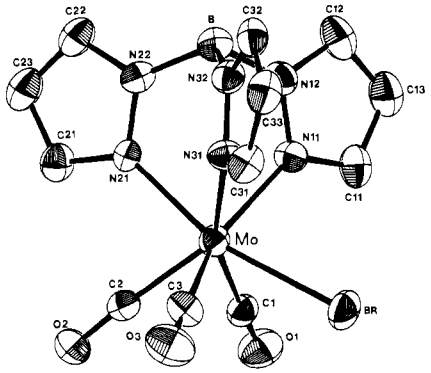


Figure 2. ORTEP plot for $TpMo(CO)_3Br$: Mo–C1 = 1.989 (7) Å, Mo–C2 = 1.957 (7) Å, Mo–C3 = 2.000 (8) Å, Mo–Br = 2.6546 (9) Å, Mo–N = 2.213 (5)–2.231 (5) Å; Br–Mo–C1 = 76.0 (2)°, Br–Mo–C2 = 118.5 (2)°, Br–Mo–C3 = 73.2 (2)°, C1–Mo–C2 = 71.7 (3)°, C1–Mo–C3 = 107.0 (3)°, C2–Mo–C3 = 68.5 (3)°.

resented in eq 1 and 2 are unprecedented in $CpMo(CO)_3R$ chemistry.[18,19]

The η^2-acetyl complex **3** readily forms adducts with phosphines and phosphites (eq 3). The crystal structure

$$\underset{\mathbf{3}}{TpMo(CO)_2(\eta^2\text{-}COMe)} + L \rightarrow \underset{\mathbf{6}}{TpMo(CO)(L)(\eta^2\text{-}COMe)} + CO \quad (3)$$

of the adduct **7** (L = $(MeO)_3P$) has been determined.[20] The Mo–C(acyl) and Mo–O(acyl) distances in **7** are each about 0.02 Å *shorter* than in **3** which suggests that back-bonding from Mo to the π^* orbital of the η^2-COR moiety is an important factor in the bonding.

Since it is unlikely that a Mo–O bond in **3** or **5** is considerably stronger than this bond in the unknown $CpMo(CO)_2(\eta^2\text{-}COMe)$, we are left with the question: why is $M(\eta^2\text{-}COR)$ more stable than $M(CO)(\sigma\text{-}R)$ in the TpMo complexes whereas the reverse stability is evident for the corresponding CpMo complexes?

We suggest that the η^2-acyl isomers are stabilized in the Tp complexes by a combination of steric and electronic effects that strongly favor octahedral coordination in TpMo complexes. The cone angle of the Tp ligand is near 180°, discouraging high coordination numbers, and the localized N_3–Mo bonding in the TpMo fragment "hybridizes" the fragment MO's into an octahedral array more efficiently than does the diffuse C_5–Mo bonding in the CpMo fragment.[21] If the η^2-COR group is considered to occupy one coordination site, then an isomerization, e.g., **2** → **3** or **4** → **5**, lowers the coordination number from seven to six, relieves steric congestion, and allows for a quais-octahedral structure about the metal.[22]

The importance of steric factors in facilitating decarbonylation finds support in the facile formation of the π-allyl complexes $XMo(CO)_2(\eta^3\text{-}C_3H_5)$ (X = indenyl,[23] Tp[15,24]) from $XMo(CO)_3^-$ and allyl halides. In contrast, $CpMo(CO)_3^-$ with allyl chloride gives the σ-allyl complex that is decarbonylated to the π-allyl dicarbonyl only under UV photolysis.[25]

In order to obtain a benchmark for a seven-coordinate TpMo complex, we have determined the structure of the previously unreported bromide $TpMo(CO)_3Br$ (**6**).[26] The ligands are arranged in a version of the four-legged piano stool geometry (Figure 2). In a vertical projection, the Br lies between two pyrazolyl rings which causes the trans-carbonyl to eclipse the third pyrazolyl ring. The net effect is to bend the trans-carbonyl down (Br–Mo–CO_t = 118.5 (2)° vs. ~132° in $CpMo(CO)_3X$ complexes)[27] and generally to compress the "legs" of the piano stool. Such compression in a $TpMo(CO)_3R$ complex would force the alkyl and cis-CO groups into close proximity, facilitating alkyl migration to form the η^2-acyl structure.

The use of sterically demanding, σ-bonded ligands to facilitate the formation of η^2-acyl or η^2-formyl complexes may have general synthetic applicability and investigations on this aspect are in progress.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. K.-B.S. also thanks the donors of the James E. Harris fellowship, administered by the Department of Chemistry, for support. We thank Dr. L. Messerle for obtaining ^{13}C NMR spectra of one of the compounds reported here, and we are grateful to Drs. F.J. Lalor and G. Ferguson for sharing their results and their helpful comments.

Registry No. 1, 47314-50-1; **2**, 22357-74-0; **3**, 86822-12-0; **5**, 86822-14-2; **6**, 86822-13-1; **7**, 86822-15-3.

