Synthesis of Tricarbonylhexachlorocyclotriphosphazenechromium

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Summary The title complex has been prepared by the reaction of hexachlorocyclotriphosphazene with $(MeCN)_3Cr(CO)_3$.

HEXACHLOROCYCLOTRIPHOSPHAZENE complexes analogous to benzenetricarbonylchromium[1] and tricarbonylhexamethylborazinechromium[2] were previously unknown. From consideration of M.O. theory of the cyclophosphazenes, $(PNX_2)_n$, ($n = 3, 4$), Brown[3] predicted that π-complexes of these compounds with metal carbonyls may exist. We now report the synthesis of the title phosphazene complex which represents the first isolation of such a complex.

Treatment of equimolar quantity of hexachlorocyclotriphosphazene[4] with $(MeCN)_3Cr(CO)_3$[5] in THF or diethyl ether at 30—40° for 2 h, yielded tricarbonylhexachlorocyclotriphosphazenechromium, $(PNCl_2)_3Cr(CO)_3$, as a bright yellow, readily sublimable crystalline solid (*ca.* 20%). The composition of the complex was established by complete elemental analysis and mass spectrometry. The complex is soluble in common organic solvents, however, it rapidly decomposes in solution, thus preventing the determination of the molecular weight osmometrically. The parent ion was not observed in the mass spectrum of the complex. The following ions however were observed and identified from the mass spectrum; $[(PNCl_2)_3Cr(CO)_2]^+$, $[(PNCl_2)_3Cr(CO)]^+$, $[(PNCl_2)_3]^+$, Cr^+, in addition to the complex fragmentation pattern of the phosphazene ligand.

The title compound shows one λ_{max} and four ν_{CO} bands, whilst hexamethylborazinetricarbonylchromium has three λ_{max} and only two ν_{CO} bands. The presence of four ν_{CO} bands has also been reported for naphthalene chromiumtricarbonyl.[6] We think the factor group approach[7] to the interpretation of the spectrum of the phosphazene complex may explain our observation. The charge-transfer u.v. bands, corresponding to those of the hexamethylborazinetricarbonylchromium complex, are not expected to be found in the tricarbonylphosphazenechromium complex, because such charge-transfer bands are absent in the u.v. spectrum of the phosphazene ligand.[8] Recently, Huttner and Krieg[9] have reported the crystal structure of hexaethylborazinetricarbonylchromium to be essentially an arene type of π-complex, as predicted earlier by Werner *et al.*[2] Therefore, we suggest that the molecular structure of our tricarbonylphosphazenechromium complex is analogous to that of the borazine complex. An *X*-ray crystallographic study is in progress.

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