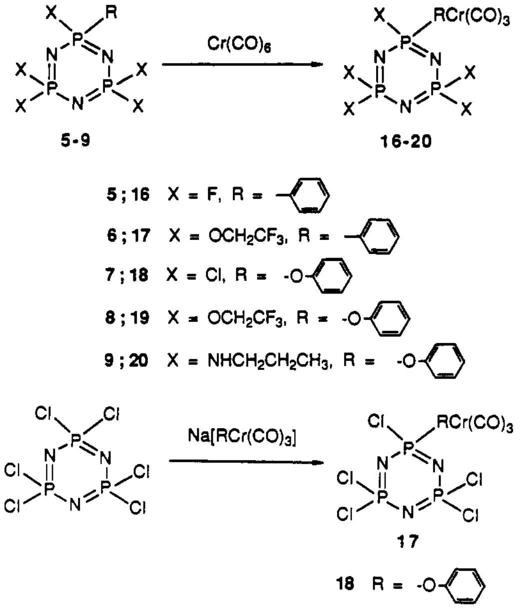
The synthesis and structure of a new class of cyclotriphosphazene transition-metal complexes is described. The complexes have the general structures $N_3P_3X_5[RCr(CO)_3]$, where the X and R substituents are fluoro and phenyl, trifluoroethoxy and phenyl, chloro and phenoxy, trifluoroethoxy and phenoxy, and *n*-propylamino and phenoxy, respectively, $N_3P_3R_5[RCr(CO)_3]$, where the R substituents are phenoxy, 4-methylphenoxy, 4-methoxyphenoxy, phenyl, 2-phenoxyethoxy, and anilino, and $N_3P_3[RCr(CO)_3]_6$, where the R substituents are phenoxy and 2-phenoxyethoxy. Species $N_3P_3[RCr(CO)_3]_6$ represent unique examples of cyclotriphosphazenes that possess one transition metal on each side-group structure. The molecular structure of $N_3P_3F_5[(C_6H_5)Cr(CO)_3]$ has been determined by X-ray diffraction. The crystals are monoclinic with space group $P2_1/c$, with $a = 6.458$ (1) Å, $b = 10.840$ (1) Å, $c = 22.122$ (3) Å, $\beta = 91.72$ (1)°, $V = 1548.0$ Å^3, and $Z = 4$.

The preparation of macromolecules that function as carrier species for transition metals is a synthetic challenge and is a subject of growing interest.[1,2] Such complexes have potential applications as electroactive or magnetic materials or polymer-supported catalysts.

In earlier papers we described several methods for the linkage of transition metals to polyphosphazenes. These methods include the linkage of metals to skeletal phosphorus atoms via covalent bonds,[3] by coordination to exocyclic phosphorus atoms in phosphino groups,[4] by coordination to skeletal nitrogen atoms,[5] or by the use of pendent organic spacer groups.[6] A necessary prerequisite in the development of such synthetic routes is to examine prototype systems at the small molecule level.[7] This protocol is followed because of the greater ease of characterization of small molecules compared to macromolecules.

Our present objective is to explore routes that allow the efficient π coordination of transition metals to pendent aryl ligands on phosphazenes. In particular, we were interested in the synthesis of phosphazene–(η^6-arene)$Cr(CO)_3$ complexes,[8] in which the arene ligand was bound either directly to the phosphazene skeleton, via an oxygen or nitrogen atom, or indirectly via an organic spacer group. The substitutive method of synthesis for phosphazenes allows the facile incorporation of a diverse range of aryl side-group structures and provides access to an interesting series of arene complexes.

Scheme I. Synthesis of $N_3P_3X_5[RCr(CO)_3]$ Complexes



Specifically, in this paper we describe the synthesis and structure of a new class of cyclotriphosphazene transition-metal complexes with the general structures $N_3P_3X_5[RCr(CO)_3]$ (1), $N_3P_3R_5[RCr(CO)_3]$ (2), and $N_3P_3[RCr(CO)_3]_6$ (3), in which the R substituents are aryl groups and the X substituents are fluoro, chloro, trifluoroethoxy, or *n*-propylamino groups. During these studies, compounds 1–3 were viewed as models for the prospective high polymeric analogues such as 4.

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(1) Reviews: (a) Andrews, M. P.; Ozin, G. A. *Chem. Mater.* **1989**, *1*, 174. (b) Zeldin, M., Wynne, K. J., Allcock, H. R., Eds. *Inorganic and Organometallic Polymers: Macromolecules Containing Silicon, Phosphorus, and Other Inorganic Elements*; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988. (c) Sheats, J. E., Carraher, C. E., Jr., Pittman, C. U., Jr., Eds. *Metal-Containing Polymeric Systems*; Plenum: New York: 1985.

(2) (a) Wright, M. E. *Macromolecules* **1989**, *22*, 3256. (b) Chaudret, B.; Chung, G.; Huang, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 749. (c) Roberts, M. F.; Jenekhe, S. A. *Chem. Mater.* **1990**, *2*, 224. (d) Andrews, M. P.; Ozin, G. A. *Inorg. Chem.* **1986**, *25*, 2587. (e) St. Clair, A. K.; Carver, V. C.; Taylor, L. T.; Furtsch, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 876.

(3) (a) Allcock, H. R.; Mang, M. N.; McDonnell, G. S.; Parvez, M. *Macromolecules* **1987**, *20*, 2060. (b) Allcock, H. R.; Riding, G. H.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 5561. (c) Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim, M. Y. *Inorg. Chem.* **1981**, *20*, 716.

(4) Allcock, H. R.; Manners, I.; Mang, M. N.; Parvez, M. *Inorg. Chem.* **1990**, *29*, 522.

(5) (a) Allcock, H. R.; Allen, R. W.; O'Brien, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 3984. (b) Allcock, H. R.; Greigger, P. P.; Gardner, J. E.; Schmutz, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 606.

(6) (a) Allcock, H. R.; Scopelianos, A. G.; O'Brien, J. P.; Bernheim, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 350. (b) Allcock, H. R.; Scopelianos, A. G.; Whittle, R. R.; Tollefson, N. M. *J. Am. Chem. Soc.* **1983**, *105*, 1316. (c) Allcock, H. R.; Lavin, K. D.; Tollefson, N. M.; Evand, T. L. *Organometallics* **1983**, *2*, 267. (d) Dubois, R. A.; Garrou, P. E.; Lavin, K. D.; Allcock, H. R. *Organometallics* **1986**, *5*, 460. (e) Allcock, H. R.; Neenan, T. X.; Boso, B. *Inorg. Chem.* **1985**, *24*, 2656. (f) Allcock, H. R.; Neenan, T. X. *Macromolecules* **1986**, *19*, 1495.

(7) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.

(8) (a) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, England, 1982; Vol. 3, p 1001 and references cited therein. (b) Sneeden, R. P. A. *Organochromium Compounds*; Academic: New York, 1975. (c) Silverthorn, W. E. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic: New York, 1975; Vol. 13, p 48.

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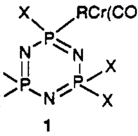

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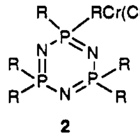

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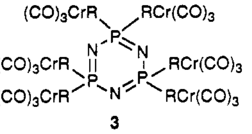

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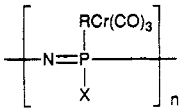

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Results and Discussion

Overview of the Synthetic Approach. Two synthetic methodologies were employed in the preparation of the cyclotriphosphazene (η^6-arene)Cr(CO)$_3$ complexes. In the first approach, an aryl-substituted phosphazene was allowed to react with Cr(CO)$_6$ in the donor solvent medium of di-*n*-butyl ether/THF.[8a] The aryl-substituted phosphazenes had the general structures $N_3P_3X_5R$ (5–9) and $N_3P_3R_6$ (10–15). Species 5–15 were prepared by conventional procedures,[9] and the specific structures and ^{1}H, ^{13}C, and ^{31}P NMR characterization data are summarized in Tables I–III, respectively.

In the second synthetic approach, $N_3P_3Cl_6$ was allowed to react with the sodium salt of an alcohol or phenolic chromium tricarbonyl complex. This approach paralleled more closely the conventional substitutive method of synthesis for phosphazenes.[9] Both approaches were successful and allowed the synthesis of a diverse range of arene complexes.

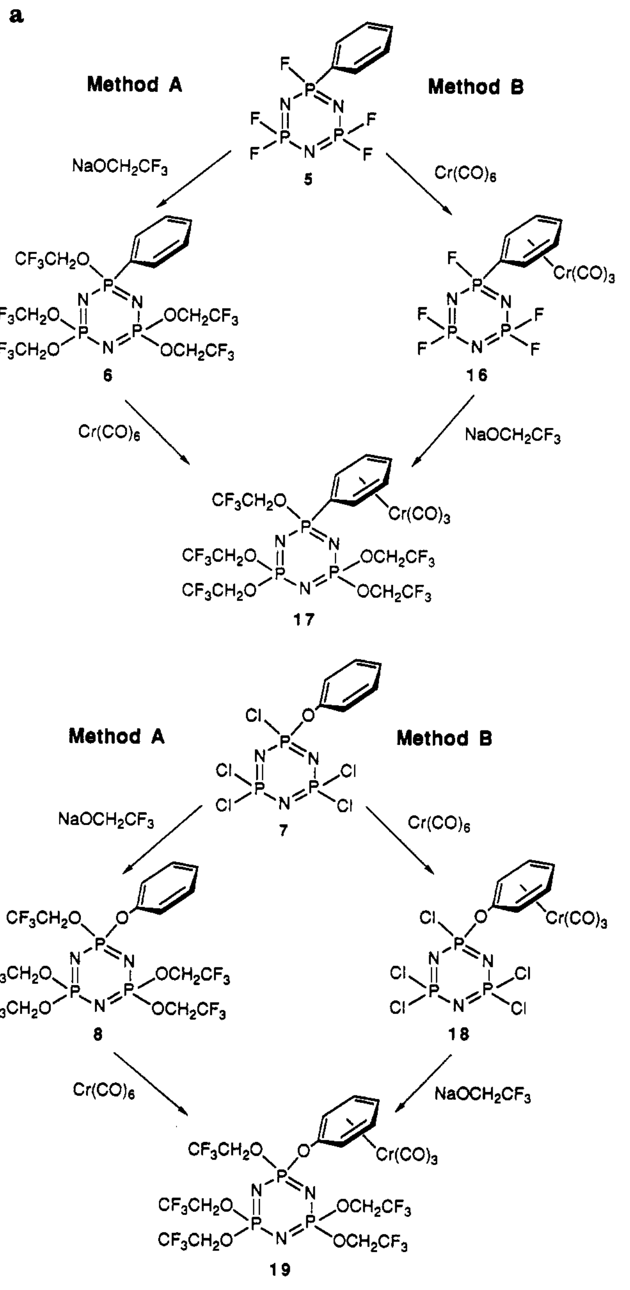
Synthesis of $N_3P_3X_5$[RCr(CO)$_3$] Complexes. The series of compounds 16–20 have the general structure $N_3P_3X_5$[RCr(CO)$_3$], where the X and R substituents were fluoro and phenyl for 16, trifluoroethoxy and phenyl for 17, chloro and phenoxy for 18, trifluoroethoxy and phenoxy for 19, and *n*-propylamino and phenoxy for 20, respectively (see Scheme I). The trifluoroethoxy and *n*-propylamino groups are representative cosubstituent nucleophiles in cyclic and polymeric phosphazene chemistry.

