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REACTION OF COORDINATED DIPHOSPHOROUS WITH METAL CARBONYL FRAGMENTS. CRYSTAL STRUCTURE OF $[(CO)_5Cr][(CO)_5W]P_2Co_2(CO)_6$

ANNA VIZI-OROSZ, GYULA PÁLYI, LÁSZLÓ MARKÓ,

Research Group for Petrochemisty of the Hungarian Academy of Sciences, H-8201 Veszprém, Schönherz Z.u.8. (Hungary)

ROLAND BOESE and GÜNTER SCHMID

Institute of Inorganic Chemistry, University of Essen, Essen (G.F.R.)

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Summary

Either one or two of the metal carbonyl fragments $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$ or $Fe(CO)_4$ can become linked to the coordinated diphosphorous molecule of $(\mu_2\text{-}P_2)Co_2(CO)_5L$ ($L = CO$, PBu_3, PPh_3) when the latter species is treated with THF adducts of these fragments. The structure of $[(CO)_5Cr][(CO)_5W]P_2Co_2(CO)_6$ has been determined by X-ray diffraction.

Introduction

The most efficient coordinative activation of molecular N_2 requires excitation of a dinitrogen ligand by interaction with several metal atom(s) [1]. The μ_2-N_2 coordination type is believed to be very favourable for such activation. Only one μ_2-N_2 type complex is known [2], and its structure shows further coordination to hard Lewis acid centers in addition to the interaction with the transition metal. The isoelectronic acetylenes yield stable $(\mu_2\text{-alkyne})Co_2(CO)_6$ compounds [3], but attempts to prepare the analogous N_2 complexes have so far failed [4].

The most obvious model for such bonding in the Vth Main Group is $(\mu_2\text{-}P_2)Co_2(CO)_6$, which was synthezised in our laboratory [5]. The P–P bond order in this complex was found to be approximately 2 [6,7], indicating a degree of activation of the P_2 entity by the $Co_2(CO)_6$ moiety similar to that observed [10] for the acetylene analogs.

In continuation of our studies along these lines we started an examination of the Lewis acid/base behaviour of the $E_n[Co(CO)_3]_{4-n}$ (E = CH, P, As, etc.) complexes. Some results with $n = 1$; E = P [11], As [12]; $n = 2$, E = CH [13,14], P, As [13,15,16]

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and $n = 3$, $E = P$, As [11,15] have already been published. For the complexes with $n = 2$, and $E = P$ or As, we observed cluster rearrangement upon irradiation in the presence of carbonylmetals. We thus attempted separate photochemical activation of the mononuclear reaction partners. While the work was in progress two relevant papers appeared: one reported the direct synthesis of carbonylmetal derivatives of $As_2Co_2(CO)_6$ [19], and the other described an indirect route to carbonylmetal derivatives of $P_2Co_2(CO)_6$ [20]. We restrict the present report to results which complement those papers.

Results and discussion

$E_2Co_2(CO)_6$ complexes or their phosphine-substituted derivatives do not react directly with $M(CO)_6$ ($M = Cr$, Mo, W) complexes or $Fe(CO)_5$. These highly symmetrical reaction partners can, however, be photochemically activated by irradiating their solutions in weakly coordinating solvents ($S = THF$, DMF or pyridine) to form $M(CO)_5(S)$ species [21]. Furthermore, $Fe(CO)_4(THF)$ can be prepared from $Fe_2(CO)_9$ in THF even without irradiation [22]. In fact we found that the THF adducts of Cr, Mo, W, and Fe carbonyls yield the desired adducts upon reaction with $P_2Co_2(CO)_6$ and its tertiary phosphine derivatives. The new complexes prepared in this way are listed in Table 1 together with their IR ν(C–O) spectra.

The mono-metallated derivatives of the $P_2Co_2(CO)_5L$ ($L = CO$, PBu_3, PPh_3)

TABLE 1

INFRARED ν(C-O) SPECTRA OF THE CARBONYLMETAL ADDUCTS OF $P_2Co_2(CO)_5L$ ($L = CO$, PBu_3, PPh_3) COMPOUNDS (n-hexane, CO gas calibration [28])

