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Preliminary communication

CHEMICAL SYNTHESIS WITH METAL ATOMS: THE REACTION OF 1,4- AND 1,3-CYCLOHEXADIENE WITH CHROMIUM ATOMS AND TRIFLUOROPHOSPHINE

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Summary

The reaction of 1,3-cyclohexadiene, chromium atoms, and PF_3 yields bis(*tetrahapto*-cyclohexadiene)bis(trifluorophosphine)chromium (I). The reaction of the 1,4-cyclohexadiene, chromium atoms and PF_3 initially yields *pentahapto*-cyclohexadienylhydridotris(trifluorophosphine)chromium (II), which rearranges to I in the presence of silica gel.

Introduction

The photochemical reaction of 1,3-butadiene with chromium hexacarbonyl [1] or the reaction of chromium atoms with 1,3-butadiene and CO [2] yields the impurity- and temperature-sensitive butadienechromium tetracarbonyl, a good hydrogenation catalyst for olefins [3]. A further substitution of two carbon monoxide molecules to yield bis-diene-chromium dicarbonyl is known only in the case of bis(1,3-cyclohexadiene)chromium dicarbonyl [4]. We wished to study these potentially useful diene—chromium systems and hoped to trap diene- or bis-diene-chromium compounds at low temperatures by cocondensation of chromium atoms and dienes and filling any remaining coordination sites of the chromium with the trifluorophosphine ligand which is more useful in NMR than carbon monoxide, although having a similar coordination capacity [5].

The reaction of chromium atoms with 1,3-cyclohexadiene at —196°C and subsequent reaction with an excess of trifluorophosphine yielded exclusively the bis(*tetrahapto*-cyclohexadiene)bis(trifluorophosphine)chromium complex I, which was quite stable even in chloroform at 50°C.

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The expectedly unstable analogous bis(1,4-cyclohexadiene)bis(trifluorophosphine)chromium complex was not formed in the reaction of 1,4-cyclohexadiene with chromium atoms and trifluorophosphine; instead we isolated *pentahapto*-cyclohexadienylhydridotris(trifluorophosphine)chromium(II), which in the absence of air was also stable in solution at 50°C. However, attempted purification by chromatography on florisil or silica gel resulted in a rearrangement to I exclusively, and not, surprisingly, to the mono (*tetrahapto*-cyclohexadiene)tetrakis(trifluorophosphine)chromium. Attempted preparations of single crystals of I or II for X-ray work proved unsuccessful, therefore we have attempted to prove their structures by spectroscopic methods.

