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A Bis(benzene)chromium-Bridged Cyclophosphazene: X-ray Structure Analysis of $N_3P_3F_4(\eta\text{-}C_6H_5)_2Cr$

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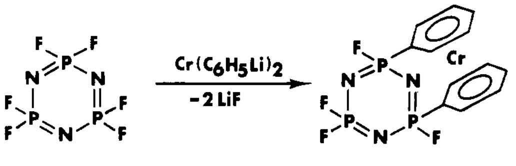
Summary: The first member of a new class of bis(arene)cyclophosphazenes, 1,3-$N_3P_3F_4(\eta\text{-}C_6H_5)_2Cr$, has been prepared by the reaction of 1,1′-dilithiobis(benzene)chromium with $(NPF_2)_3$, and the structure was confirmed by X-ray diffraction techniques.

Recent investigations into the reactions of halogenophosphazenes with a variety of organometallic reagents have yielded several new classes of cyclic and high polymeric phosphazenes that bear transition-metal elements in the side group structure.[1] One aspect of this subject, reported recently, is the synthesis of phosphazene cyclic trimers and polymers that bear ferrocenyl or ruthenocenyl side groups, some of which involve a transannular spanning of the cyclophosphazene ring by the metallocene.[2-4] Several of these metallocenylcyclophosphazenes have been polymerized to the analogous linear high polymer.

We report here the first bis(benzene)chromium-linked cyclophosphazene (2), a species that contains a transannular-linked organometallic unit. Species 2 was prepared by the reaction of 1,1′-dilithiobis(benzene)chromium with excess hexafluorocyclotriphosphazene (1) in cyclohexane at 25 °C for 4 h. The dilithio reagent was prepared from bis(benzene)chromium and *n*-butyllithium/tetramethylethylenediamine in cyclohexane at 70 °C, by the method of Elschenbroich.[5] Treatment of the mixture containing 2 with 2-propanol, filtration, and crystallization at −10 °C yielded dark orange crystals of 2 (35%), mp 191 °C. Elemental analyses were consistent with structure 2.[6] Because of the sensitivity of the reagents and products to air, all synthetic procedures were carried out under an atmosphere of dry nitrogen.



1 **2**

The ¹H-decoupled ³¹P NMR spectrum of 2 consisted of a doublet of multiplets at 57.4 ppm (J_{PF} = 950 Hz), assigned to the two phosphorus atoms that bear the bridging bis(benzene)chromium unit, and a triplet of multiplets at 20.0 ppm (J_{PF} = 920 Hz), assigned to the PF_2 unit. The ¹⁹F NMR spectrum of 2 consisted of three doublets of multiplets at 44.3 ppm (J_{PF} = 895 Hz, 1 F) and at 43.9 ppm (J_{PF} = 951 Hz, 1 F), assigned to the two inequivalent fluorine atoms of the PF_2 unit, and at 39.4 ppm (J_{PF} = 958 Hz, 2 F), assigned to the two equivalent fluorine atoms of the PFBz units. The ¹H NMR spectrum showed four broad multiplets at δ 5.30 (2 H), 4.76 (2 H), 4.09 (2 H), and 3.95 (4 H) for the five inequivalent protons on the phenyl rings. The infrared spectrum of 2 contained an aromatic C–H stretching peak at 3060 cm^{-1} and two different P–N stretching peaks at 1220 and 1192 cm^{-1}. An electron-impact mass spectrum contained the expected molecular ion at *m*/*e* 417.

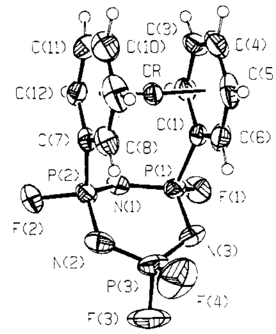


Figure 1. The molecular structure of 2.

