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SYNTHESIS AND STRUCTURE OF R—P-BRIDGED TRINUCLEAR HETEROMETALLIC CLUSTERS OF MANGANESE AND CHROMIUM

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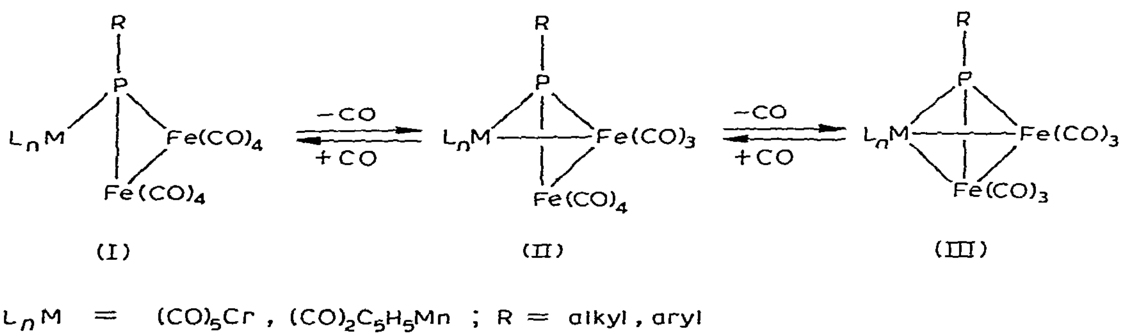
Summary

Complexes of the type L_nMPRCl_2 (L_nM = $(CO)_5Cr$ or $C_5H_5(CO)_2Mn$), on treatment with $C_5H_5Co(CO)_2$, undergo dehalogenation giving mixed metal clusters, $L_nMPR[CoC_5H_5(CO)]_2$. The molecular structure of $(C_5H_5)_3Co_2Mn(CO)_4$-$PCH_2C_6H_5$ is described. Monoclinic, space group $P2_1/c$ with *a* 9.579, *b* 14.338, *c* 17.650 Å, $Z = 4$.

Introduction

Dehalogenation of complexed dihalophosphanes by $Fe(CO)_9$ has been found to lead to the heterometallic R—P-bridged clusters I—III [1], which are of



special interest because of the fact that they can be reversibly transformed into each other [2]. We report here on the similar use of $C_5H_5Co(CO)_2$ as a dehalogenating agent. The reaction leads to mixed cobalt clusters (IV). The compounds IV are structurally analogous to the open type iron clusters I, but in

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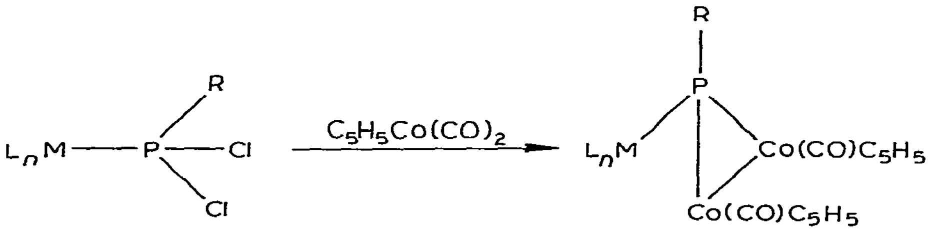
contrast to the latter, cannot be transformed to closed cluster systems analogous to II or III.



(IV)

L_nM = $(CO)_5Cr$, $(CO)_2C_5H_5Mn$; R = C_6H_5 , $CH_2C_6H_5$

Results and discussion

Preparation and spectra

When solutions of L_nMPRCl_2 and $C_5H_5Co(CO)_2$ are mixed at room temperature, no reaction takes place even on prolonged stirring (30 h), as revealed by the ^{31}P NMR spectra. Reaction starts only at around 100°C, while at temperature above 120°C, both the manganese and chromium complexes are found to undergo appreciable decomposition. The products IV are separated from other materials by column chromatography. Final purification is by crystallisation, and gives complexes IV as dark brown crystalline solids. Attempts to induce the formation of additional metal—metal bonds, analogous to the formation of II or III from I, by either prolonged heating or UV irradiation of the clusters (IV) did not lead to compounds similar to II or III, but only to partial decomposition.

It may be inferred from the structure analysis performed on IV (R = C_6H_5-CH_2, L_nM = $(CO)_2C_5H_5Mn$) that the bulky cyclopentadienyl groups at the cobalt centers do not permit stable manganese cobalt interactions in the initial stages of the presumed cluster closing reaction.