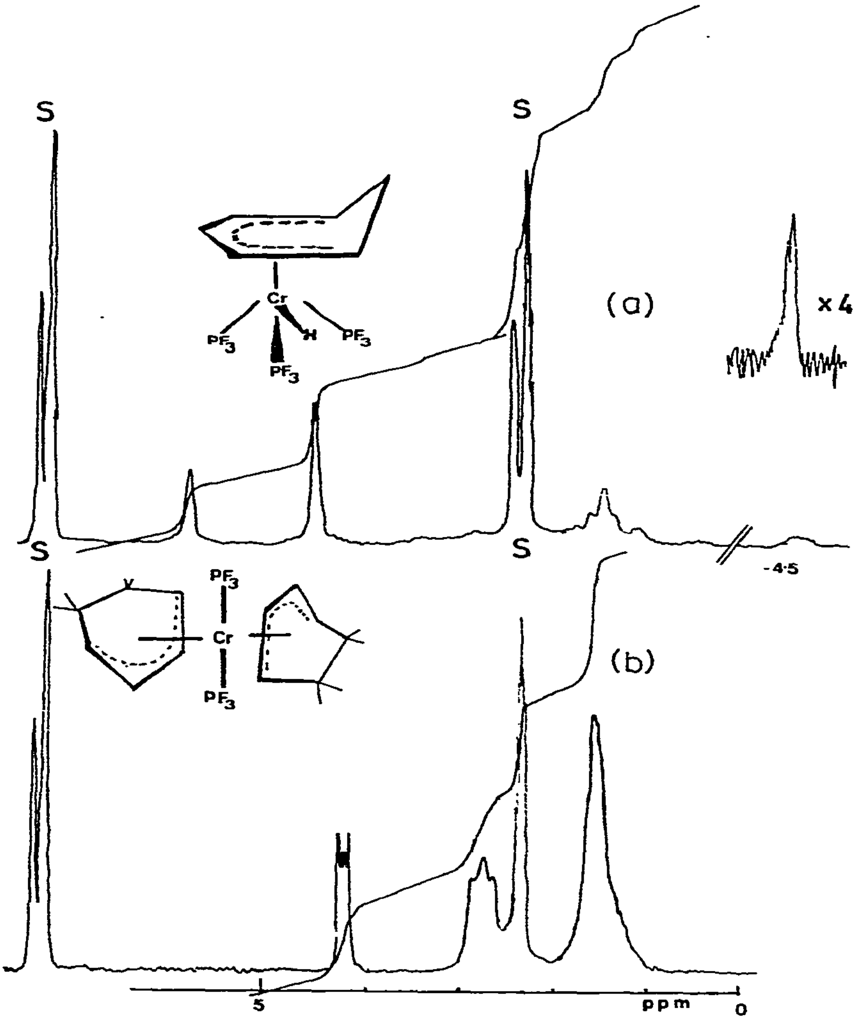

Fig. 1. ^{1}H NMR spectrum of (a) *pentahapto*-cyclohexadienylhydridotris(trifluorophosphine)chromium and (b) bis(*tetrahapto*-cyclohexadiene)bis(trifluorophosphine)chromium.

Structure of I

There are two possible *trans* and three possible *cis* isomers of I excluding enantiomers. The *trans* isomers may be distinguished by the orientations of the two *tetrahapto*-cyclohexadiene ring systems: *syn* or *anti*, similarly the *cis* isomers have one distinguishable *anti* and two distinguishable *syn* orientations of the cyclohexadiene ring systems.

The ^{1}H NMR spectrum of I (Fig. 1) shows two pairs of equivalent protons (attached to *hapto*-bonded carbons) τ 5.7, 7.3 ppm and four protons τ 8.5 ppm attributable to equivalent methylene groups, over the temperature range +50°C to —30°C. The ^{19}F NMR shows over the same temperature range, a spectrum interpretable only in terms of the X and X′ components of an $AX_3A'X'_3$ system [6] implying magnetically distinguishable but chemically equivalent PF_3 groups (Fig. 2).

Excluding a rapid interconversion of isomers, or a rotational motion of the organic rings, the only structure consistent with these data is that of the *trans* isomer with an *anti* orientation of the two ring systems (Fig. 1). The intricacies of the ^{19}F spectra (relative signs of coupling constants, ^1J(PF), ^3J(PMP) etc.) will be dealt with in another publication.

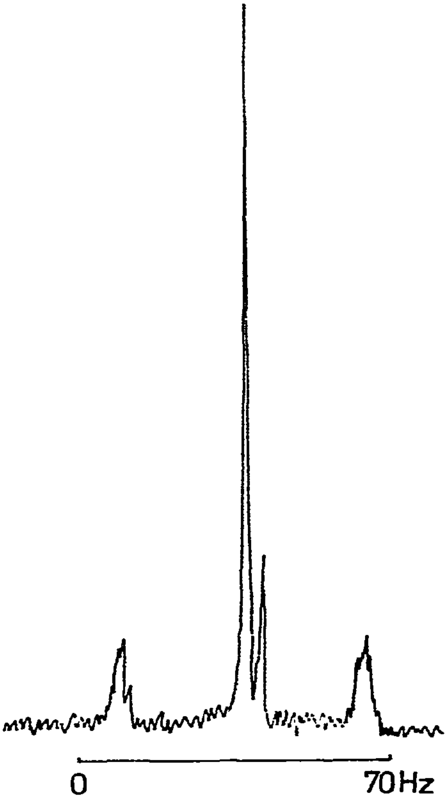

Fig. 2. ^{19}F NMR spectrum of bis(*tetrahapto*-cyclohexadienebis(trifluorophosphine)chromium; only the low-field half is shown (experimental). The spectrum is temperature independent from 20°C to —50°C.

