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Preliminary Communication

P_x ligands with a maximum of electron-donating ability

VI *. $[CoCp''(\eta^4\text{-}P_4)\{Cr(CO)_5\}_3]$ ($Cp'' = \eta^5\text{-}C_5H_3{}^tBu_2\text{-}1,3$), the product of the reaction between P_4 and $[CoCp''(\mu\text{-}CO)]_2$ in the presence of $[Cr(CO)_5THF]$ **

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Abstract

The reaction of P_4 with $[CoCp''(\mu\text{-}CO)]_2$ in the presence of $[Cr(CO)_5THF]$ leads to $[CoCp''(\eta^4\text{-}P_4)\{Cr(CO)_5\}_3]$ ($Cp'' = \eta^5\text{-}C_5H_3{}^tBu_2\text{-}1,3$) (IUPAC formula $[CoCp''\{[\{Cr(CO)_5\}_3(P_H\text{-}1\kappa P^1,2\kappa P^2,3\kappa P^3)](\kappa\text{-}P^1,P^2,P^3,P^4)\}]$) as a final product. An X-ray structural study reveals a complex with a planar *cyclo*-P_4 ligand capped by a Cp″Co unit. Three of the phosphorus atoms are also coordinated to $[Cr(CO)_5]$ groups.

The reaction of P_4 with appropriate transition metal complexes results in complexes containing P_x ligands [2]. In a three-component reaction system the stepwise transformation of tetrahedral P_4 can be observed. Recently we reported the reaction between P_4 and $[RhCp'(CO)_2]$ ($Cp' = \eta^5\text{-}C_5H_4{}^tBu$) in the presence of $[Cr(CO)_5THF]$; in this reaction the bicyclotetraphosphine complex was by-passed and $[RhCp'(\eta^4\text{-}P_4)\{Cr(CO)_5\}_4]$ was isolated as a final product [3]. The crystal structure shows that all P atoms are coordinated to $Cr(CO)_5$ moieties. Because of the steric hindrance by the t-butyl group of the Cp′ ring one $Cr(CO)_5$ unit is bent out of the plane of the remaining Cr atoms. It was thus of particular interest to study the influence of the additional t-butyl group present in the Cp″ ligand ($Cp'' = \eta^5\text{-}C_5H_3{}^tBu_2\text{-}1,3$) on the coordination behaviour of the *cyclo*-P_4 unit. Furthermore, this modification could also be extended to other types of complexes containing the *cyclo*-P_4 ligand; only two of such species are known, *viz.*, $[M(CO)_4(\eta^4\text{-}P_4)\{M(CO)_5\}_4]$ (M = Cr [4], W [4,5]) and $[NbCp^*(CO)_2(\eta^4\text{-}P_4)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) [6].

Under thermal conditions up to 110°C no reaction occurs between P_4 and $[CoCp''(CO)_2]$ with or without $[Cr(CO)_5THF]$ present*, and so the more reactive dimer $[CoCp''(\mu\text{-}CO)]_2$ has to be used as the starting material. The reaction between $[CoCp''(\mu\text{-}CO)]_2$ and P_4 in the presence of $[Cr(CO)_5THF]$ takes place at about 70°C in THF. The ^{31}P-NMR spectrum of the crude product reveals traces of $[CoCp''(CO)(\eta^2\text{-}P_4)\{Cr(CO)_5\}_4]$ **1** along with $[CoCp''(\eta^4\text{-}P_4)\{Cr(CO)_5\}_3]$ **2** as the main product. This indicates that the reaction pathway (Scheme 1) is analogous to that recently found for the corresponding Rh complexes [3]. In contrast to $[RhCp'(\eta^4\text{-}P_4)\{Cr(CO)_5\}_4]$ [3], in product **2** only three of the P atoms are able to coordinate to $Cr(CO)_5$ groups owing to the steric effect of the Cp″ group.

Because only very small amounts of **1** were obtained this complex was not isolated analytically pure. However, the similarity of its ^{31}P-NMR data of **1** ** with those for the corresponding Rh compound $[RhCp'(\eta^2\text{-}P_4)\{Cr(CO)_5\}_4]$ [3] indicates that they have analogous structures. Complex **2** forms red plates, which are obtained analytically pure by fractional crystallization or column chromatography. It is moderately soluble in n-pentane and readily soluble in benzene, CH_2Cl_2 and THF.

Compound **2** was characterized by NMR and IR spectroscopy and mass spectrometry ***. The ^{31}P NMR spectrum (Fig. 1) is an AM_2X spin system. The IR spectra exhibit carbonyl absorption patterns characteristic of the C_{4v} symmetry of two different $Cr(CO)_5$ moieties in the ratio 1:2. The mass spectrum (FAB/30 eV) reveals peaks arising from carbonyl loss.