Complexes 16–20 were prepared by the use of the two synthetic strategies, as illustrated in Scheme I and described above. In the first strategy, the monoaryl-substituted phosphazenes $N_3P_3X_5R$ (5–9) were allowed to react with an excess of Cr(CO)$_6$ to yield the corresponding arene complexes $N_3P_3X_5$[RCr(CO)$_3$] (16–20). Because species $N_3P_3X_5R$ possess only one aryl group per molecule of cyclic trimer, the use of excess Cr(CO)$_6$ was feasible and proved to be an efficient route for the preparation of the corresponding arene complexes.

Compound 18, $N_3P_3Cl_5$[(OC$_6$H$_5$)Cr(CO)$_3$], was also prepared by the second strategy, specifically via the reaction of $N_3P_3Cl_6$ with 1 equiv of (NaOC$_6$H$_5$)Cr(CO)$_3$. Note that (NaOC$_6$H$_5$)Cr(CO)$_3$ was prepared by the facile reaction of (HOC$_6$H$_5$)Cr(CO)$_3$ with NaH. This strategy for the introduction of the Cr(CO)$_3$ unit into the phosphazene was very effective and, as will be discussed in a later section, provided an important route to the synthesis of phosphazenes with high loadings of transition metals.

The trifluoroethoxy-substituted trimers $N_3P_3(OCH_2CF_3)_5$[(C$_6$H$_5$)Cr(CO)$_3$] (17) and $N_3P_3(OCH_2CF_3)_5$[(OC$_6$H$_5$)Cr(CO)$_3$] (19) were synthesized by two different pathways, which are designated as methods A and B. The methods differed in the order of addition of NaOCH$_2$CF$_3$ and Cr(CO)$_6$ to $N_3P_3X_5R$. The syntheses are outlined in Scheme IIa for 17 and Scheme IIb for 19.

Scheme II



For the synthesis of 17 (Scheme IIa), in method A, $N_3P_3F_5(C_6H_5)$ (5) was allowed to react first with NaOCH$_2$CF$_3$ in order to replace the P–F bonds and yield species $N_3P_3(OCH_2CF_3)_5(C_6H_5)$ (6). Compound 6 was then allowed to react with Cr(CO)$_6$ to yield the arene complex $N_3P_3(OCH_2CF_3)_5$[(C$_6$H$_5$)Cr(CO)$_3$] (17). In method B, $N_3P_3F_5(C_6H_5)$ (5) was allowed to react first with Cr(CO)$_6$ to yield the arene complex $N_3P_3F_5$[(C$_6$H$_5$)Cr(CO)$_3$] (16), which then reacted further with NaOCH$_2$CF$_3$ to yield the product 17. No displacement of the Cr(CO)$_3$ unit from the phenyl ring, or of the (C$_6$H$_5$)Cr(CO)$_3$ group from the cyclic trimer, was detected during the reaction of 16 with NaOCH$_2$CF$_3$.

The analogous synthesis of $N_3P_3(OCH_2CF_3)_5$[(OC$_6$H$_5$)Cr(CO)$_3$] (19) (Scheme IIb) was accomplished by both methods A and B with the use of $N_3P_3Cl_5(OC_6H_5)$ (7) as the starting compound. Thus, in method A, 7 was allowed to react with NaOCH$_2$CF$_3$ to yield $N_3P_3(OCH_2CF_3)_5$[(OC$_6$H$_5$)Cr(CO)$_3$] (8), which was treated with Cr(CO)$_6$ to yield

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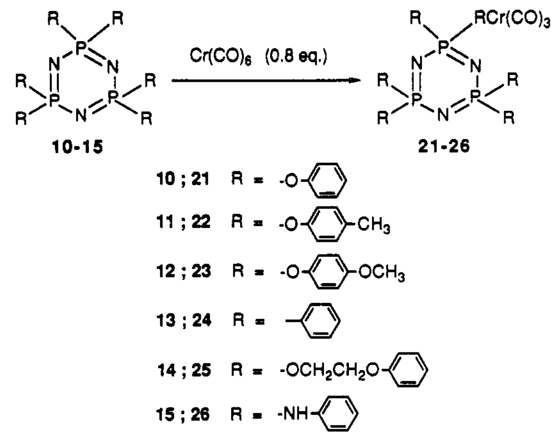
(9) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic: New York, 1972 and references cited therein.

Scheme III. Synthesis of $N_3P_3R_5[RCr(CO)_3]$ Complexes



the product 19. In method B, 7 was allowed to react first with $Cr(CO)_6$ to yield $N_3P_3Cl_5[(OC_6H_5)Cr(CO)_3]$ (18), which was then allowed to react with $NaOCH_2CF_3$ to yield product 19. However, in several experiments, the reaction of 18 with $NaOCH_2CF_3$ resulted in displacement of the (arene)$Cr(CO)_3$ group from the cyclic trimer. The products of the substitution reaction were identified as $N_3P_3(OCH_2CF_3)_6$ and $(HOC_6H_5)Cr(CO)_3$. This displacement reaction was minimized by the use of (a) low reaction temperatures (0 °C), (b) stoichiometric quantities of $NaOCH_2CF_3$ (i.e., 5 equiv), and (c) dilute reaction conditions.

Synthesis of $N_3P_3R_5[RCr(CO)_3]$ Complexes. The series of compounds 21–26 have the general structure $N_3P_3R_5[RCr(CO)_3]$, where the R substituents were phenoxy (21), 4-methylphenoxy (22), 4-methoxyphenoxy (23), phenyl (24), 2-phenoxyethoxy (25), and anilino (26) (see Scheme III).

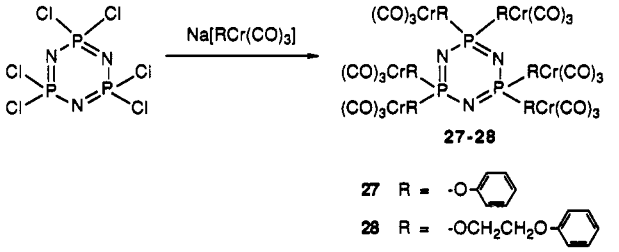
The synthesis of complexes 21–26 is summarized in Scheme III and was accomplished by the reaction of the hexaaryl-substituted trimers $N_3P_3R_6$ (10–15) with a deficiency of $Cr(CO)_6$ (i.e., 0.8 equiv). The use of a deficiency of $Cr(CO)_6$, as opposed to 1 equiv, favored the formation of the desired monosubstituted arene complex. In general, the disubstituted arene complex, $N_3P_3R_4[RCr(CO)_3]_2$, was formed in very low yield and could be differentiated clearly from $N_3P_3R_6$ and $N_3P_3R_5[RCr(CO)_3]$ by thin-layer chromatography.

Additional hexaaryl-substituted cyclotriphosphazenes were studied with the use of this synthetic scheme. Examples include 2-napthoxy, 4-phenylphenoxy, and 4-fluorophenoxy derivatives. Arene complexes of the 2-napthoxy and 4-phenylphenoxy derivatives were prepared. However, the availability of two aryl rings per side group for π coordination yielded isomers for the $N_3P_3R_5[RCr(CO)_3]$ complexes.[8] These isomers were difficult to separate completely by chromatography. In the case of the 4-fluorophenoxy derivative, no arene complex formation was detected after extended reaction times with excess $Cr(CO)_6$. Presumably, the electron-withdrawing fluoro substituent deactivated the phenoxy ring to π complexation.[8]

Synthesis of $N_3P_3[RCr(CO)_3]_6$ Complexes. Compounds 27 and 28 have the general structure $N_3P_3[RCr(CO)_3]_6$, where the R substituents were phenoxy (27) and 2-phenoxyethoxy (28) (see Scheme IV).

The synthesis of the hexaarene-substituted trimers 27 and 28 is outlined in Scheme IV and was accomplished by the reaction of $N_3P_3Cl_6$ with an excess of $(NaOC_6H_5)Cr(CO)_3$ or $(NaOCH_2CH_2OC_6H_5)Cr(CO)_3$, respectively. The substitution reaction took place readily and was quantitative by ^{31}P NMR spectroscopy. Singlet ^{31}P NMR resonances at +8.5 and +17 ppm, respectively, were detected for the fully substituted species. Species 27 and 28 represent unique examples of cyclotriphosphazenes that possess one transition metal on every side-group unit.

Scheme IV. Synthesis of $N_3P_3[RCr(CO)_3]_6$ Complexes



An alternative synthesis of $N_3P_3[(OC_6H_5)Cr(CO)_3]_6$ (27) was attempted by the reaction of $N_3P_3(OC_6H_5)_6$ (10) with a large excess of $Cr(CO)_6$ (i.e., up to ca. 18 equiv) in di-*n*-butyl ether/THF for 7 days at reflux. The progress of the reaction was monitored by thin-layer chromatography and the various substitution products could be identified clearly. After 7 days of reaction, the major products were found to be the tri-, tetra-, and pentaarene-substituted complexes.

Thus, the synthetic strategy of the reaction of $Cr(CO)_6$ with $N_3P_3(OC_6H_5)_6$ (10) or other $N_3P_3R_6$ species was successful for the incorporation of *moderate loadings* of $Cr(CO)_3$ units, while the protocol of the reaction of $N_3P_3Cl_6$ with $(NaOC_6H_5)Cr(CO)_3$ or $(NaOCH_2CH_2OC_6H_5)Cr(CO)_3$ provided a controlled method for the incorporation of *high loadings* of $Cr(CO)_3$ units. Although the second approach has been developed only for compounds with phenoxy and 2-phenoxyethoxy as the arene ligands, the strategy should be applicable to a wide variety of phenoxides and aryl-containing alkoxides.

General Properties. Arene complexes 16–28 were yellow in color and were fully soluble in common organic solvents such at THF, methylene chloride, and acetone. In the solid state, the products were reasonably air and moisture stable. However, after several hours in solution in contact with air or moisture, the complexes decomposed to yield a green residue. This was presumably a consequence of oxidation of the chromium center from Cr(0) to a paramagnetic Cr(III) species.[8]

Structural Proof of Cyclotriphosphazene–Chromium Tricarbonyl Complexes. Compounds 16–28 were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, infrared spectroscopy, mass spectrometry, and elemental microanalysis. The NMR spectroscopic data are summarized in Tables I–III, and the analytical data are shown in Table IV. In the tables of NMR data, the spectra of the $N_3P_3X_5R$ (5–9) and $N_3P_3R_6$ (10–15) species are included for comparison with those of the corresponding arene products (16–28).