X-ray investigation of $(C_5H_5)_3MnCo_2(CO)_4CH_2C_6H_5$

Satisfactory crystals were obtained by chilling the 1/1 methylenechloride/pentane solution of the compound at −20°C. The crystals separate in monoclinic form. Space group $P2_1/c$, a 9.579, b 14.338, c 17.650 Å, α 90, β 99.08, γ 90°, Z = 4. The structure was solved by conventional methods and refined to R_1 = 0.054 on 2396 independent reflections ($I > 3\,\sigma$). Diffractometer: Syntex P3, ω-scan, $\Delta\omega$ 1°, $1 \leqslant \omega \leqslant 29.3°$ min^{-1}, $2 \leqslant 2\theta \leqslant 40°$, λ-Mo 71.069 pm, Graphite monochromator, T −100°C. Syntex-EXTL, structure solving system. Tables of structure factors may be obtained from the authors.

A perspective view of the molecular structure is shown in Fig. 1 which also illustrates the numbering of atoms used throughout. Fractional atomic coordinates are given in Table 1. Table 2 lists the bond lengths and bond angles. Anisotropic temperature factors are presented in Table 3. Estimated standard

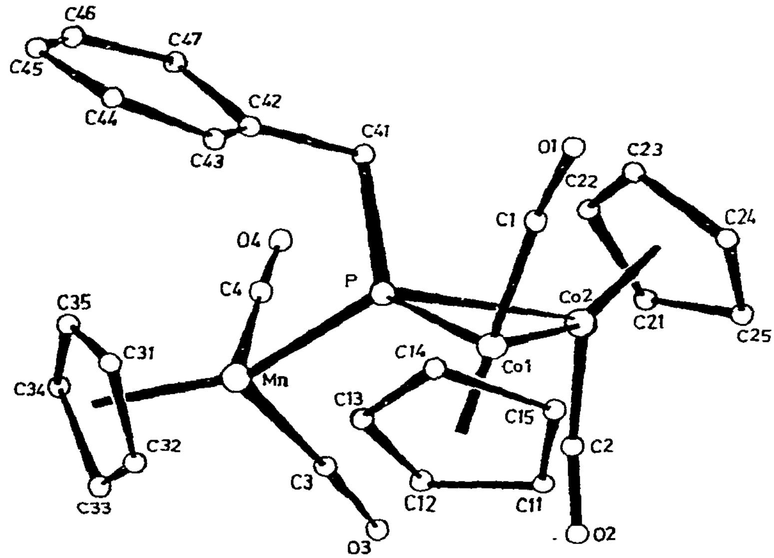


Fig. 1. Molecular structure of $(C_6H_5)_3MnCo_2(CO)_4PCH_2C_6H_5$, also illustrating the atom numbering.

TABLE 1

FRACTIONAL ATOMIC COORDINATES

Atom	*x/a*	*y/b*	*z/c*	B (Å^2)
Co(1)	0.2143(1)	−0.2000(1)	0.3442(1)	
Co(2)	0.1990(1)	−0.3766(1)	0.3572(1)	
Mn	0.5532(2)	−0.3278(1)	0.2775(1)	
P	0.3982(3)	−0.2972(2)	0.3573(1)	
O(1)	0.1965(1)	−0.1886(7)	0.5044(7)	
O(2)	0.0945(10)	−0.3774(6)	0.1946(6)	
O(3)	0.3707(13)	−0.4502(8)	0.1722(7)	
O(4)	0.6345(12)	−0.4889(8)	0.3742(6)	
C(1)	0.2046(14)	−0.1966(10)	0.4416(9)	
C(2)	0.1403(13)	−0.1723(9)	0.2586(8)	
C(3)	0.4378(14)	−0.3987(10)	0.2144(8)	
C(4)	0.6015(13)	−0.4222(9)	0.3362(7)	
C(11)	0.0601(14)	−0.1675(9)	0.2467(7)	5.40(28)
C(12)	0.2004(13)	−0.1656(9)	0.2282(7)	4.94(27)
C(13)	0.2774(14)	−0.0950(9)	0.2758(7)	5.11(29)
C(14)	0.1906(15)	−0.0566(10)	0.3256(8)	6.09(33)
C(15)	0.0539(15)	−0.1018(10)	0.3042(1)	5.65(31)
C(21)	0.1810(13)	−0.5205(9)	0.3718(7)	4.83(27)
C(22)	0.2782(14)	−0.4805(10)	0.4341(8)	5.32(30)
C(23)	0.2098(15)	−0.4139(10)	0.4736(8)	5.80(31)
C(24)	0.0634(15)	−0.4131(10)	0.4381(8)	5.69(31)
C(25)	0.0477(13)	−0.4779(9)	0.3757(7)	4.85(27)
C(31)	0.6386(14)	−0.1846(9)	0.2799(8)	5.63(28)
C(32)	0.5772(15)	−0.2109(9)	0.2037(8)	5.77(31)
C(33)	0.6542(15)	−0.2903(10)	0.1834(8)	5.90(32)
C(34)	0.7561(15)	−0.3137(10)	0.2451(8)	6.29(33)
C(35)	0.7473(14)	−0.2474(10)	0.3051(7)	5.74(29)
C(41)	0.4956(11)	−0.2952(7)	0.4613(6)	3.39(22)
C(42)	0.6147(11)	−0.2285(7)	0.4763(6)	3.42(22)
C(43)	0.5957(14)	−0.13050(9)	0.4679(7)	5.26(29)
C(44)	0.7147(16)	−0.0711(11)	0.4854(8)	6.79(35)
C(45)	0.8434(16)	−0.1052(10)	0.5140(8)	6.44(33)
C(46)	0.8617(14)	−0.2007(10)	0.5249(8)	5.93(30)
C(47)	0.7470(12)	−0.2630(8)	0.5053(7)	4.05(25)