The crystal structure analysis of **2** *** (Fig. 2) shows that a square planar *cyclo*-P_4 ligand is capped by a Cp″Co unit and three P atoms are coordinated to $Cr(CO)_5$ moieties. The *cyclo*-P_4 ligand supplies 10 valence electrons to the overall complex. The various

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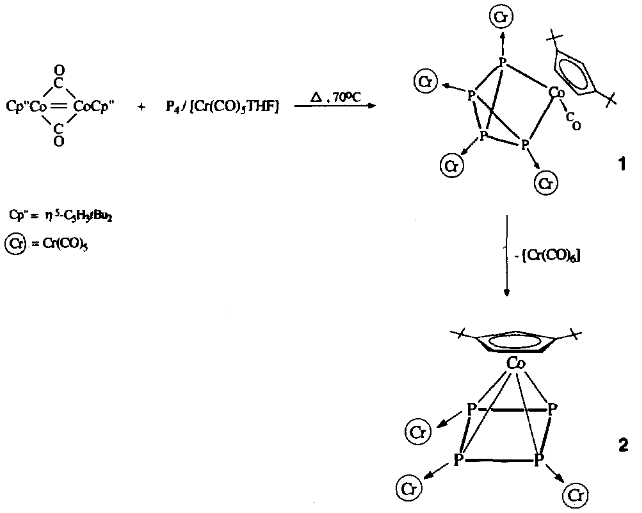
* For Part 5, see Ref. 1.

** Dedicated to Professor Otto J. Scherer on the occasion of his 60th birthday.

*** In the case of $[RhCp'(CO)_2]$ the reaction with P_4 proceeds only in the presence of $[Cr(CO)_5THF]$ [3].



Scheme 1. Proposed reaction pathway for the formation of 2.

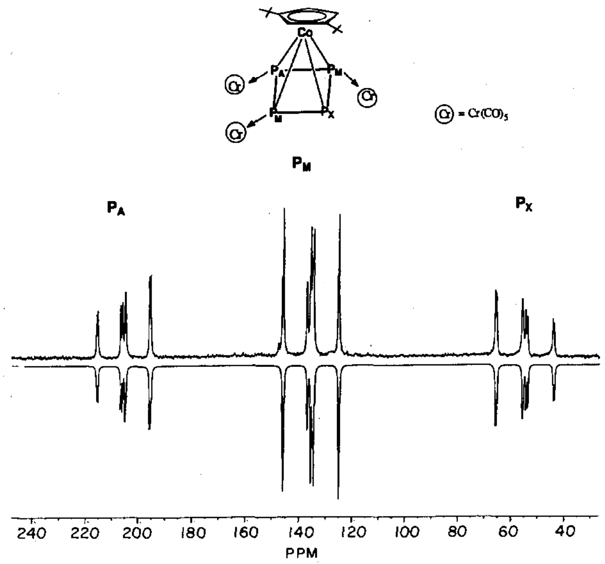


Fig. 1. Experimental and calculated ^{31}P NMR spectrum of [CoCp″(η^4-P_4){Cr(CO)$_5$}$_3$] 2 (Cp″ = η^5-$C_5H_3{}^tBu_2$-1,3) at 32.438 MHz.

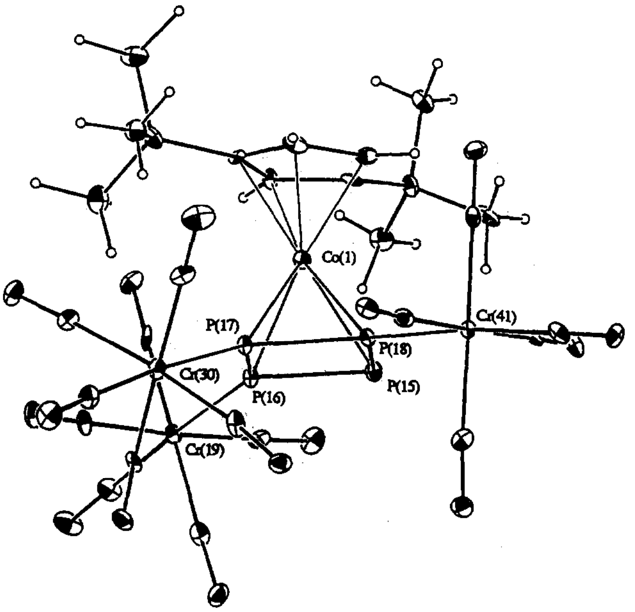


Fig. 2. The molecular structure of [CoCp″(η^4-P_4){Cr(CO)$_5$}$_3$] (2). Selected bond lengths (Å) and bond angles (°): P(15)–P(16), 2.144(5); P(15)–P(18), 2.144(4); P(16)–P(17), 2.137(4); P(17)–P(18); 2.143(4); Cr(19)–P(16), 2.318(4); Cr(30)–P(17), 2.333(3); Cr(41)–P(18), 2.319(3); Co–Cp′$_{cent}$, 1.687(2); P(16)–P(15)–P(18), 87.54(16); P(15)–P(16)–P(17), 92.44(17); P(16)–P(17)–P(18), 87.75(16); P(15)–P(18)–P(17), 92.25(16); Cr(19)–P(16)–P(15), 127.47(17); Cr(30)–P(17)–P(16), 134.35(17); Cr(41)–P(18)–P(15), 126.46(17).

