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Preliminary communication

The reaction of $(\eta^3\text{-}C_3H_5)_3Cr$ with P-donor ligands *

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Abstract

$(\eta^3\text{-}C_3H_5)_3Cr$ reacts with P-donor ligands to give 1/1 adducts. The product of the reaction with bis(dimethylphosphino)ethane has been shown by X-ray diffraction to contain η^4-1,3-hexadiene and η^3-allyl groups.

The recognition by G. Wilke over 25 years ago that the η^3-allyl group alone is sufficient to stabilize a transition metal atom was one of the more important landmarks in the development of post-ferrocene organotransition metal chemistry and homogeneous catalysis [1,2].

One of the first homoleptic $(\eta^3\text{-allyl})_nM$ compounds to be prepared was $(\eta^3\text{-}C_3H_5)_3Cr$. This was synthesized in high yield by the classic reaction between the metal chloride and allylmagnesium chloride [3–5] and the crystal structure was later confirmed by X-ray diffraction [6]. Although this compound attracted attention in the late 60's as a non-Ziegler catalyst for the polymerization of ethylene, substituted alkenes and butadiene [2,3,7], its chemistry has received surprisingly little attention and is apparently limited to degradation studies and to the reactions shown below. Many of the products of these reactions are paramagnetic and their nature remains unclear.

As part of an investigation of the chemistry of the η^3-allyl complexes of the Group VI metals [14], we have turned our attention to chromium and report here the reaction with P-donor ligands.

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* Dedicated to Prof.Dr.mult. G. Wilke on the occasion of his 65th birthday.

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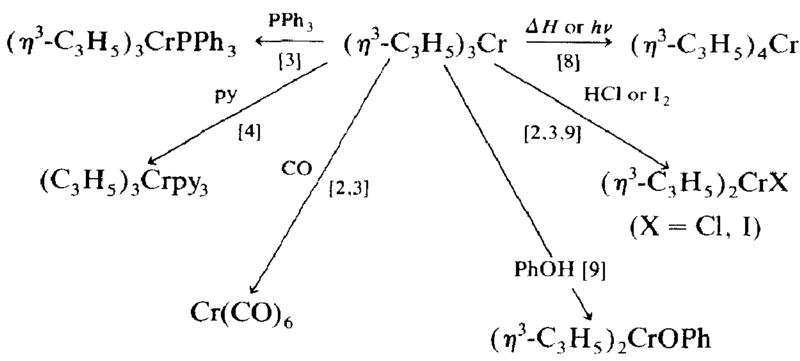

$(\eta^3\text{-}C_3H_5)_3Cr$ reacts with a variety of P-donor ligands, in addition to triphenylphosphine [3], to give $(C_3H_5)_3CrPR_3$ species (R = Ph, OMe, Me, i-C_3H_7, Cy). However, the products are brown, insoluble, paramagnetic amorphous powders which decompose above 0 °C with ligand dissociation and which have successfully resisted further investigation. Fortunately the reaction with bidentate ligands was more productive: tris(η^3-allyl)chromium reacts with bis(dimethylphosphino)ethane or bis(dicyclohexylphosphino)ethane in ether at −10 °C to give dark green, paramagnetic compounds in ca. 60% yield.

The mass spectrum of the $Me_2PC_2H_4PMe_2$ compound confirms the formation of a 1/1 adduct (m/e 325 M^+). The compound is paramagnetic (17 valence electrons) and its crystal structure has been determined by X-ray diffraction at low temperature (Fig. 1) [10*].

The chromium atom lies in a distorted tetrahedral environment. Two coordination sites are occupied by phosphorus, and interaction with η^4-1,3-hexadiene and an η^3-allyl group completes the coordination sphere. Bond distances and angles of these groups are similar to reported values [11–13]. A slightly distorted complexation of

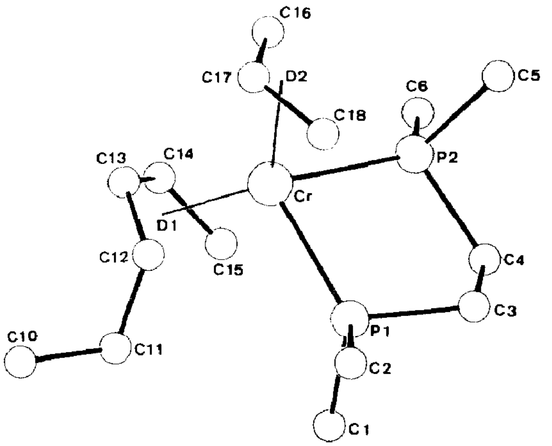

Fig. 1. Molecular structure of $(\eta^4\text{-}1\text{-}EtC_4H_5)(\eta^3\text{-}C_3H_5)Cr(PMe_2C_2H_4PMe_2)$; C(12)–Cr 2.215(5), C(13)–Cr 2.118(4), C(14)–Cr 2.127(4), C(15)–Cr 2.206(4), C(16)–Cr 2.224(4), C(17)–Cr 2.088(5), C(18)–Cr 2.186(4), Cr–P(1) 2.335(1), Cr–P(2) 2.378(1), C(10)–C(11) 1.518(7), C(11)–C(12), 1.445(8), C(12)–C(13) 1.450(7), C(13)–C(14) 1.404(6), C(14)–C(15), 1.402(6), C(16)–C(17) 1.436(7), C(17)–C(18) 1.415(6) Å; C(16)–C(17)–C(18) 120.4, P(1)–Cr–P(2) 79.7°.

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* Reference number with asterisk indicates a note in the list of references.

the hexadiene group is induced by the non-symmetric substitution of this ligand. Remarkable is that the ligand induced reductive coupling of two allyl groups in the starting material does not lead to the more familiar formation of an η^2,η^2-bonded 1,5-diene molecule [14–16] but instead isomerization to the conjugated diene occurs.

The similarity between the IR spectrum of this compound and those of the adducts with monodentate ligands (in particular the presence of absorptions at ca. 2900, 1120, 720 and 650 cm^{-1} as well as bands assignable to the η^3-allyl group) suggest that they may all contain the same organic ligands.

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10 Crystal structure analysis: space group *Pbca*, a 14.956(1), b 15.243(3), c 15.178(2) Å, V 3460.2 Å^3, T $-173°$ C, D_{calc} 1.25 g cm^{-3}, $Z = 8$, (μ-Mo-K_α) 8.12 cm^{-1}, 10339 measured reflections ($\pm h, +k, +l$), averaged to 4990 independent reflections, 3742 observed ($I > 2\sigma(I)$), 163 refined parameters, $R = 0.065$, $R_w = 0.074$, residual electron density ρ 1.65 e Å^{-3}. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 53893, the names of the authors, and the journal citation.

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