TABLE 2

BOND DISTANCES AND BOND ANGLES

(A) Bond distances (Å)

Co(1)—Co(2)	2.549(2)	C(1)—O(1)	1.13(2)
Co(1)—P	2.229(3)	C(2)—O(2)	1.15(2)
Co(2)—P	2.222(3)	C(3)—O(3)	1.18(2)
Mn—P	2.246(3)	P(1)—C(41)	1.92(1)
Co(1)—C(1)	1.74(2)	Co—C(C_5H_5)	2.08(1)—2.14(1)
Co(2)—C(2)	1.74(1)		average, 2.11(1)
Mn—C(3)	1.76(2)	Mn—C[C_5H_5]	2.12(2)—2.21(1)
Mn—C(4)	1.72(1)		average, 2.16(2)

(B) Bond angles (deg)

Co(2)—Co(1)—P	54.9(1)	Co(2)—P—C(41)	107.1(3)
P—Co(1)—C(1)	94.6(5)	Mn—P—C(41)	109.4(3)
Co(2)—Co(1)—C(1)	85.7(5)	P—Mn—C(3)	95.6(5)
Co(1)—Co(2)—P	55.2(1)	P—Mn—C(4)	85.2(5)
P—Co(2)—C(2)	97.1(4)	P—C(41)—C(42)	115.1(8)
Co(1)—Co(2)—C(2)	83.6(4)	C(3)—Mn—C(4)	90.5(6)
Co(1)—P—Co(2)	69.9(1)	Mn—C(3)—O(3)	175(1)
Co(2)—P—Mn	123.5(1)	Mn—C(4)—O(4)	178(1)
Co(1)—P—Mn	130.4(1)	Co(1)—C(1)—O(1)	176(1)
Co(1)—P—C(41)	110.2(3)	Co(2)—C(2)—O(2)	173(1)

deviations are always given in parenthesis and are right adjusted.

The complex may be described as composed of a metallocyclic phosphane ligand $C_6H_5CH_2PCo_2(C_5H_5)_2(CO)_2$ complexed to a $C_5H_5(CO)_2Mn$ moiety. The two cycopentadienyl rings at the $Co_2(C_5H_5)_2(CO)_2$ fragment are in *trans* positions to each other, presumably because the *cis* orientation would involve severe steric strain. The individual distances within the molecule are well within the range observed for compounds containing comparable structural units [3].

TABLE 3

ANISOTROPIC TEMPERATURE FACTORS [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co(1)	3.6(1)	2.6(1)	4.0(1)	0.1(1)	0.6(1)	0.5(1)
Co(2)	3.8(1)	2.6(1)	3.0(1)	−0.5(1)	0.0(1)	0.4(1)
Mn	4.1(1)	3.6(1)	2.5(1)	0.4(1)	0.7(1)	0.0(1)
P	3.4(1)	2.6(1)	2.6(1)	−0.0(1)	0.3(1)	0.2(1)
O(1)	7.4(6)	8.6(6)	5.5(6)	0.4(4)	2.8(5)	−0.7(5)
O(2)	7.3(5)	6.4(3)	4.3(3)	−0.8(4)	−1.1(4)	0.3(5)
O(3)	9.5(7)	8.1(7)	7.7(7)	−0.7(6)	−0.2(6)	−2.8(6)
O(4)	12.1(7)	6.9(7)	5.8(7)	4.0(5)	1.9(5)	1.2(6)
C(1)	4.9(8)	5.0(8)	5.3(8)	0.9(6)	1.5(6)	0.4(7)
C(2)	4.6(6)	3.7(7)	4.4(7)	−0.2(5)	−0.1(5)	0.7(5)
C(3)	6.0(8)	5.8(8)	3.7(8)	0.3(6)	0.9(6)	−0.1(6)
C(4)	6.5(7)	5.1(7)	3.4(7)	2.2(5)	1.7(5)	0.3(5)

[a] The anisotropic temperature factor is defined as $T = \exp[-1/4(h^2a^{*2}B_{11} + ... + 2hka^*b^*B_{12} + ...)]$, B in Å^2.