(a) NMR Spectroscopy. The ^1H NMR spectra of 16–28 confirmed the metal coordination to the aryl substituent. A characteristic feature of the spectra was that the (η^6-arene)$Cr(CO)_3$ protons resonated at significantly higher field (ca. 2 ppm) than the corresponding uncomplexed ligands (see Table I).[8] In general, the protons on the uncomplexed arene ligand were in the region from 7.9 to 6.7 ppm, while the protons on the complexed arene ligand were at 6.0–4.5 ppm. This upfield shift of the aromatic protons can be ascribed to a reduction in the ring current and an overall withdrawal of π electrons from the arene ring by the $Cr(CO)_3$ unit.[8] The cummulative effect is a reduction in the deshielding of the aromatic protons.

Similarily, the ^{13}C NMR spectra of 16–28 provided evidence for complex formation (see Table II). This was

Table I. ^{1}H NMR Characterization Data

compd	^{1}H NMR, ppm[a]
	$N_3P_3X_5R$
X = F, R = C_6H_5 (5)	7.87–7.81 (m, 2 H, Ar H), 7.62–7.60 (m, 1 H, Ar H), 7.55–7.48 (m, 2 H, Ar H)
X = OCH_2CF_3, R = C_6H_5 (6)	7.87–7.81 (m, 2 H, Ar H), 7.62–7.60 (m, 1 H, Ar H), 7.55–7.49 (m, 2 H, Ar H), 4.38–4.30 (m, 4 H, OCH_2CF_3), 4.24–4.10 (m, 6 H, OCH_2CF_3)
X = Cl, R = OC_6H_5 (7)	7.44–7.19 (m, Ar H)
X = OCH_2CF_3, R = OC_6H_5 (8)	7.39–7.35 (m, 2 H, Ar H), 7.25–7.21 (m, 3 H, Ar H), 4.48–4.39 (m, 2 H, gem OCH_2CF_3), 4.31–4.22 (m, 4 H, non-gem OCH_2CF_3), 3.92–3.78 (m, 4 H, non-gem OCH_2CF_3)
X = $NHCH_2CH_2CH_3$, R = OC_6H_5 (9)	7.18–6.95 (m, 5 H, Ar H), 2.93–2.89 (m, 2 H, $NHCH_2$), 2.78–2.73 (m, 4 H, $NHCH_2$), 2.56–2.53 (m, 5 H, NH and $NHCH_2$), 2.07–2.01 (m, 2 H, NH), 1.79–1.70 (m, 2 H, NH), 1.49–1.37 (m, 6 H, CH_2), 1.29–1.22 (m, 4 H, CH_2), 0.85–0.78 (m, 9 H, CH_3), 0.73–0.69 (m, 6 H, CH_3)
	$N_3P_3R_6$
R = OC_6H_5 (10)	7.26–7.09 (m, 3 H, Ar H), 6.97–6.89 (m, 2 H, Ar H)
R = $OC_6H_4CH_3$-4 (11)	6.96 (d, 2 H, Ar H), 6.81 (d, 2 H, Ar H), 2.32 (s, 3 H, CH_3)
R = $OC_6H_4OCH_3$-4 (12)	6.85 (d, 2 H, Ar H), 6.68 (d, 2 H, Ar H), 3.77 (s, 3 H, OCH_3)
R = C_6H_5 (13)	7.80–7.74 (m, 2 H, Ar H), 7.35–7.27 (m, 3 H, Ar H)
R = $OCH_2CH_2OC_6H_5$ (14)	7.26–7.20 (m, 2 H, Ar H), 6.95–6.84 (m, 3 H, Ar H), 4.29–4.27 (m, 2 H, OCH_2), 4.13–4.10 (m, 2 H, OCH_2)
R = NHC_6H_5 (15)	7.20–7.17 (m, 2 H, Ar H), 7.05–6.99 (m, 2 H, Ar H), 6.72–6.68 (m, 1 H, Ar H), 6.54–6.52 (m, 1 H, NH)[b]
	$N_3P_3X_5[RCr(CO)_3]$[c]
X = F, R = C_6H_5 (16)	**5.9–5.8 (m, 2 H, Ar H), 5.7–5.6 (m, 1 H, Ar H), 5.3–5.1 (m, 2 H, Ar H)**
X = OCH_2CF_3, R = C_6H_5 (17)	**5.9–5.7 (m, 2 H, Ar H), 5.6–5.5 (m, 1 H, Ar H), 5.4–5.1 (m, 2 H, Ar H)**, 4.5–4.1 (m, 10 H, OCH_2CF_3)
X = Cl, R = OC_6H_5 (18)	**5.7–4.8 (m, Ar H)**
X = OCH_2CF_3, R = OC_6H_5 (19)	**5.7–4.8 (m, 5 H, Ar H)**, 4.6–3.7 (m, 10 H, OCH_2CF_3)
X = $NHCH_2CH_2CH_3$, R = OC_6H_5 (20)	**5.6–5.4 (m, 4 H, Ar H), 4.8–4.7 (m, 1 H, Ar H)**, 2.9–2.5 (m, 11 H, $NHCH_2$ (10 H) and NH (1 H)), 2.2–1.7 (m, 4 H, NH), 1.5–1.2 (m, 10 H, CH_2), 0.9–0.6 (m, 15 H, CH_3)
	$N_3P_3R_5[RCr(CO)_3]$[c]
R = OC_6H_5 (21)	7.5–6.4 (m, 25 H, Ar H), **5.3–4.6 (m, 5 H, Ar H)**
R = $OC_6H_4CH_3$-4 (22)	7.2–6.7 (m, 20 H, Ar H), **5.1–4.9 (m, 4 H, Ar H)**, 2.5–2.3 (s, 15 H, CH_3), **2.1–2.0 (s, 3 H, CH_3)**
R = $OC_6H_4OCH_3$-4 (23)	7.0–6.7 (m, 20 H, ArH), **5.2–4.8 (dd, 4 H, Ar H)**, 3.8–3.7 (br s, 15 H, OCH_3), **3.6–3.5 (br s, 3 H, OCH_3)**
R = C_6H_5 (24)	8.3–7.1 (m, 25 H, Ar H), **5.6–4.8 (m, 5 H, Ar H)**
R = $OCH_2CH_2OC_6H_5$ (25)	7.4–6.7 (m, 25 H, Ar H), **5.5–4.7 (m, 5 H, Ar H)**, 4.5–4.1 (m, 20 H, OCH_2), **4.0–3.7 (m, 4 H, OCH_2)**
R = NHC_6H_5 (26)	7.2–6.5 (m, 30 H, Ar H, NH), **5.7–5.5 (m, 4 H, Ar H), 5.0–4.9 (m, 1 H, Ar H)**[b]
	$N_3P_3[RCr(CO)_3]_6$[c]
R = OC_6H_5 (27)	**5.8–5.1 (m, Ar H)**[b]
R = $OCH_2CH_2OC_6H_5$ (28)	**5.8–5.4 (m, 12 H, Ar H), 5.3–5.0 (m, 12 H, Ar H), 4.9–4.7 (m, 6 H, Ar H), 4.3–4.1 (m, 12 H, OCH_2), 4.3–4.0 (m, 12 H, OCH_2)**

[a] In $CDCl_3$ solvent. [b] In acetone-d_6 solvent. [c] Resonances in boldface correspond to $RCr(CO)_3$ complex.

Table II. ^{13}C NMR Characterization Data

compd	^{13}C NMR, ppm[a–c]
	$N_3P_3X_5R$
X = F, R = C_6H_5 (5)	134.2 (d, $^4J_{CP}$ = 3 Hz), 130.5 (d, $^3J_{CP}$ = 12 Hz), 128.9 (d, $^2J_{CP}$ = 17 Hz), 126.4 (dd, $^1J_{CP}$ = 203 Hz, $^2J_{CF}$ = 32 Hz)
X = OCH_2CF_3, R = C_6H_5 (6)	133.0 (d, $^4J_{CP}$ = 3 Hz), 130.3 (d, $^3J_{CP}$ = 11 Hz), 129.8 (d, $^1J_{CP}$ = 184 Hz), 128.8 (d, $^2J_{CP}$ = 16 Hz), 122.5 (q, $^1J_{CF}$ = 280 Hz, CF_3), 62.9 (q, $^2J_{CF}$ = 38 Hz, OCH_2), 61.2 (q, $^2J_{CF}$ = 38 Hz, OCH_2)
X = Cl, R = OC_6H_5 (7)	149.4, 129.9, 126.7, 121.4
X = OCH_2CF_3, R = OC_6H_5 (8)	147.7, 129.9, 126.3, 122.3 (q, $^1J_{CF}$ = 270 Hz, CF_3), 121.3, 62.8 (q, $^2J_{CF}$ = 38 Hz, OCH_2)
X = $NHCH_2CH_2CH_3$, R = OC_6H_5 (9)	151.8, 128.6, 123.7, 121.7, 42.6 (CH_2), 42.5 (CH_2), 42.3 (CH_2), 24.8 (CH_2), 24.7 (CH_2), 24.6 (CH_2), 11.2 (CH_3), 11.1 (CH_3)
	$N_3P_3R_6$
R = OC_6H_5 (10)	150.7, 129.4, 124.8, 121.0
R = $OC_6H_4CH_3$-4 (11)	148.4, 134.0, 129.7, 120.8, 20.8 (CH_3)
R = $OC_6H_4OCH_3$-4 (12)	156.4, 144.2, 120.8, 114.2, 55.4 (OCH_3)
R = C_6H_5 (13)	138.3 (d, $^1J_{CP}$ = 133 Hz), 130.6 (d, $^3J_{CP}$ = 12 Hz), 130.2, 127.7 (d, $^2J_{CP}$ = 14 Hz)
R = $OCH_2CH_2OC_6H_5$ (14)	158.4, 129.4, 120.9, 114.5, 66.5 (CH_2), 64.4 (CH_2)
R = NHC_6H_5 (15)	143.0, 129.1, 120.5, 118.5[d]
	$N_3P_3X_5[RCr(CO)_3]$[e]
X = F, R = C_6H_5 (16)	**229.1 (CO), 95.4, 94.9 (d, $^3J_{CP}$ = 11 Hz), 86.9 (d, $^2J_{CP}$ = 13 Hz)**
X = OCH_2CF_3, R = C_6H_5 (17)	**230.5 (CO)**, 122.5 (q, $^1J_{CF}$ = 275 Hz, CF_3), **95.5, 95.0 (d, $^3J_{CP}$ = 10 Hz), 91.7 (d, $^1J_{CP}$ = 210 Hz), 88.0 (d, $^2J_{CP}$ = 12 Hz)**, 63.1 (q, $^2J_{CF}$ = 38 Hz, OCH_2), 62.8 (q, $^2J_{CF}$ = 38 Hz, OCH_2)
X = Cl, R = OC_6H_5 (18)	**231.1 (CO), 130.9, 92.2, 87.8, 84.3**
X = OCH_2CF_3, R = OC_6H_5 (19)	**231.6 (CO), 131.7**, 122.3 (q, $^1J_{CF}$ = 279 Hz, CF_3), **93.0, 87.2, 83.7**, 63.1 (q, $^2J_{CF}$ = 38 Hz, OCH_2)
X = $NHCH_2CH_2CH_3$, R = OC_6H_5 (20)	**232.3 (CO), 135.4, 93.8, 86.2, 84.5**, 42.6 (CH_2), 42.5 (CH_2), 42.4 (CH_2), 24.8 (CH_2), 24.7 (CH_2), 24.6 (CH_2), 11.2 (CH_3), 11.1 (CH_3)
	$N_3P_3R_5[RCr(CO)_3]$[e]
R = OC_6H_5 (21)	**232.0 (CO)**, 150.4, **132.5**, 129.7, 125.2, 121.0, **93.0, 86.9, 84.9**
R = $OC_6H_4CH_3$-4 (22)	**232.5 (CO)**, 148.3, **134.6**, 134.1, 129.8, 120.8, **103.9, 93.1, 86.4**, 20.8 (CH_3), **19.9 (CH_3)**
R = $OC_6H_4OCH_3$-4 (23)	**232.3 (CO)**, 156.7, 144.2, **138.7, 125.1**, 121.8, 114.3, **87.3, 77.2, 56.0 (OCH_3)**, 55.4 (OCH_3)
R = C_6H_5 (24)	**231.5 (CO)**, 138.3 (d, $^1J_{CP}$ = 134 Hz), 131.2, 130.5 (d, $^2J_{CP}$ = 27 Hz), 127.8 (d, $^3J_{CP}$ = 12 Hz), **103.5 (d, $^1J_{CP}$ = 139 Hz), 96.1 (d, J_{CP} = 9 Hz), 94.8, 87.8 (d, J_{CP} = 9 Hz)**
R = $OCH_2CH_2OC_6H_5$ (25)	**233.1 (CO)**, 158.4, **142.0**, 129.5, 121.0, 114.5, **94.9, 85.4, 78.6, 67.4 (CH_2)**, 66.6 (CH_2), 64.5 (CH_2), **63.6 (CH_2)**
R = NHC_6H_5 (26)	**227.9 (CO)**, 143.0, 129.3, **121.4**, 120.6, 118.6, **97.3, 87.5, 82.9**[d]
	$N_3P_3[RCr(CO)_3]_6$[e]
R = OC_6H_5 (27)	**230.9 (CO), 133.2, 95.8, 90.1, 86.2**[d]
R = $OCH_2CH_2OC_6H_5$ (28)	**233.2 (CO), 142.2, 95.5, 85.9, 78.9, 67.5 (CH_2), 64.0 (CH_2)**