Supplementary Material Available: Tables I, II, and III, fractional atomic coordinates for $TpMo(CO)_2(\eta^2\text{-}COMe)$ (**3**), $TpMo(CO)_2(\eta^2\text{-}COPh)$ (**5**), and $TpMo(CO)_3Br$ (**6**), respectively, and Tables IV, V, and VI, listings of F_o vs. F_c for **3**, **5**, and **6**, respectively (29 pages). Ordering information is given on any current masthead page.

(18) (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (c) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417.

(19) The reaction of $CpMo(CO)_3^-$ with PhCOX gives low yields of $CpMo(CO)_3COPh$ that thermally decompose to $(PhC_5H_4)_2Mo_2(CO)_6$ and $Cp_2Mo_2(CO)_6$: Nesmayonov, A. N.; Markova, L. G.; Ustynyuk, N. A.; Bogatyreva, L. V. *J. Organomet. Chem.* **1972**, *46*, 105. Similarly, $CpMo(CO)_3Et$ decomposes by radical pathways to $Cp_2Mo_2(CO)_6$ or $(EtC_5H_4)_2Mo_2(CO)_6$ depending on conditions: McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 4096.

(20) Shiu, K.-B.; Curtis, M. D., to be submitted for publication.

(21) To our knowledge, the only seven-coordinate $TpMo(CO)_3X$ complexes known are $TpMo(CO)_3H$,[15] the new halides $TpMo(CO)_3X$ (X = Br, I), and the related $TpMo(CO)_2(CS)I$: Greaves, W. W.; Angelici, R. J. *J. Organomet. Chem.* **1980**, *191*, 49.

(22) The propensity of the TpMo fragment for octahedral coordination is also manifested in the stability of the complexes $TpMo(CO)_3\cdot$ and $Tp_2Mo_2(CO)_4(Mo{\equiv}Mo)$: Shiu, K.-B.; Curtis, M. D.; Huffman, J. C. *Organometallics* **1983**, *2*, 936.

(23) King, R. B.; Bisnette, M.B. *Inorg. Chem.* **1965**, *4*, 475.

(24) Cotton, F. A.; Murillo, C. A.; Stults, B. R. *Inorg. Chim. Acta* **1977**, *22*, 75.

(25) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1973**, 889.

(26) The structure of $TpMo(CO)_3Br$ was refined with anisotropic temperature factors for all non-hydrogen atoms to final R values of R = 0.036 and R_w = 0.058 using 1902 reflections with $I \geq 3\sigma(I)$: a = 8.305 (1) Å, b = 12.032 (1) Å, c = 8.570 (2) Å, α = 104.39 (1)°, β = 93.42 (1)°, γ = 92.03 (1)°, V = 826.9 (2) Å^3, Z = 2, space group $P\bar{1}$ (No. 2).

(27) Mawby, A.; Pringle, G. E. *Inorg. Nucl. Chem. Lett.* **1972**, *34*, 525.

A New Route to the Synthesis of Highly Alkylated Cyclic Chlorophosphazenes

Paul J. Harris* and Logan A. Jackson

Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Received May 31, 1983

Summary: The reactions of hexachlorocyclotriphosphazene with trimethylaluminum have been examined. These reactions lead to good yields of a new series

of tetraalkylated chlorocyclotriphosphazenes via a predominantly geminal substitution pathway.

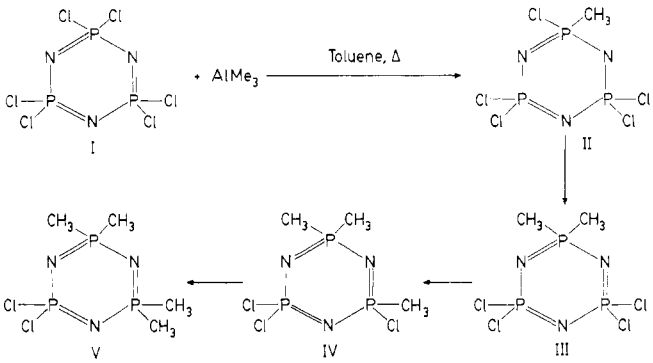
The reactions of organometallic reagents with chlorocyclophosphazenes are some of the most complex in main-group chemistry. The reactions of organolithium reagents with hexachlorocyclotriphosphazene (I) have been shown to lead to degradation of the phosphazene ring,[1] while the reactions with Grignard reagents are found to proceed via a metal–halogen exchange pathway.[2,3] With both these reagents, only traces of simple alkylated cyclic phosphazenes of general structure II and III have been observed. Compounds of type II[4] and III[5,6] can be synthesized, indirectly, via the reactions of I with organocopper reagents. These reactions follow a somewhat complex pathway involving a metallophosphazene intermediate.[6-8] Higher degrees of alkylation of hexachlorocyclotriphosphazene have not been observed in any of the reactions discussed above.

We report here the unusual results of a series of reactions between hexachlorocyclotriphosphazene (I) and trimethylaluminum. Surprisingly, these reactions led to good yields of a white crystalline compound identified as 1,1,3,3-tetramethyl-5,5-dichlorocyclotriphosphazene (V). This is the first time that high degrees of alkylation have been achieved in a reaction between hexachlorocyclotriphosphazene and an organometallic reagent. The extension of these results to the reactions of organoaluminum reagents with poly(dichlorophosphazene) may have important consequences.