A detailed structural insight was obtained from an X-ray analysis of 2 derived from a single crystal grown from chloroform.[7] The structure is shown in Figure 1. A bis(benzene)chromium unit is linked in a nongeminal, transannular manner through the two P–C covalent bonds to the cyclotriphosphazene ring. The bis(benzene)chromium portion of the molecule is virtually unaffected by the presence of the phosphazene ring. The phenyl groups are planar and virtually coplanar, with the dihedral angle between the rings being only 2.1°. The rings are almost equally separated from the chromium atom by distances of 1.617 (1) and 1.621 (1) Å. These are slightly longer distances than the 1.606 (1) Å reported for the equivalent values in bis(benzene)chromium.[8]

However, the influence by the bis(benzene)chromium group on the phosphazene ring is quite marked. The phosphazene ring is distorted appreciably, and the bond lengths and angles vary considerably from those in $(NPF_2)_3$. The nitrogen atom N(1), between the two phosphorus atoms that bear the phenyl groups, is displaced 0.66 Å from the plane defined by the remaining five skeletal atoms of the phosphazene ring. Moreover, the bond angle at that nitrogen atom (110.8 (2)°) is narrower than that at the other two nitrogen atoms (118.1 (2)°). The phosphazene ring angles at phosphorus vary from 115.4 (1)° for N(1)–P(1)–N(3) and 114.9 (1)° for N(1)–P(2)–N(2) to 120.6 (2)° for N(2)–P(3)–N(3). The four P–N bonds adjacent to the benzene linkage sites are almost identical and longer than expected (average 1.592 (3) Å), while the two P–N bonds flanking P(3) are slightly shorter than expected (average 1.558 (3) Å). These distortions of the phosphazene ring undoubtedly represent a response to the constraints imposed by the more rigid bis(benzene)chromium unit.

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(7) Crystal data for complex 2: triclinic space group $P\bar{1}$ (No. 2); a = 7.874 (1) Å, b = 8.725 (2) Å, c = 11.618 (3) Å; α = 82.86 (2)°, β = 88.48 (2), γ = 67.8 (1)°; V = 733.1 Å^3; Z = 2, D_{calcd} = 1.89 g cm^{-3}; $F(000)$ = 416; Mo Kα radiation; λ = 0.71073 Å; μ(Mo Kα) = 11.27 cm^{-1}; 2575 reflections were measured at 20 °C; θ limits, 2.0–25°. The structure was solved by direct methods and refined by full-matrix least-squares calculations to final R and R_w values of 0.033 and 0.040, respectively, using 1885 independent reflections with $I \leqslant 3\sigma(I)$.

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Supplementary Material Available: Listings of the positional and thermal parameters from the final cycle of refinement (Tables I and II), the interatomic distances (Table III), and bond angles (Table IV) (6 pages); a list of observed and calculated structure factors (Table V) (19 pages). Ordering information is given on any current masthead page.

Nitrogen-Nitrogen Double-Bond Scission of Azoarenes by $Ru_3(NAr)(CO)_{10}$. Structure and Catalytic Activity of $H_2Ru_3(NAr)_2(CO)_8$

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Summary: Azoarenes react with $Ru_3(NAr)(CO)_{10}$ giving $Ru_3(NAr)(NAr')(CO)_9$ in high yields. These bis(imido) clusters react with H_2 to give $H_2Ru_3(NAr)(NAr')(CO)_8$, which can be used to catalyze the hydrogenation of olefins.

The cleavage of strong multiple bonds using polynuclear metal complexes is an interesting facet of cluster reactivity. Small molecules such as CO and NO are the sources for the main-group atoms in carbido[3] and nitrido[4] clusters, while larger molecules such as acetylenes[5] and coordinated acyl groups[6] have led to the alkylidyne ligand. In this communication we describe the use of a trinuclear ruthenium cluster to cleave the N–N double bond in azoarenes, the use of the product as a homogeneous catalyst for olefin hydrogenation, and the structure of a new hydrido cluster obtained from the active solutions. The symmetric cleavage of azoarenes is uncommon.[7-9]

The reaction of $Ru_3(NAr)(CO)_{10}$[10,11] with azoarenes was complete in refluxing hexane in 20–24 h (or 6 h in heptane). It was dependent upon the nature of the para substituent on the azoarene with electron-withdrawing groups improving the yield of the bis(imido) clusters (eq 1). Typically, the yields were greater than 50% with 4,4'-dinitroazobenzene forming $Ru_3(NPh)(NC_6H_4NO_2)(CO)_9$ in 85% isolated yield. Both infrared spectroscopy and gas chromatography were used to verify that the second half of the azoarene was converted into an arene isocyanate. An important observation was the complete selectivity for the formation of the unsymmetric product. None of the original arylimido ligand was displaced as the isocyanate.