[a] In $CDCl_3$ solvent. [b] Resonances are singlets unless coupling is noted. [c] *Resonances correspond to aromatic carbon atoms unless noted.* [d] In acetone-d_6 solvent. [e] Resonances in boldface correspond to $RCr(CO)_3$ complex.

indicated by an upfield shift of ca. 35–40 ppm in the resonances of the arene carbon atoms.[8] In general, the carbon atoms of the uncomplexed arene ligand resonated in the region from 158 to 114 ppm, while the carbon atoms of the complexed arene ligand were in the region from 142 to 77 ppm. This characteristic of an upfield shift in the arene carbon resonances is illustrated clearly in Figure 1, by a comparison of the aromatic region of the ^{13}C NMR spectra of the series of compounds $N_3P_3(OC_6H_5)_6$ (10), $N_3P_3(OC_6H_5)_5[(OC_6H_5)Cr(CO)_3]$ (21), and $N_3P_3[(OC_6H_5)$-

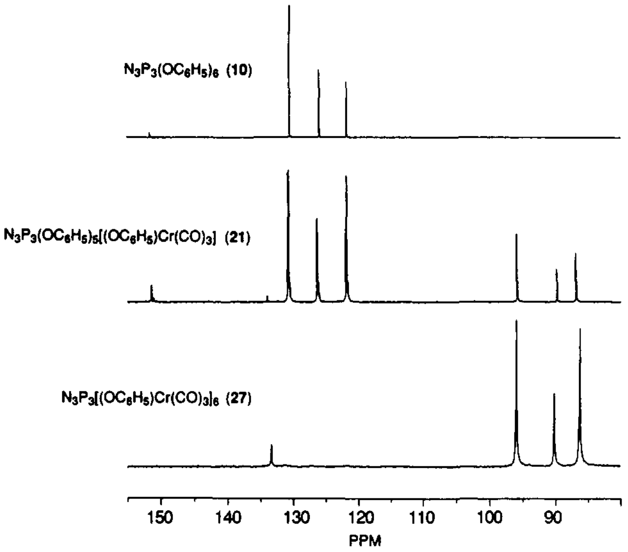


Figure 1. Aromatic region of the ^{13}C NMR spectra (90.0 MHz) of $N_3P_3(OC_6H_5)_6$ (**10**), $N_3P_3(OC_6H_5)_5[(OC_6H_5)Cr(CO)_3]$ (**21**), and $N_3P_3[(OC_6H_5)Cr(CO)_3]_6$ (**27**) in acetone-d_6.

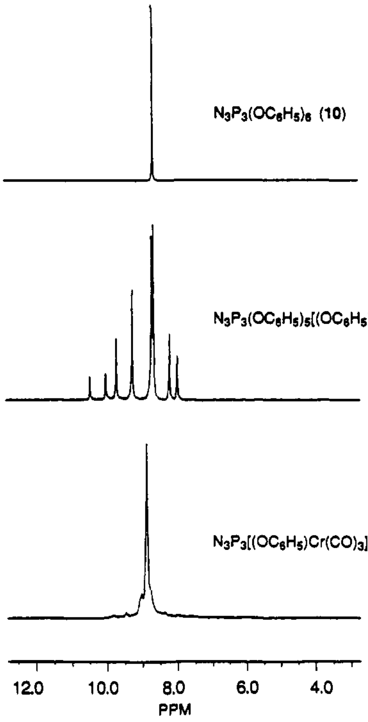


Figure 2. ^{31}P NMR spectra (145.8 MHz) and $N_3P_3(OC_6H_5)_6$ (**10**), $N_3P_3(OC_6H_5)_5[(OC_6H_5)Cr(CO)_3]$ (**21**), and $N_3P_3[(OC_6H_5)Cr(CO)_3]_6$ (**27**) in acetone-d_6.

Table III. ^{31}P NMR Characterization Data

compd	^{31}P NMR, ppm[a]
$N_3P_3X_5R$	
X = F, R = C_6H_5 (**5**)	34.3 (d, $^2J_{PNP}$ = 77 Hz, $^1J_{PF}$ = 988 Hz), 8.3 (t, $^2J_{PNP}$ = 77 Hz, $^1J_{PF}$ = 988 Hz)
X = OCH_2CF_3, R = C_6H_5 (**6**)	28.9 (t, $^2J_{PNP}$ = 54 Hz), 15.9 (d, $^2J_{PNP}$ = 54 Hz)
X = Cl, R = OC_6H_5 (**7**)	22.2 (d, $^2J_{PNP}$ = 61 Hz), 12.0 (t, $^2J_{PNP}$ = 61 Hz)
X = OCH_2CF_3, R = OC_6H_5 (**8**)	AB_2 (ν_A = 13.2, ν_B = 16.7, $^2J_{PNP}$ = 90 Hz)[b]
X = $NHCH_2CH_2CH_3$, R = OC_6H_5 (**9**)	AB_2 (ν_A = 18.2, ν_B = 17.3, $^2J_{PNP}$ = 45 Hz)[b]
$N_3P_3R_6$	
R = OC_6H_5 (**10**)	8.5 (s)
R = $OC_6H_4CH_3$-4 (**11**)	8.9 (s)
R = $OC_6H_4OCH_3$-4 (**12**)	9.8 (s)
R = C_6H_5 (**13**)	14.9 (s)
R = $OCH_2CH_2OC_6H_5$ (**14**)	17.7 (s)
R = NHC_6H_5 (**15**)	2.3 (s)[c]
$N_3P_3X_5[RCr(CO)_3]$	
X = F, R = C_6H_5 (**16**)	34.4 (d, $^2J_{PNP}$ = 84, $^1J_{PF}$ = 978), 7.7 (t, $^2J_{PNP}$ = 84, $^1J_{PF}$ = 978)
X = OCH_2CF_3, R = C_6H_5 (**17**)	28.5 (t, $^2J_{PNP}$ = 55 Hz), 14.9 (d, $^2J_{PNP}$ = 55 Hz)
X = Cl, R = OC_6H_5 (**18**)	22.3 (d, $^2J_{PNP}$ = 62 Hz), 12.7 (t, $^2J_{PNP}$ = 62 Hz)
X = OCH_2CF_3, R = OC_6H_5 (**19**)	AB_2 (ν_A = 12.7, ν_B = 16.2, $^2J_{PNP}$ = 90 Hz)[b]
X = $NHCH_2CH_2CH_3$, R = OC_6H_5 (**20**)	AB_2 (ν_A = 19.0, ν_B = 17.6, $^2J_{PNP}$ = 45 Hz)[b]
$N_3P_3R_5[RCr(CO)_3]$	
R = OC_6H_5 (**21**)	AB_2 (ν_A = 9.7, ν_B = 8.4, $^2J_{PNP}$ = 45 Hz)[b]
R = $OC_6H_4CH_3$-4 (**22**)	AB_2 (ν_A = 10.0, ν_B = 8.7, $^2J_{PNP}$ = 45 Hz)[b]
R = $OC_6H_4OCH_3$-4 (**23**)	AB_2 (ν_A = 10.6, ν_B = 9.5, $^2J_{PNP}$ = 45 Hz)[b]
R = C_6H_5 (**24**)	14.2 (m)[d]
R = $OCH_2CH_2OC_6H_5$ (**25**)	17.7 (s)
R = NHC_6H_5 (**26**)	2.0 (m)[c,d]
$N_3P_3[RCr(CO)_3]_6$	
R = OC_6H_5 (**27**)	8.8 (s)[c]
R = $OCH_2CH_2OC_6H_5$ (**28**)	17.6 (s)

[a] In $CDCl_3$ solvent. [b] Coupling determined by Bruker NMR Simulation Program PANIC. [c] In acetone-d_6 solvent. [d] Coupling not resolved.