A typical experimental procedure was as follows. Hexachlorocyclotriphosphazene (I; 5.0 g, 0.014 mol) was dissolved in dry, degassed toluene (~150 mL) under an atmosphere of dry nitrogen. Trimethylaluminum (8 mL, pure liquid) was then carefully added by using Schlenk techniques. The reaction mixture was heated at reflux for 150 h, and the solvent was then removed in vacuo. The residue was extracted with dry CH_2Cl_2 (2 × 150 mL), and this solution was then filtered through neutral alumina. This gave the crude product in 40% yield (1.5 g). This material was recrystallized from CH_2Cl_2/hexane to give V as air- and moisture-stable white crystals, mp 240–242 °C. The structure of V was established from the following data.[9]

The mass spectrum showed the molecular ion at m/z 265 ($^{35}Cl_2$) with a Cl_2 isotope pattern. Fragment ions were observed at m/z 250 ($M^+ - CH_3$; base peak), and at m/z 230 ($M^+ - Cl$). The infrared spectrum showed bands for the CH_3 group at 2995 (mw) and 2920 (mw), P–CH_3 at 1300 (m), and PN bonds at 1180 (vs) cm^{-1}. The proton-decoupled ^{31}P NMR spectrum showed a simple AB_2 spin system with peaks at 16.56 ppm (a triplet, J_{PNP} = 3.6 Hz; assigned to the PCl_2 group) and 31.61 ppm (a doublet, J_{PNP} = 3.6 Hz; this peak broadened significantly upon ^1H coupling and was assigned to the $P(CH_3)_2$ groups). From these

Scheme I



data, it is clear that the four methyl groups are bound to two of the phosphorus atoms in the phosphazene ring and are arranged in a geminal orientation. This was confirmed by an inspection of the ^1H NMR spectrum (200 MHz) that showed the resonance assigned to the $P(CH_3)_2$ groups as a doublet centered at δ 1.60 (J_{PCH} = 12.9 Hz) with further unresolved fine structure. These data indicate that all four of the methyl groups are magnetically equivalent, and this can only be achieved by the geminal substitution pattern suggested for compound V. Correct microanalytical data were also obtained.[10]

Following the isolation of compound V, it was of interest to determine the substitution pattern involved during its formation from I. At several stages during a typical reaction, a 10-mL aliquot of the reaction mixture was withdrawn by syringe and worked up as previously described. Proton NMR of the crude product revealed the presence of mono-[4] and dimethylcyclotriphosphazenes[6] and a new set of resonances at δ 2.0 (doublet of quartets) and 1.65 (doublet of multiplets) tentatively assigned to the molecule 1,1,3-trimethyl-3,5,5-trichlorocyclotriphosphazene. This product was also observed in the mass spectrum of the reaction mixture.[11]

These results indicated a predominantly geminal mode of halogen replacement. This was confirmed by reactions of methylpentachlorocyclotriphosphazene (II) and 1,1-dimethyltetrachlorocyclotriphosphazene (III) with trimethylaluminum, which led to good yields of compound V. (In both cases traces of compound IV were detected during the reaction). The substitution pathway is summarized in Scheme I. This predominantly geminal mode of substitution for chlorocyclotriphosphazenes is in marked contrast to fluorophosphazenes where both geminal and nongeminal substitution pathways are observed.[12] However, the fact that substitution appears to stop after the introduction of the fourth methyl group is not fully understood and is under further investigation at the present time.

Acknowledgment. This work was supported by the Virginia Polytechnic Institute and State University.

Registry No. I, 940-71-6; V, 86748-46-1; $AlMe_3$, 75-24-1.

(1) Harris, P. J.; Fadeley, C. L. *Inorg. Chem.* **1983**, *22*, 561.
(2) Harris, P. J.; Desorcie, J. L.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1981**, 852.
(3) Allcock, H. R.; Desorcie, J. L.; Harris, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 2814.
(4) Allcock, H. R.; Harris, P. J. *Inorg. Chem.* **1981**, *20*, 2844.
(5) Harris, P. J.; Allcock, H. R. *J. Chem. Soc.*, Chem. *Commun.* **1979**, 714.
(6) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *21*, 11.
(7) Harris, P. J.; Allcock, H. R. *J. Am. Chem. Soc.* **1978**, *101*, 6512.
(8) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.
(9) All NMR data were obtained in $CDCl_3$ solution. Positive ^{31}P chemical shifts are downfield from an internal capillary of H_3PO_4. Proton chemical shifts are downfield from internal $(CH_3)_4Si$.
(10) Correct elemental analyses were obtained for C, H, N, P, and Cl (±0.5%).
(11) Harris, P. J.; Minard, R. D.; Allcock, H. R. *Org. Mass Spectrom.* **1982**, *17*, 351; **1983**, *18*, 178, 268.
(12) Ramachandran, K.; Allen, C. W. *J. Am. Chem. Soc.* **1982**, *104*, 2396.