Structure of II

The ^1H NMR of II is shown in Fig. 1. The symmetry of the protons bonded to the *pentahapto* system (2:2:1, τ 7.5, 5.5, 4.2 ppm) (Fig. 1) implies five coplanar CH groups as the bonding unit as expected. The hydride resonance appears at surprisingly low field but no fluxional behaviour could be detected. The presence of any chromatographic material converts II to I.

Skell [7] reports the catalytic conversion of 1,4-cyclohexadiene by chromium atoms to yield benzene and cyclohexene. It is therefore not surprising that such a reaction should go via hydrogen abstraction, through a cyclohexadienylhydridochromium intermediate. Most of the first row transition metals, especially chromium exhibit the ability to abstract hydrogen from coordinating diene ligands in metal atoms reactions [8] and it is possible that the disproportionation of 1,4-cyclohexadiene in the presence of chromium atoms proceeds via a relatively stable cyclohexadienylhydrido-1,4-cyclohexadiene sixteen electron species. We may have been fortunate in trapping such a species which can then easily lose the 1,4-cyclohexadiene ligand in exchange for trifluorophosphine giving the stable eighteen electron species II.

Experimental

Thermal evaporation of chromium in a steel vessel has been described previously [5]; in a typical experiment n-hexane (150 ml) was condensed on the walls of the steel vessel at —196°C; chromium (2 g) was then cocondensed with 1,3- or 1,4-cyclohexadiene (40 ml) over a 1 h period (10^{-4} Torr), the cocondensation was stopped and trifluorophosphine (11 l) was then introduced and the vessel brought to atmospheric pressure with argon. As the matrix melted, the products were collected in a flask attached to the base of the vessel. The solution was then filtered through glass wool, evaporated to dryness and the residue chromatographed (Merck 7734) in n-hexane under argon. (No chromatography was performed when the reactant was 1,4-cyclohexadiene). The orange red solutions (I on II) obtained were left to crystallise at —80°C. All operations were conducted below —30°C under argon.

Analysis (I): Found: C, 36.85; H, 4.6; Cr, 13.41; F, 29.22; P, 15.90; mol.wt. 386 (benzene). $C_{12}H_{16}CrF_6P_2$ calcd.: C, 37.12; H, 4.16; Cr, 13.40; F, 29.36; P, 15.96%; mol.wt. 388. Mass spectrum 388(M^+), 300($M^+ - PF_3$), 212($M^+ - 2PF_3$), 130($C_6H_6Cr^+$). ^1H NMR: 5.7 (2), 7.3 (2), 8.5 (4). ^{19}F NMR: XX' part of $AX_3A'X'_3$ 0.67 ppm(CCl_3F) ^1J(PF) 1250 Hz.

Analysis II: Found: C, 18.1; H, 2.3; Cr, 13.4; F, 43.4; P, 23.2. $C_6H_8CrP_3F_9$ calcd.: C, 18.18; H, 2.02; Cr, 13.13; F, 43.18; P, 23.48%. Mass spectrum: 396(M^+), 395($M^+ - H$), 394($M^+ - 2H$), 306($M^+ - 2H - PF_3$), 130($C_6H_6Cr^+$), 88, 78, 52. ^1H NMR: 4.2 (1), 5.5 (2), 7.5 (2), 8.5 (2), 14.5 (1). Solutions of II in n-hexane chromatographed on silica gel (Merck 7734) yielded after work up I. Analysis: Found C, 37.32; H, 4.30; Cr, 13.26; F, 29.16; P, 16.01; mol.wt. 372 (benzene). ^1H NMR spectra were recorded in toluene-d_8 and the τ scale is used throughout.

Acknowledgements

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