$Cr(CO)_3]_6$ (**27**). Note that the ^{13}C NMR spectrum of $N_3P_3[(OC_6H_5)Cr(CO)_3]_6$ (**27**) supports the hexaarene-substituted structure.

In the ^{13}C NMR spectra, the CO ligands for the (η^6-arene)$Cr(CO)_3$ species **16–28** were detected as a single resonance in the region 233–228 ppm. This single resonance arises from the equivalence of the three CO ligands.[8]

An additional interesting feature in the ^{13}C NMR spectra was the detection of new resonances for substituents on the (η^6-arene)$Cr(CO)_3$ groups. As an example, for $N_3P_3(OC_6H_4CH_3\text{-}4)_5[(OC_6H_4CH_3\text{-}4)Cr(CO)_3]$ (**22**), the methyl group on the uncomplexed phenoxy ligand was detected at 20.8 ppm, while a new resonance of lesser intensity was detected at 19.9 ppm and was assigned to the methyl group on the complexed phenoxy ligand (see Table II). This was also apparent in complexes **23** and **25**, which possessed a methoxy para substituent and a connecting ethylene oxide group, respectively.

In selected cases, characterization of complexes **16–28** by ^{31}P NMR spectroscopy was important in order to illustrate the effect of the π coordination of a transition metal to an aryl substituent on the environment at the phosphorus atom, as well as to monitor the progress of the substitution reaction in the synthesis of **27** and **28**, as mentioned previously (see Table III).

^{31}P NMR spectroscopy was particularily interesting for the $N_3P_3R_5[RCr(CO)_3]$ complexes **21–24** and **26**. In these complexes, incorporation of one $Cr(CO)_3$ unit generated an inequivalent phosphorus atom. This feature is illustrated clearly in Figure 2, where the ^{31}P NMR spectra of $N_3P_3(OC_6H_5)_6$ (**10**), $N_3P_3(OC_6H_5)_5[(OC_6H_5)Cr(CO)_3]$ (**21**), and $N_3P_3[(OC_6H_5)Cr(CO)_3]_6$ (**27**) are shown. The ^{31}P NMR spectrum for **10** was a singlet resonance at +8.5 ppm, for **21** was a second-order AB_2 spin system, with ν_A = +9.7 ppm, ν_B = +8.4 ppm, and $^2J_{PNP}$ = 45 Hz,[10] and for **27** was a broad singlet at +8.8 ppm.

The second-order AB_2 spectrum for **21** arises from the inequivalent nature of the two phosphorus atoms that bear

Table IV. Analytical Data for Cyclotriphosphazene–Chromium Tricarbonyl Complexes

		mass spectral data, *m*/*e*		anal.		
compd	IR: ν_{CO}, cm^{-1}[a]	calcd	found	elem	calcd, %	found, %
		$N_3P_3X_5[RCr(CO)_3]$				
X = F, R = C_6H_5 (**16**)	1992, 1925	443	443	C	24.40	24.59
				H	1.14	1.13
				N	9.49	9.47
X = OCH_2CF_3, R = C_6H_5 (**17**)	1985, 1916	843	787 (M^+ − 2CO)	C	27.06	27.33
				H	1.79	2.51
				N	4.98	4.84
X = Cl, R = OC_6H_5 (**18**)	1982, 1908	541	485 (M^+ − 2CO)[b]	C	19.97	21.64
				H	0.93	1.64
				N	7.76	7.38
X = OCH_2CF_3, R = OC_6H_5 (**19**)	1980, 1905	859	803 (M^+ − 2CO)	C	26.56	27.50
				H	1.76	2.29
				N	4.89	4.41
X = $NHCH_2CH_2CH_3$, R = OC_6H_5 (**20**)	1970, 1890	654	655 (M^+ + 1)[c]	C	44.03	44.42
				H	6.93	8.09
				N	17.12	18.44
		$N_3P_3R_5[RCr(CO)_3]$				
R = OC_6H_5 (**21**)	1976, 1899	829	745 (M^+ − 3CO)	C	56.46	56.10
				H	3.65	3.77
				N	5.07	4.99
R = $OC_6H_4CH_3$-4 (**22**)	1971, 1893	913	829 (M^+ − 3CO)	C	59.15	58.77
				H	4.63	4.89
				N	4.60	4.62
R = $OC_6H_4OCH_3$-4 (**23**)	1971, 1892	1009	1010 (M^+ + 1)[c]	C	53.52	51.85
				H	4.19	5.48
				N	4.16	3.92
R = C_6H_5 (**24**)	1974, 1900	733	649 (M^+ − 3CO)	C	63.85	62.50
				H	4.12	4.45
				N	5.73	5.91
R = $OCH_2CH_2OC_6H_5$ (**25**)	1967, 1887	1093	1094 (M^+ + 1)[c]	C	55.99	55.10
				H	4.98	5.46
				N	3.84	3.49
R = NHC_6H_5 (**26**)	1962, 1883	823	824 (M^+ + 1)[c]	C	56.87	57.23
				H	4.41	4.64
				N	15.31	15.40
		$N_3P_3[RCr(CO)_3]_6$				
R = OC_6H_5 (**27**)	1979, 1904	1509	1510 (M^+ + 1)[c]	C	42.96	42.73
				H	2.00	2.54
				N	2.78	2.75
R = $OCH_2CH_2OC_6H_5$ (**28**)	1969, 1887	1733	1734 (M^+ + 1)[c]	C	44.68	44.34
				H	3.07	3.33
				N	2.37	2.31

[a] In CH_2Cl_2 solution. [b] Cl_5 isotope pattern detected. [c] Determined by positive fast atom bombardment.

phenoxy groups compared to the phosphorus atom that bears a phenoxy group and a phenoxy chromium tricarbonyl group.[10] It is interesting to note that the ^{31}P NMR spectrum of a cyclotriphosphazene that bears five phenoxy groups and one para-substituted phenoxy group, for example $N_3P_3(OC_6H_5)_5(OC_6H_4Br\text{-}4)$ or $N_3P_3(OC_6H_5)_5(OC_6H_4CH_3\text{-}4)$, consists of a singlet resonance at +8.5 ppm. Therefore, the introduction of a $Cr(CO)_3$ unit perturbates the electronic environment at the phosphorus center to a greater extent than does the incorporation of a *p*-halogeno- or *p*-alkyl-substituent.

One exception to the ^{31}P NMR spectral behavior of $N_3P_3R_5[RCr(CO)_3]$ complexes was species $N_3P_3(OCH_2CH_2OC_6H_5)_5[(OCH_2CH_2OC_6H_5)Cr(CO)_3]$ (**25**). The ^{31}P NMR spectrum of **25** was a singlet resonance at +17.7 ppm, which was unchanged from the starting compound $N_3P_3(OCH_2CH_2OC_6H_5)_6$ (**14**). This reflects the ability of an ethylene oxide unit to decouple the electronic properties of the (η^6-arene)$Cr(CO)_3$ group from the phosphazene ring.

(b) Infrared Spectroscopy. The IR spectra of **16**–**28** in solution showed two intense C–O stretching absorptions, one in the region 1992–1962 cm^{-1} and the other in the region 1925–1883 cm^{-1}.[8] The specific ν_{CO} absorption values for **16**–**28** are listed in Table IV. The presence of these two bands is a characteristic feature of (η^6-arene)$Cr(CO)_3$ complexes. In general, the ν_{CO} shifts to lower frequency with increased electron density on the arene substituent.[8] Thus, for species **16**–**28**, the frequency of the stretching absorption could be used as a probe of the overall electron density at the arene ligand. This electron density was determined by the electronic properties of the phosphazene cosubstituents and the arene para substituents.

For the series $N_3P_3X_5[RCr(CO)_3]$ (**16**–**20**), the CO stretching frequency decreased in order from species **16** to **20**. Thus, $N_3P_3F_5[(C_6H_5)Cr(CO)_3)]$ (**16**) had the highest CO stretching frequency (1992, 1925 cm^{-1}) and, hence, the most electron-deficient arene ligand. This resulted from a combination of the strong electron-withdrawing fluoro cosubstituents and the direct attachment of the phenyl ligand to the electron-withdrawing phosphazene skeleton. Replacement of the fluoro substituent in **16** by the less electron-withdrawing trifluoroethoxy group in **17** shifted ν_{CO} absorption to lower frequencies (1985, 1916 cm^{-1}).

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[10] (a) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd ed.*; Pergamon: Oxford, England, 1969. (b) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959. (c) $^2J_{PNP}$ coupling constants for second-order AB_2 spin systems were determined with the use of the Bruker NMR Simulation Program PANIC.

Table V. Summary of Crystal Data and Intensity Collection Parameters for $N_3P_3F_5[(C_6H_5)Cr(CO)_3]$ (16)

formula	$C_9H_5F_5N_3O_3P_3Cr$
fw	443.07
cryst size, mm	0.14 × 0.08 × 0.45
space group	$P2_1/c$
a, Å	6.458 (1)
b, Å	10.840 (1)
c, Å	22.122 (3)
α, deg	
β, deg	91.72 (1)
γ, deg	
V, Å^3	1548.0
Z	4
d(calcd), g/cm^3	1.901
θ limits, deg	5–65
μ, cm^{-1}	99.12
radiation (λ, Å)	Cu Kα
T, K	293 (1)
scan method	$\omega/2\theta$
ω-scan width, deg	0.60 + 0.14 tan θ
cryst decay, %	2.5
empirical abs cor	
min cor factor	0.703
max cor factor	1.000
no. of unique data measd	2789
no. of data used [$I > 3\sigma(I)$]	1946
data:param ratio	9
R, R_w ($=(\sum\Delta^2/\sum wF_o^2)^{1/2}$)	0.0456, 0.0643
$(\Delta/\sigma)_{max}$ in last cycle	<0.05
$\Delta\rho$ in final ΔF map, e Å^{-3}	0.384
p (weighting factor)	0.080
error in weights	1.358

This trend in the relationship of the CO stretching frequencies to the electronic properties of the phosphazene cosubstituent was also found in the analogous phenoxy-substituted arene complexes **18–20**. In this series, the ν_{CO} absorption for the chloro-substituted species (**18**) (1982, 1908 cm^{-1}) shifted to lower frequency following replacement of a chloro group with a trifluoroethoxy group (**19**) (1980, 1905 cm^{-1}) and to even lower frequencies following replacement by an electron-donating n-propylamino group (**20**) (1970, 1908 cm^{-1}). A comparison between the ν_{CO} values for the trifluoroethoxy-substituted complexes **17** and **19** illustrated that a phenoxy substituent linked to a cyclotriphosphazene was indeed more electron-rich than a phenyl group attached to the same ring.