Experimental

Phenyldichlorophosphane, $PC_6H_5Cl_2$; benzyldichlorophosphane, $PCH_2C_6H_5$-Cl_2 and their corresponding manganese and chromium complexes C_5H_5Mn-$(CO)_2PC_6H_5Cl_2$, $C_5H_5Mn(CO)_2PCH_2C_6H_4Cl_2$ and $Cr(CO)_5PCH_2C_6H_5Cl_2$ were prepared by literature methods [4,5]. Cyclopentadienylcobaltdicarbonyl, C_5H_5-$Co(CO)_2$, purchased from E. Merck, was used without further purification. Solvents were purified by standard methods. All reactions and handling of chemicals were performed under dry nitrogen.

Infrared spectra are measured in CaF_2 cells using methylene chloride solutions by means of a ZEISS Infrared Spectrophotometer IMR-40; a BRUKER WP 80 FT-NMR-Spectrometer is used to record the ^{31}P NMR spectra.

$(C_5H_5)_3MnCo_2(CO)_4PCH_2C_6H_5$

3.69 g (10 mmol) of $C_5H_5Mn(CO)_2PCH_2C_6H_5Cl_2$ and 4.5 g (25 mmol) of $C_5H_5Co(CO)_2$ are mixed in 70 ml of toluene. The mixture is then warmed slowly and kept at 115—116°C for 15 h. The solvent is removed and the product chromatographed on silica gel. The compound is obtained by elution with pentane/toluene (1/1) and recrystallisation from pentane/CH_2Cl_2 (1/1) as dark-brown crystals with 0.52 g (8.6%) yield. Found: C, 51.70; H, 3.49; Co, 20.01; Mn, 9.15; P, 5.31. Calcd. for $C_{26}H_{22}Co_2MnO_4P$: C, 51.82; H, 3.64; Co, 19.60; Mn, 9.13; P, 5.14%. IR (ν(CO) cm^{-1}): 1985(sh); 1968s; 1918s; 1857s. ^{31}P FT NMR: δ, 397 ppm (acetone-d_6, ext. H_3PO_4).

$(C_5H_5)_3MnCo_2(CO)_4PC_6H_5$

This compound is made by the method described above, using C_5H_5Mn-$(CO)_2PC_6H_5Cl_2$ (3.55 g, 10 mmol) instead of the benzyl analog, as dark-brown crystals with 0.81 g (13.8%) yield. Found: C, 51.32; H, 3.42; Co, 20.18; Mn, 9.20; P, 5.44. Calcd. for $C_{25}H_{20}Co_2MnO_4P$: C, 51.02; H, 3.40; Co, 19.88; Mn, 9.35; P, 5.27%. IR (ν(CO) cm^{-1}): 1985(sh); 1968s; 1912s; 1856s. ^{31}P FT NMR: δ, 375.8 ppm (acetone-d_6, ext. H_3PO_4).

$(C_5H_5)_2CrCo_2(CO)_7PCH_2C_6H_5$

3.85 (10 mmol) $Cr(CO)_5 \cdot PCH_2C_6H_5Cl_2$ and 4.5 g (25 mmol) of C_5H_5Co-$(CO)_2$ are mixed in 70 ml of toluene. The mixture is warmed slowly and kept at 100—101°C for 15 h. The solvent is removed and the product chromatographed on silica gel. The compound is obtained by elution with pentane/toluene (3/1) and recrystallisation from pentane/toluene (2/1) as dark-brown crystals with 0.30 g (4.9%) yield. Found: C, 45.81; H, 2.81; Co, 19.19; Cr, 8.24; P, 5.22. Calcd. for $C_{24}H_{17}Co_2CrO_7P$: C, 46.60; H, 2.75; Co, 19.08; Cr, 8.41; P, 5.02%. IR (ν(CO) cm^{-1}): 2070w; 2055s; 1978s; 1940vs; 1920vs. ^{31}P FT NMR: δ, 326.7 ppm (acetone-d_6, ext. H_3PO_4).

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