P–P bond distances (mean 2.142(4) Å) are identical within the limits of error and shorter than single bonds (2.21 Å [7]). The four P atoms lie in a plane, and the Co atom is 1.754 Å above this. The two ^{t}Bu groups of the Cp″ ligand are so orientated that one is above the uncoordinated P atom and the other is slightly staggered with respect to the P atom *trans* to the uncoordinated one. As a consequence, the atom Cr(30) is pushed further away from the P_4 plane than the other Cr atoms. Because of this steric repulsion, the Cp″ plane and the *cyclo*-P_4 ligand are inclined to each other by about 4°. In [RhCp′(η^4-P_4){Cr(CO)$_5$}$_4$], in which all the P-atoms can still coordinate to Cr(CO)$_5$ groups, this angle is 7° [3]. Thus, the presence of the additional t-butyl group in the case of the Cp″ ligand results in steric modification of the coordination behaviour of the *cyclo*-P_4 ring, which can coordinate to only three Cr(CO)$_5$ centres.

** ^{31}P NMR data for **1** (CD_2Cl_2, ADEM spinsystem): $\delta(P_A) = -52.5$, $\delta(P_D) = -56.84$, $\delta(P_E) = -58.19$, $\delta(P_M) = -125.7$, $J(P_A, P_E) = 139.1$, $J(P_A, P_M) = 133.5$, $J(P_D, P_E) = 122.7$, $J(P_D, P_M) = 140.0$, $J(P_E, P_M) = 132.4$. Spectroscopic data for **2**: IR ν(CO): 2078m, 2063s, 2001w, 1967br, vs, 1958br, vs (CH_2Cl_2); 2078s, 2062vs, 2014m, 1934br, vs (KBr) cm^{-1}. MS: m/z 794.3 (M^+ − 5CO, 30%), 740.7 (M^+ − Cr(CO)$_5$, 16%), 563.6 (M^+ − Cr(CO)$_5$Cp″, 25%). ^{31}P NMR (CD_2Cl_2, AM_2X spinsystem): $\delta(P_A) = 203.2$, $\delta(P_M) = 133.8$, $\delta(P_X) = 54.0$, $J(P_A, P_M) = 328.4$, $J(P_A, P_X) = 10.3$, $J(P_M, P_X) = 355.9$. ^1H NMR (C_6D_6) $\delta = 1.14$ (s, 18H), $\delta = 5.53$ (d, 2H), $\delta = 6.03$ (t, 1H), $J(H, H) = 1.7$.

*** Crystal data for 2. $C_{28}H_{21}O_{15}P_4Cr_3Co$, $M = 936.28$, monoclinic, space group $P2_1/n$, $a = 12.017(4)$, $b = 20.395(7)$, $c = 15.093(5)$ Å, $\beta = 98.48(1)°$, $V = 3658.52$ Å^3, $Z = 4$, $D_c = 1.7$ g cm^{-3}, $F(000) = 1878$, $T = -174$°C, Mo Kα radiation, $\lambda = 0.71069$ Å, μ(Mo-Kα) = 15.284 cm^{-1}, 2522 observed diffractometer data [$F > 3\sigma(F)$]. The structure was solved by direct methods (MULTAN78) and standard Fourier techniques, refined by full matrix least-square analysis to $R = 0.052$ and $R_w = 0.045$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

1. Experimental details

All manipulations were performed under N_2 in dry solvents by use of standard Schlenk techniques.

A solution of 280 mg (0.5 mmol) of [CoCp$''$(μ-CO)]$_2$ [8], 124 mg (1 mmol) of P_4 and 6 mmol of [Cr(CO)$_5$THF] in 250 ml of THF was heated under reflux for 20 min. The solvent was then removed during 20 min under vacuum at a bath temperature of 70–80°C during which the green mixture turned brown. Unchanged P_4 and [Cr(CO)$_6$] were removed by sublimation (50°C, 10^{-3} Torr) and the residue was extracted with 40 ml of pentane and the extract filtered through a frit. The solid remaining on the frit was further extracted with hot pentane by warming the filtrate solution to reflux so that hot pentane was continually dripping on to the solid. Upon slow evaporation of the extract complex **1** crystallized out (90 mg, 9.4%).

The chromatographic separation of the initial product mixture on a silica gel column (1.5 × 40 cm; Merck 230–400 mesh) saturated with hexane yielded a small amount of the green [CoCp$''$(μ-CO)]$_2$, which was eluted with hexane, followed by a deep red product (80 mg, 8.5% yield after recrystallization), which was eluted with 3:1 hexane/CH_2Cl_2.

Acknowledgments

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