In a similar manner, the ν_{CO} shifts for the $N_3P_3R_5[RCr(CO)_3]$ complexes **21–26** depended on the para substituents on the arene ligand. In the series **21–23**, the ν_{CO} absorption shifted to lower frequencies following the replacement of the phenoxy group in **21** (1976, 1899 cm^{-1}) by the electron-donating p-methylphenoxy (**22**) (1971, 1983 cm^{-1}) and p-methoxyphenoxy (**23**) (1971, 1892 cm^{-1}) groups. Surprisingly, ν_{CO} absorption for the phenyl-substituted trimer **24** (1974, 1900 cm^{-1}) was similar to that for the phenoxy-substituted trimer **21** (1976, 1899 cm^{-1}).

The most electron-rich arene ligand in the series **21–26** was found to be the anilino unit in **26** (1962, 1883 cm^{-1}). Presumably this was a consequence of the stronger electron-donating ability of the nitrogen atom in the anilino structure than the oxygen atom in the phenoxy structure. Note that ν_{CO} absorption for the 2-phenoxyethoxy-substituted trimer **25** (1967, 1887 cm^{-1}) was identical with that for (2-phenoxyethanol)chromium tricarbonyl (1968, 1887 cm^{-1}), which confirms the ability of the ethylene oxide group to decouple the electronic characteristics of the phosphazene ring from the arene.

(c) Mass Spectrometry. Mass spectral analysis of **16–28** confirmed the target structures (see Table IV). Characteristic M$^+$ – 2CO and M$^+$ – 3CO losses were detected from electron impact (EI) mass spectral analysis.

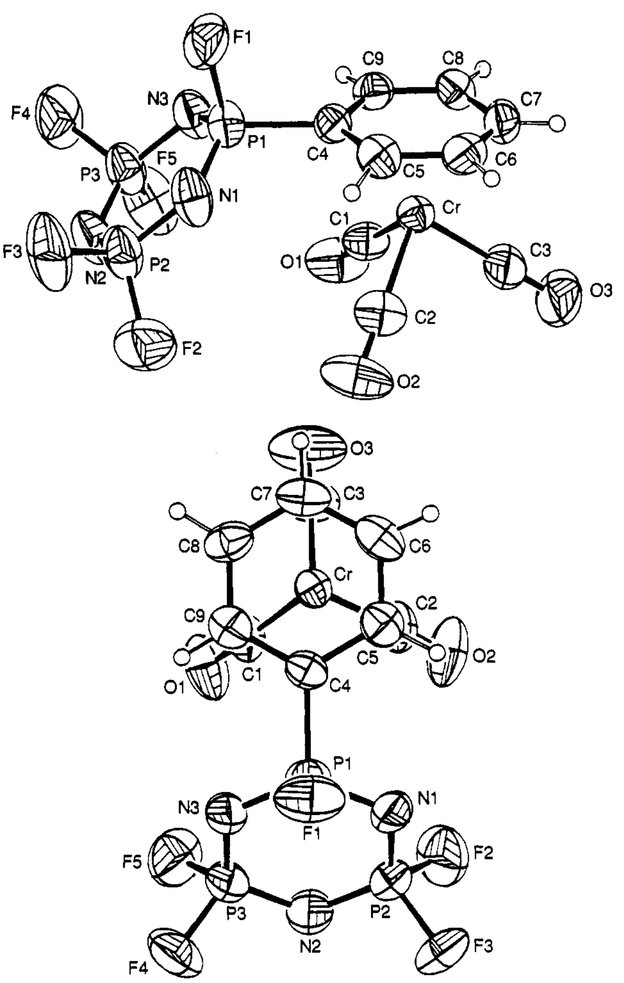

Figure 3. (a) Top: Molecular structure of $N_3P_3F_5[(C_6H_5)Cr(CO)_3]$ (**16**). (b) Bottom: Molecular structure of $N_3P_3F_5[(C_6H_5)Cr(CO)_3]$ (**16**), which shows the anti-eclipsed conformation of the $Cr(CO)_3$ group relative to the phenyl ligand.

Table VI. Selected Bond Distances (Å) for $N_3P_3F_5[(C_6H_5)Cr(CO)_3]$ (16)

Cr–C(1)	1.838 (5)	P(2)–N(1)	1.558 (5)
Cr–C(2)	1.845 (5)	P(2)–N(2)	1.542 (5)
Cr–C(3)	1.860 (5)	P(3)–F(4)	1.529 (4)
Cr–C(4)	2.194 (4)	P(3)–F(5)	1.517 (5)
Cr–C(5)	2.187 (5)	P(3)–N(2)	1.553 (5)
Cr–C(6)	2.208 (5)	P(3)–N(3)	1.565 (4)
Cr–C(7)	2.203 (5)	O(1)–C(1)	1.159 (6)
Cr–C(8)	2.208(5)	O(2)–C(2)	1.153 (7)
Cr–C(9)	2.185(4)	O(3)–C(3)	1.138 (7)
P(1)–F(1)	1.554 (3)	C(4)–C(5)	1.420 (6)
P(1)–N(1)	1.570 (4)	C(4)–C(9)	1.417 (6)
P(1)–N(3)	1.567 (5)	C(5)–C(6)	1.392 (7)
P(1)–C(4)	1.767 (5)	C(6)–C(7)	1.407 (7)
P(2)–F(2)	1.522 (4)	C(7)–C(8)	1.400 (7)
P(2)–F(3)	1.527 (4)	C(8)–C(9)	1.389 (7)

In several cases, the use of positive fast atom bombardment (FAB) mass spectroscopy allowed the detection of the molecular ion. Most notably, FAB mass spectroscopy allowed the detection of the molecular ion for the hexa-arene-substituted trimers $N_3P_3[(OC_6H_5)Cr(CO)_3]_6$ (**27**) (m/z 1509) and $N_3P_3[(OCH_2CH_2OC_6H_5)Cr(CO)_3]_6$ (**28**) (m/z 1733).

X-ray Structure Determination of $N_3P_3F_5[(C_6H_5)Cr(CO)_3]$ (16). An X-ray structure determination of $N_3P_3F_5[(C_6H_5)Cr(CO)_3]$ (**16**) was undertaken in order to confirm the η^6-coordination of the $Cr(CO)_3$ unit to the pendent arene ligand. The molecular structure of **16** is shown in Figures 3a,b. A summary of cell constants and

Table VII. Bond Angles (deg) for $N_3P_3F_5[(C_6H_5)Cr(CO)_3]$ (16)

C(1)–Cr–C(2)	87.5 (2)	F(2)–P(2)–F(3)	98.3 (2)
C(1)–Cr–C(3)	88.1 (2)	F(2)–P(2)–N(1)	110.1 (2)
C(1)–Cr–C(4)	101.7 (2)	F(2)–P(2)–N(2)	109.0 (3)
C(1)–Cr–C(5)	135.5 (3)	F(3)–P(2)–N(1)	109.5 (3)
C(1)–Cr–C(6)	167.4 (2)	F(3)–P(2)–N(2)	108.5 (2)
C(1)–Cr–C(7)	137.8 (3)	N(1)–P(2)–N(2)	119.4 (2)
C(1)–Cr–C(8)	103.9 (3)	F(4)–P(3)–F(5)	97.8 (2)
C(1)–Cr–C(9)	88.4 (2)	F(4)–P(3)–N(2)	109.7 (2)
C(2)–Cr–C(3)	88.7 (2)	F(4)–P(3)–N(3)	109.5 (2)
C(2)–Cr–C(4)	104.2 (3)	F(5)–P(3)–N(2)	109.8 (2)
C(2)–Cr–C(5)	87.6 (3)	F(5)–P(3)–N(3)	109.7 (2)
C(2)–Cr–C(6)	100.8 (3)	N(2)–P(3)–N(3)	118.5 (2)
C(2)–Cr–C(7)	133.8 (3)	P(3)–F(4)–F(5)	41.0 (1)
C(2)–Cr–C(8)	166.8 (3)	P(3)–F(5)–F(4)	41.3 (1)
C(2)–Cr–C(9)	139.3 (2)	P(1)–N(1)–P(2)	121.0 (3)
C(3)–Cr–C(4)	164.0 (3)	P(2)–N(2)–P(3)	121.5 (3)
C(3)–Cr–C(5)	136.0 (2)	P(1)–N(3)–P(3)	121.5 (3)
C(3)–Cr–C(6)	101.6 (2)	Cr–C(1)–O(1)	177.8 (4)
C(3)–Cr–C(7)	84.7 (3)	Cr–C(2)–O(2)	178.0 (4)
C(3)–Cr–C(8)	98.2 (3)	Cr–C(3)–O(3)	178.2 (5)
C(3)–Cr–C(9)	131.5 (2)	Cr–C(4)–P(1)	130.0 (2)
C(4)–Cr–C(5)	37.8 (2)	Cr–C(4)–C(5)	70.9 (3)
C(4)–Cr–C(6)	67.2 (2)	Cr–C(4)–C(9)	70.8 (3)
C(4)–Cr–C(7)	79.5 (2)	P(1)–C(4)–C(5)	120.4 (3)
C(4)–Cr–C(8)	67.3 (2)	P(1)–C(4)–C(9)	120.8 (3)
C(4)–Cr–C(9)	37.8 (2)	C(5)–C(4)–C(9)	118.9 (4)
C(5)–Cr–C(6)	36.9 (2)	Cr–C(5)–C(4)	71.4 (3)
C(5)–Cr–C(7)	67.1 (2)	Cr–C(5)–C(6)	72.4 (3)
C(5)–Cr–C(8)	79.6 (2)	C(4)–C(5)–C(6)	119.9 (4)
C(5)–Cr–C(9)	67.9 (2)	Cr–C(6)–C(5)	70.7 (3)
C(6)–Cr–C(7)	37.2 (2)	Cr–C(6)–C(7)	71.2 (3)
C(6)–Cr–C(8)	66.8 (2)	C(5)–C(6)–C(7)	120.4 (4)
C(6)–Cr–C(9)	79.2 (2)	Cr–C(7)–C(6)	71.7 (3)
C(7)–Cr–C(8)	37.1 (2)	Cr–C(7)–C(8)	71.7 (3)
C(7)–Cr–C(9)	66.8 (2)	C(6)–C(7)–C(8)	120.1 (4)
C(8)–Cr–C(9)	36.9 (2)	Cr–C(8)–C(7)	71.3 (3)
F(1)–P(1)–N(1)	106.2 (2)	Cr–C(8)–C(9)	70.6 (3)
F(1)–P(1)–N(3)	107.3 (2)	C(7)–C(8)–C(9)	120.0 (4)
F(1)–P(1)–C(4)	102.2 (2)	Cr–C(9)–C(4)	71.5 (2)
N(1)–P(1)–N(3)	117.8 (2)	Cr–C(9)–C(8)	72.5 (3)
N(1)–P(1)–C(4)	111.4 (2)	C(4)–C(9)–C(8)	120.8 (4)
N(3)–P(1)–C(4)	110.7 (2)		