Compound	Absorption maxima (cm^{-1})
$Cr(CO)_5P_2Co_2(CO)_6$	2107.5(m), 2703.09(vs), 2065.4(vs), 2052.1(s), 2047.1(m), 2037.1(w), 1999(vw,vbr), 1986.1(w), 1972.0(s), 1963.18(vs), 1930(w,br)
$[Cr(CO)_5]_2P_2Co_2(CO)_6$	2112.0(w), 2077.5(s), 2068.2(vs), 2052.0(w), 2043.0(vw), 2024(vw,vbr), 1972(vs), 1957(m), 1935(w,vbr)
$Cr(CO)_5P_2Co_2(CO)_5(PBu_3)$	2084.4(s), 2057.4(vs), 2035.9(vs), 2028.9(m), 2013.2(w), 1990.0(w), 1957.2(vs), 1952.4(s), 1944.2(m)
$[Cr(CO)_5]_2P_2Co_2(CO)_5(PBu_3)$	2092.0(s), 2061.0(vs), 2044.6(s), 2036.2(m), 2002.4(w), 1992.68(vw), 1958.6(vs), 1943.6(s)
$Cr(CO)_5P_2Co_2(CO)_5(PPh_3)$	2085.0(s), 2058.3(s), 2038.5(s), 2031.0(m), 1994(w,br), 1954.0(vs), 1948(sh)
$[Cr(CO)_5]_2P_2Co_2(CO)_5(PPh_3)$	2092.6(m), 2061.7(vs), 2047.4(m), 2037.6(m), 1995 (w,vbr), 1961.6(vs), 1956(vs), 1944.6(m)
$W(CO)_5P_2Co_2(CO)_5(PPh_3)$	2086.8(m), 2063.8(s), 2038.8(m), 2031.5(m), 1986(w,vbr), 1949.0(vs), 1941.8(vs)
$[W(CO)_5]_2P_2Co_2(CO)_5(PPh_3)$	2072.6(s), 2027.6(m), 2021.2(m), 1981(w,br), 1942(vs,br)
$Mo(CO)_5P_2Co_2(CO)_5(PPh_3)$	2086.6(m), 2065.4(s), 2037.7(m), 2030.6(m), 1993(w,br), 1957.2(vs), 1951.6(vs)
$Cr(CO)_5W(CO)_5P_2Co_2(CO)_6$	2112(w), 2077.5(s), 2074.2(s), 2068.5(s), 2054.0(w), 1972.0(s), 1968(vs), 1956(m)
$Cr(CO)_5W(CO)_5P_2Co_2(CO)_5(PBu_3)$	2093.6(m), 2067.6(s), 2061.6(s), 2047.6(s)

complexes were formed in a smooth reaction under mild conditions in short reaction times (0.5–1 h). The bis-metallated derivatives could be prepared under similar conditions using either an appropriate excess of the THF adduct or starting from the mono-metallated $P_2Co_2(CO)_5L$ and adding a further portion of the adduct. Thus the bis-metallated derivatives could also be prepared in two steps, and this provided a key to the preparation of a new type of metallated derivative containing two different transition metals linked to the coordinated P_2 moiety, e.g. $[W(CO)_5][Cr(CO)_5]P_2Co_2(CO)_5(PBu_3)$. The Cr, Mo, and W complexes are fairly stable, while the Fe derivatives are much more labile: the $Fe(CO)_4$ fragment readily dissociates off, and the corresponding non-metallated complex is reformed.

The new compounds can be identified by their characteristic IR spectra (Fig. 1 and Table 1). The complete vibrational analysis of the ν(C–O) spectra would require a separate study with such relatively complicated models but three less qualitative features can be noted:

(i) The spectra show more absorption bands than would be expected from the local symmetry of the various carbonylmetal fragments (e.g. $Co_2(CO)_6$ vs. $Cr(CO)_5$ $Co_2(CO)_6$ vs. $Fe(CO)_4$ etc.). This is a new feature since similar observations are not possible with the neutral $(CO)_nMECo_3(CO)_9$ ($E = P$, As; $Me = Cr$, Mo, W, $n = 5$; $M = Fe$, $n = 4$) [11,12] or anionic $[(CO)_5MSFe_3(CO)_9]^{2-}$ [23] complexes because of eventual rotational coupling [24];

(ii) The vibrational coupling between the carbonyl groups on different metals seems not to be very strong since the absorption bands fall into groups which can be attributed to vibrations similar to those of carbonyls in related chemical environments (i.e. in species involving only one transition metal).

(iii) The shapes of the spectra are very similar within one type, and thus the main value of the ν(C–O) spectra is in showing that the geometry established by an X-ray structural study for one example can be generalized over the whole group.

Since the structure of a homo-bis-metallated derivative of $P_2Co_2(CO)_6$ is known from the parallel study by Huttner et al. [20], we report here the structure of a