$$Ru_3(NAr)(CO)_{10} + Ar'NNAr' \rightarrow Ru_3(NAr)(NAr')(CO)_9 + Ar'NCO \quad (1)$$

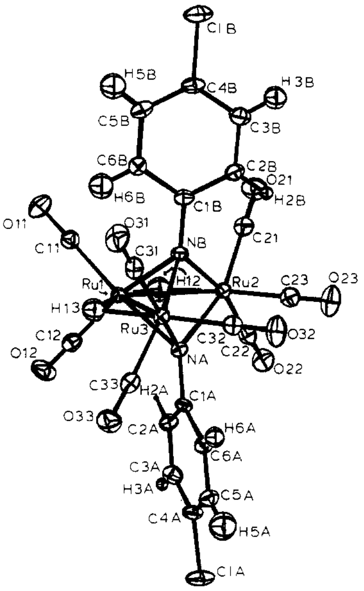
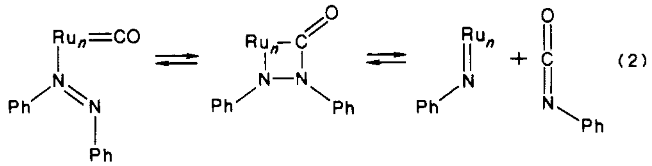


Figure 1. View of $H_2Ru_3(NC_6H_4Cl)_2(CO)_8$ showing the atom labels. Selected distances (Å): Ru1–Ru2, 2.686 (1); Ru1–Ru3, 2.673 (1); Ru2–Ru3, 3.322 (1); Ru1–NA, 2.100 (3); Ru2–NA 2.092 (3); Ru3–NA, 2.077 (3), Ru1–H12, 1.74 (5); Ru1–H13, 1.64 (4); Ru2–H12, 1.89 (5); Ru3–H13, 1.90 (4). Selected angles (deg): Ru2–Ru1–Ru3, 76.62 (1); Ru1–NA–Ru2, 79.7 (1); Ru2–NA–Ru3, 105.7 (1); Ru1–NA–C1A, 128.2 (2); Ru2–NA–C1A, 122.3 (2); Ru1–H12–Ru2, 95 (2); Ru1–H13–Ru3, 98 (2), H12–Ru1–H13, 164 (2); NA–Ru3–NB, 70.4 (1); C32–Ru3–H13, 177 (1).

Although inhibited by CO, suggesting that CO dissociation is important in the mechanism, reactions run under an atmosphere of CO gave improved yields (77–97% in refluxing heptane for ~12 h).[12]

Two recent reports of N–N double-bond scission in azoarenes involved a metathesis-like reaction. Cotton and co-workers reported[8] the formation of $[NbCl_2(Me_2S)(NPh)]_2(\mu\text{-}Cl)_2$ in the reaction between azobenzene and the Nb–Nb doubly bonded dimer $Nb_2Cl_6(Me_2S)_3$. Hegedus and co-workers found[9] that photolysis of $Cr(CO)_5[C(OMe)Me]$ and azoarenes led to products that could be explained via metathesis intermediates. One view (eq 2) of the current reaction could involve metathesis of the N–N double bond with the Ru–C bond which clearly has some π character to it. It is also possible that the conversion may occur on more than one of the metal atoms, possibly through an intermediate with a five-membered ring instead of four.



The two triply bridging arylimido ligands are responsible for the robust nature of these clusters. One use of other such stabilizing ligands has been to maintain the integrity of the cluster throughout a catalytic reaction. This has been reported in several cases using phosphinidene (PR), alkylidyne (CR), or sulfur stabilized homo- or heteronu-

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[12] In the absence of CO, $Ru_3(NAr)(CO)_{10}$ will slowly decompose in refluxing heptane. In a typical synthesis, $Ru_3(NAr)(CO)_{10}$ (21.4 mg, 0.032 mmol) and 4,4'-dinitroazobenzene (40.1 mg, 0.147 mmol) was dissolved in 12 mL of heptane in a 40-mL Schlenk tube. A slow stream of CO was passed over the refluxing solution, and the reaction was monitored by infrared spectroscopy. This particular reaction was complete after 13 h, and the product $Ru_3(NPh)(NC_6H_4NO_2)(CO)_9$ was purified by chromatography on silica gel (eluent, 8% CH_2Cl_2/hexane) and isolated in 97% yield. The para substituents studied were MeO, Me, H, Cl, and NO_2.

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