Table VIII. Final Fractional Atomic Coordinates for $N_3P_3F_5[(C_6H_5)Cr(CO)_3]$ (16)

atom	*x*	*y*	*z*
Cr	0.61970 (11)	0.02352 (7)	0.34693 (3)
P(1)	0.9218 (2)	−0.2365 (1)	0.3984 (1)
P(2)	0.6751 (3)	−0.4365 (1)	0.3771 (1)
P(3)	0.7114 (3)	−0.3431 (1)	0.4901 (1)
F(1)	1.1595 (5)	−0.2581 (3)	0.3974 (2)
F(2)	0.4766 (6)	−0.4407 (4)	0.3383 (2)
F(3)	0.7612 (8)	−0.5628 (3)	0.3606 (2)
F(4)	0.8195 (7)	−0.4108 (4)	0.5428 (2)
F(5)	0.5391 (6)	−0.2844 (4)	0.5253 (2)
O(1)	0.3494 (6)	−0.0284 (5)	0.4517 (2)
O(2)	0.3447 (6)	−0.1504 (4)	0.2764 (2)
O(3)	0.3287 (6)	0.2304 (4)	0.3148 (2)
N(1)	0.8213 (7)	−0.3338 (4)	0.3539 (2)
N(2)	0.6185 (8)	−0.4383 (4)	0.4444 (2)
N(3)	0.8582 (7)	−0.2405 (4)	0.4662 (2)
C(1)	0.4573 (8)	−0.0091 (5)	0.4119 (2)
C(2)	0.4523 (8)	−0.0831 (5)	0.3026 (2)
C(3)	0.4381 (7)	0.1508 (5)	0.3262 (3)
C(4)	0.8979 (7)	−0.0853 (4)	0.3693 (2)
C(5)	0.8854 (7)	−0.0650 (5)	0.3059 (2)
C(6)	0.8716 (7)	0.0547 (5)	0.2833 (2)
C(7)	0.8631 (7)	0.1557 (5)	0.3230 (2)
C(8)	0.8751 (7)	0.1367 (4)	0.3856 (2)
C(9)	0.8900 (7)	0.0177 (4)	0.4086 (2)
H(5)	0.855 (8)	−0.137 (5)	0.278 (2)
H(6)	0.858 (9)	0.060 (5)	0.243 (2)
H(7)	0.843 (8)	0.235 (5)	0.309 (2)
H(8)	0.865 (8)	0.209 (5)	0.411 (2)
H(9)	0.886 (9)	0.003 (5)	0.450 (3)

data collection parameters is given in Table V. Selected bond lengths, bond angles, and final fractional atomic coordinates are shown in Tables VI–VIII, respectively.

An X-ray single-crystal analysis of 16 confirmed that the molecule consists of a pentafluorocyclotriphosphazene ring with a phenyl side group. A $Cr(CO)_3$ unit lies directly below the center of the phenyl ring. The average $Cr–C_{ar}$ (ar = arene) bond distance in 16 is 2.198 Å, which is consistent with π coordination of the $Cr(CO)_3$ group to the phenyl substituent in an η^6 manner.[8,11] The $Cr(CO)_3$ groups adopts a "piano-stool" structure that is typical of (η^6-arene)$Cr(CO)_3$ complexes.[8,11]

Interestingly, the $Cr(CO)_3$ group occupies an anti-eclipsed conformation relative to the carbon atoms of the phenyl ligand.[8] This feature can be seen clearly in the molecular structure shown in Figure 3b. The anti-eclipsed conformation is typical for (η^6-arene)$Cr(CO)_3$ derivatives in which the arene bears a strong electron-withdrawing substituent.[8] Thus, the solid-state conformation of the $Cr(CO)_3$ unit is in accordance with the known electron-withdrawing characteristics of the phosphazene ring.

Specific structural features of the (η^6-C_6H_5)$Cr(CO)_3$ group in 16 can be compared with (η^6-benzene)$Cr(CO)_3$.[8,11] In particular, the average $Cr–C_{CO}$ bond length in 16 of 1.848 Å is close to the average value of 1.842 Å found for the analogous benzene complex. The average C–O bond length in 16 of 1.150 Å is slightly longer than the average value of 1.145 Å for (η^6-benzene)$Cr(CO)_3$. The average $Cr–C_{ar}$ length in 16 is slightly shorter than that found in (η^6-benzene)$Cr(CO)_3$, with values of 2.198 and 2.221 Å, respectively. The average $C_{CO}–Cr–C_{CO}$ angle in 16 of 88.1° is close to the average value of 89° for the benzene analogue.

The P–N bond lengths and bond angles of the trimeric ring are similar to those in other fluoro-substituted cyclophosphazenes.[9,12,14] Specifically, the average P–N bond length in 16 is 1.559 Å, which is similar to the value of 1.560 Å for $N_3P_3F_6$. Additionally, the N–P–N average is 118.5°, and the P–N–P average is 121.3°. The P(1)–C(4) distance is 1.767 (5) Å, which is similar to that reported for other phenyl-substituted cyclotriphosphazenes.[9,13,14]

The P–F bonds at P(2) and P(3) are equal in length, with an average bond distance of 1.525 Å. This value is similar to that found for $N_3P_3F_6$ (1.521 Å).[12] The P(1)–F(1) bond (1.554 (3)Å) is lengthened considerably, presumably a consequence of the presence of the geminal (phenyl)-$Cr(CO)_3$ group. Because a (phenyl)$Cr(CO)_3$ group is more electron-donating than a fluorine atom, the extra electron density serves to lengthen the geminal P–F bond.

Conclusions

η^6-Coordination of transition metals to pendent aryl ligands linked to a cyclotriphosphazene ring is possible. The use of the two synthetic strategies allowed the preparation of a representative series of arene complexes. In particular, the $N_3P_3[RCr(CO)_3]_6$ complexes, with one transition metal on each side group, provide the highest loading of transition-metal atoms on any phosphazene studied that we are aware of.

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(11) (a) Mills, O. S. *Pure Appl. Chem.* **1969**, *20*, 117. (b) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1314. (c) Corradini, P.; Allegra, G. *J. Am. Chem. Soc.* **1959**, *81*, 2271.

(12) Dougill, M. W. *J. Chem. Soc. A* **1963**, 3211.

(13) Allcock, H. R.; Connolly, M. S.; Whittle, R. R. *Organometallics* **1983**, *2*, 1514.

(14) Allen, C. W. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic: London, 1987; Vol. 2, Chapter 20 and references cited therein.

Future research in this area will involve the thermal and photolytic ligand replacement reactions of the (η^6-arene)$Cr(CO)_3$ complexes and the synthesis and structural characterization of the corresponding Mo and W species. An extension of this small-molecule work to the more challenging macromolecular level will be presented in a forthcoming publication.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (provided by Ethyl Corp.), chromium hexacarbonyl (Strem), phenol (Aldrich), 4-methylphenol (Aldrich), and 4-methoxyphenol (Aldrich) were purified by vacuum sublimation before use. 2-Phenoxyethanol (Aldrich), 2,2,2-trifluoroethanol (Halocarbon), and aniline (Aldrich) were distilled from calcium hydride. All other reagents (Aldrich) were used as received. Column chromatography was carried out under an atmosphere of argon with the use of dry *n*-hexane/THF as elution solvents and with the use of silica gel (60–200 mesh, Fisher) as packing material. The reactions of cyclotriphosphazenes with chromium hexacarbonyl were carried out in a solvent system of di-*n*-butyl ether/THF (10:1 v/v).[8] All reactions and manipulations were carried out under an atmosphere of dry argon or nitrogen by using standard Schlenk and drybox techniques. Solvents were dried and distilled under nitrogen by standard methods.

Equipment. ^{31}P (145.8 MHz), ^1H (360.0 MHz) and ^{13}C (90.0 MHz) NMR spectra were recorded with use of a Bruker WM360 spectrometer. Chemical shifts are relative to external 85% H_3PO_4 (^{31}P) or tetramethylsilane (^1H and ^{13}C). All heteronuclear NMR spectra were proton decoupled. Infrared spectra were recorded with the use of a Perkin-Elmer Model 1710 FTIR instrument interfaced with a Perkin-Elmer 3600 data station. Electron-impact mass spectra were obtained with the use of a Kratos MS9/50 spectrometer. Positive fast atom bombardment mass spectra were obtained with the use of a Kratos MS50 spectrometer. Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN.

Synthesis of $(HOC_6H_5)Cr(CO)_3$. (Phenol)chromium tricarbonyl was prepared by following a modified literature procedure.[15] A solution of phenol (6.0 g, 0.064 mol) and $Cr(CO)_6$ (15.5 g, 0.071 mol, 10% excess) in di-*n*-butyl ether/THF (250 mL) was stirred and heated at reflux for 48–72 h. The solvent was removed in vacuo, and the residue was transferred to a water-cooled sublimator, which was evacuated to 10^{-3} mmHg. After the mixture was warmed at 30 °C for 2 h, phenol and $Cr(CO)_6$ were collected on the cold finger and removed. Additional warming at 45 °C for 16 h allowed the isolation of the product as yellow crystals: yield 35–70%; MS calcd *m/z* 230, found *m/z* 230; ^1H NMR ($CDCl_3$) 5.8–4.6 ppm (m, ArH); ^{13}C NMR ($CDCl_3$) 233.3 (CO), 139.3, 95.4, 85.2, 79.6 ppm; IR (CH_2Cl_2) ν_{CO} 1969, 1887 cm^{-1}. Anal. Calcd for $C_9H_6O_4Cr$: C, 46.97; H, 2.63. Found: C, 47.06; H, 2.79.

Synthesis of $(HOCH_2CH_2OC_6H_5)Cr(CO)_3$. A solution of $C_6H_5OCH_2CH_2OH$ (20.0 g, 0.145 mol) and $Cr(CO)_6$ (35 g, 0.159 mol, 10% excess) in di-*n*-butyl ether/THF (300 mL) were stirred and heated at reflux for 48–72 h. The solvent and excess $Cr(CO)_6$ were removed in vacuo, and the excess $C_6H_5OCH_2CH_2OH$ was removed by vacuum distillation (ca. 70 °C at 10^{-3} mmHg). The residue was dissolved in THF (50 mL), and the solution was filtered through silica gel (ca. 1 in.). The solvent was removed in vacuo, and the product was further purified by recrystallization from *n*-hexane/methylene chloride to yield $(HOCH_2CH_2OC_6H_5)Cr(CO)_3$ as yellow crystals: yield 45–80%; MS calcd *m/z* 274, found *m/z* 274; ^1H NMR ($CDCl_3$) 5.6–5.4 (m, 2 H, ArH), 5.2–5.0 (m, 2 H, ArH), 4.9–4.7 (m, 1 H, ArH), 4.1–3.8 ppm (m, 4 H, OCH_2); ^{13}C NMR ($CDCl_3$) 233.1 (CO), 142.1, 95.0, 85.5, 78.6, 70.0, 60.9 ppm; IR (CH_2Cl_2) ν_{CO} 1968, 1887 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_5Cr$: C, 48.18; H, 3.68. Found: C, 47.96; H, 3.77.

Synthesis of $N_3P_3X_5R$ (5–9) and $N_3P_3R_6$ (10–15). Compounds $N_3P_3F_5(C_6H_5)$ (**5**), $N_3P_3Cl_5(OC_6H_5)$ (**7**), $N_3P_3(OC_6H_5)_6$ (**10**), $N_3P_3(OC_6H_4CH_3\text{-}4)_6$ (**11**), $N_3P_3(OC_6H_4OCH_3\text{-}4)_6$ (**12**), $N_3P_3(C_6H_5)_6$ (**13**), $N_3P_3(OCH_2CH_2OC_6H_5)_6$ (**14**), and $N_3P_3(NHC_6H_5)_6$ (**15**) were prepared by conventional procedures reported in the literature.[9]

Compounds $N_3P_3(OCH_2CF_3)_5(C_6H_5)$ (**6**) and $N_3P_3(OCH_2CF_3)_5(OC_6H_5)$ (**8**) were prepared from $N_3P_3F_5(C_6H_5)$ (**5**) and $N_3P_3Cl_5(OC_6H_5)$ (**7**), respectively, in a similar manner. The following procedure for the preparation of **6** is typical. To a solution of $N_3P_3F_5(C_6H_5)$ (**5**) (2.0 g, 6.51 mmol) in THF (30 mL) was added slowly a solution of sodium trifluoroethoxide in THF (30 mL), which was prepared by the reaction of sodium (1.12 g, 48.7 mmol) and trifluoroethanol (5.4 g, 54.0 mmol) in THF. The reaction mixture was stirred at 25 °C for 15 h. After evaporation of the solvent, the product **6** was purified by column chromatography with *n*-hexane/methylene chloride.

Compound $N_3P_3(NHCH_2CH_2CH_3)_5(OC_6H_5)$ (**9**) was prepared from $N_3P_3Cl_5(OC_6H_5)$ (**7**) in the following manner. To a solution of $N_3P_3Cl_5(OC_6H_5)$ (**7**) (4.5 g, 0.011 mol) in THF (150 mL) was added slowly a solution of *n*-propylamine (ca. 25 g, excess) in THF (50 mL). The reaction mixture was stirred at room temperature for 1 h and heated at reflux for 1 h. After evaporation of the solvent and excess *n*-propylamine, the residue was dissolved in diethyl ether (100 mL), washed with water (3 × 100 mL), and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the product **9** was purified by recrystallization from *n*-hexane/methylene chloride.

The ^1H, ^{13}C, and ^{31}P NMR characterization data for compounds **5**–**15** are listed in Tables I–III, respectively.

Synthesis of $N_3P_3F_5[(C_6H_5)Cr(CO)_3]$ (16). Compound **16** was prepared by two methods. In method 1, $Cr(CO)_6$ (0.5 g, 2.27 mmol) was added to a solution of $N_3P_3F_5(C_6H_5)$ (**5**) (1.00 g, 3.26 mmol) in di-*n*-butyl ether/THF (30 mL). The reaction mixture was allowed to stir at reflux for 96 h. After removal of the solvent in vacuo, the product was isolated and purified by column chromatography to yield **16** as a yellow solid. Yield: 0.95 g, 66%.

In method 2, $N_3P_3F_5(C_6H_5)$ (**5**) (ca. 5.0 g, excess) was added to $Cr(CO)_6$ (1.0 g, 4.55 mmol) in the absence of solvent and the reaction mixture was heated to reflux for 12 h. The product was isolated and purified as described above. Typical yield: 62–73%. Characterization data for **16** are listed in Tables I–IV.

Synthesis of $N_3P_3(OCH_2CF_3)_5[(C_6H_5)Cr(CO)_3]$ (17). Compound **17** was prepared by two methods. In method A, $Cr(CO)_6$ (0.14 g, 0.63 mmol, 20% excess) was added to a solution of $N_3P_3(OCH_2CF_3)_5(C_6H_5)$ (**6**) (0.37 g, 0.52 mmol) in di-*n*-butyl ether/THF (20 mL). The reaction mixture was allowed to stir at reflux for 12 h. The solvent was removed in vacuo, and the product was isolated and purified by column chromatography to yield **17** as a yellow solid. Yield: 0.23 g, 52%.

In method B, a solution of sodium trifluoroethoxide in THF (30 mL), which was prepared by the reaction of trifluoroethanol (0.333 g, 3.33 mmol) with sodium (0.084 g, 3.65 mmol) in THF, was added to a solution of $N_3P_3F_5[(C_6H_5)Cr(CO)_3]$ (**16**) (0.30 g, 0.55 mmol) in THF (25 mL) at 0 °C. The reaction mixture was allowed to warm to 25 °C and was stirred at 25 °C for 16 h. The product was purified by column chromatography. Yield: 0.38 g, 81%. Characterization data for **17** are listed in Tables I–IV.

Synthesis of $N_3P_3Cl_5[(OC_6H_5)Cr(CO)_3]$ (18). Compound **18** was prepared by two methods. In method 1, a solution of $(HOC_6H_5)Cr(CO)_3$ (0.20 g, 0.87 mmol) in THF (15 mL) was added to a suspension of NaH (0.035 g, 0.87 mmol) in THF (15 mL) at 0 °C. After the mixture was warmed to 25 °C and stirred at 25 °C for 5 h, this $Na[(OC_6H_5)Cr(CO)_3]$ was added slowly dropwise to a solution of $N_3P_3Cl_6$ (0.35 g, 1.00 mmol) in THF (20 mL). The reaction mixture was allowed to stir at 25 °C for 12 h. The solvent was removed in vacuo, and the product was purified by column chromatography to yield **18** as a yellow solid. Yield: 0.40 g, 74%.

In method 2, $N_3P_3Cl_5(OC_6H_5)$ (**7**) (0.50 g, 1.23 mmol) and $Cr(CO)_6$ (0.41 g, 1.85 mmol) were dissolved in di-*n*-butyl ether/THF (75 mL). The reaction mixture was allowed to stir at reflux for 24 h, the solvent was removed in vacuo, and the product was isolated and purified by column chromatography to yield **18** as a yellow solid. Yield: 0.42 g, 63%. Characterization data for **18** are listed in Tables I–IV.

Synthesis of $N_3P_3(OCH_2CF_3)_5[(OC_6H_5)Cr(CO)_3]$ (19). Compound **19** was prepared from $N_3P_3(OCH_2CF_3)_5(OC_6H_5)$ (**8**) and $N_3P_3Cl_5[(OC_6H_5)Cr(CO)_3]$ (**18**) by following the same procedures, method A and method B, respectively, described for **17**. Typical yield: 60–82%. Characterization data for **19** are listed in Tables I–IV.

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[15] Heppert, J. A.; Boyle, T. J.; Takusagawa, F. *Organometallics* **1989**, *8*, 461.

Synthesis of $N_3P_3(NHCH_2CH_2CH_3)_5[(OC_6H_5)Cr(CO)_3]$ (20). $N_3P_3(NHCH_2CH_2CH_3)_5(OC_6H_5)$ (9) (1.00 g, 1.93 mmol) and $Cr(CO)_6$ (0.85 g, 3.86 mmol) were dissolved in di-*n*-butyl ether/THF (60 mL). The reaction mixture was allowed to stir at reflux for 24 h, the solvent was removed in vacuo, and the product was isolated and purified by column chromatography to yield **20** as a yellow solid. Yield: 0.59 g, 47%. Characterization data for **20** are listed in Tables I-IV.

Synthesis of $N_3P_3R_5[RCr(CO)_3]$ Complexes 21-26. Compounds **21-26** were prepared in the same manner by the reaction of the corresponding $N_3P_3R_6$ (**10-15**) with $Cr(CO)_6$ (0.8 equiv). The following procedure for the preparation of $N_3P_3(OC_6H_5)_5[(OC_6H_5)Cr(CO)_3]$ (**21**) is typical. $N_3P_3(OC_6H_5)_6$ (**10**) (1.00 g, 1.44 mmol) and $Cr(CO)_6$ (0.25 g, 1.15 mmol, 0.8 equiv) were dissolved in di-*n*-butyl ether/THF (75 mL). The reaction mixture was heated to reflux for 12-48 h. The solvent was removed in vacuo, and the product was isolated and purified from the starting compound, $N_3P_3(OC_6H_5)_6$ (**10**), by column chromatography. Further purification by recrystallization from *n*-hexane/methylene chloride yielded **21** as yellow crystals. Typical yields for **21-26**: 40-70%. Characterization data for **21-26** are listed in Tables I-IV.

Synthesis of $N_3P_3[(OC_6H_5)Cr(CO)_3]_6$ (27). A solution of $(HOC_6H_5)Cr(CO)_3$ (0.62 g, 2.69 mmol) in THF (25 mL) was added to a suspension of NaH (0.11 g, 2.69 mmol) in THF (30 mL) at 0 °C. After the mixture was warmed to 25 °C and stirred at 25 °C for 5 h, this $Na[(OC_6H_5)Cr(CO)_3]$ was added slowly dropwise to a solution of $N_3P_3Cl_6$ (0.13 g, 0.37 mmol) in THF (25 mL). The reaction mixture was allowed to stir at 40-45 °C for 12 h. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. The solvent was removed in vacuo, and the product was purified by column chromatography to yield **27** as a yellow solid. Yield: 0.47 g, 84%. Characterization data for **27** are listed in Tables I-IV.

Synthesis of $N_3P_3[(OCH_2CH_2OC_6H_5)Cr(CO)_3]_6$ (28). Compound **28** was prepared from $(HOCH_2CH_2OC_6H_5)Cr(CO)_3$ by following the same procedure described for **27**. Yield: 89%. Characterization data for **28** are listed in Tables I-IV.

X-ray Structure Determination Technique. Our general technique is described elsewhere,[16] and only details related to the present work will be given here. Crystals of **16** were grown by slow diffusion of hexanes into a methylene chloride/hexanes solution of **16** at -20 °C. A summary of the important crystallographic data is presented in Table V.

The structures were solved by direct methods (using MULTAN 82[17]) and Fourier methods. All structures were refined by full-matrix, least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms.

Acknowledgment. We thank the U.S. Army Research Office and the Air Force Office of Scientific Research for financial support.

Supplementary Material Available: Tables of complete bond lengths and anisotropic thermal parameters for **16** (2 pages); a table of calculated and observed structure factors for **16** (20 pages). Ordering information is given on any current masthead page.

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[16] Allcock, H. R.; Mang, M. N.; Riding, G. H.; Whittle, R. R. *Organometallics* **1986**, *5*, 2244.

[17] Main, P.; Fiske, S. J.; Hull, S.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN 82. Universities of York, England, and Louvain, Belgium, 1982.