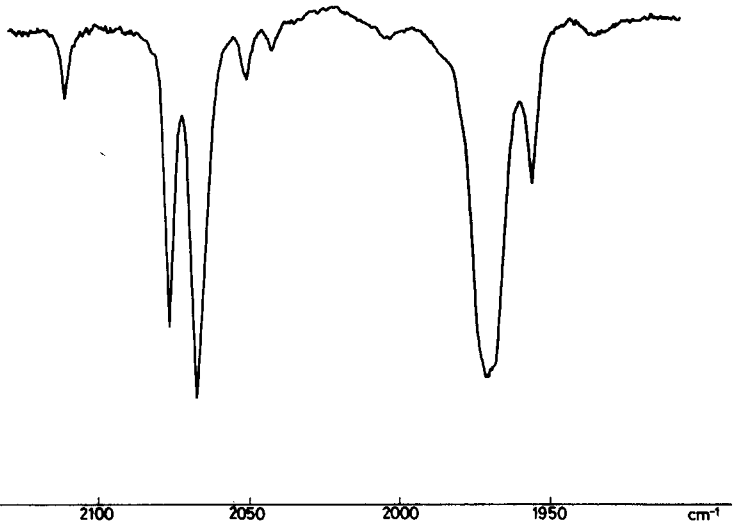

Fig. 1. Infrared ν(C–O) spectrum of $[Cr(CO)_5]_2P_2Co_2(CO)_6$ complex in hexane solution.

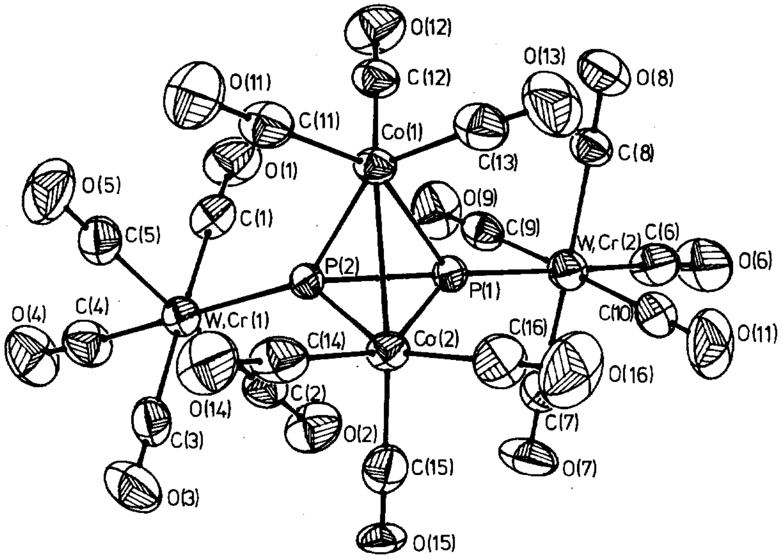

Fig. 2. The molecular structure of $[(CO)_5W][(CO)_5Cr]P_2Co_2(CO)_6$.

derivative in which the side-on coordinated P_2 moiety bears two further different metals. The molecular structure of $[(CO)_5Cr][(CO)_5W]P_2Co_2(CO)_6$ is shown in Fig. 2, and some relevant structural parameters are shown in Table 2.

The overall geometry of the molecule corresponds to that expected from the way in which it was made. It is noteworthy that the two bulky $M(CO)_5$ (M = Cr or W) fragments do not change the geometry of the $Co_2(CO)_6$ fragment with respect to that in less crowded molecules; e.g. compare, the Co–Co distances in $Co_2(CO)_8$ (bridged isomer) (252.4 pm [25]), $P_2Co_2(CO)_5PPh_3$ (257.4 pm [6]), and $As_2Co_2(CO)_5PPh_3$ (259.4 pm [26]), etc..

Thus the $M(CO)_5$ (M = Cr, Mo, W) group can be regarded as a ligand attached

TABLE 2

BOND LENGTHS (pm) AND BOND ANGLES (°) IN $[(CO)_5Cr][(CO)_5W]P_2Co_2(CO)_6$ (STANDARD DEVIATIONS IN PARENTHESES.)

Bond lengths		Angles	
Co(1)-Co(2)	257.3(1)	Co(1)-P(1)-Co(2)	69.7(1)
Co(1)-P(1)	225.8(2)	P(2)-P(1)-Co(2)	62.9(1)
Co(1)-P(2)	224.5(2)	P(2)-P(1)-Co(1)	62.4(1)
Co(2)-P(1)	224.6(2)	Co(1)-P(2)-Co(2)	69.8(1)
Co(2)-P(2)	225.2(2)	P(1)-P(2)-Co(2)	62.6(1)
P(1)-P(2)	206.1(3)	P(1)-P(2)-Co(1)	63.1(1)
P(1)-W, Cr(1)	236.5(2)	P(1)-Co(1)-P(2)	54.5(1)
P(2)-W, Cr(2)	235.7(2)	P(2)-Co(1)-Co(2)	55.2(1)
Co(1)-C(O) (average)	180.5	P(1)-Co(1)-Co(2)	54.9(1)
Co(2)-C(O) (average)	182.8	P(1)-Co(2)-P(2)	54.5(1)
W, Cr(1)-C(O) (average)	193.6	Co(1)-Co(2)-P(2)	55.0(1)
W, Cr(2)-C(O) (average)	194.0	Co(1)-Co(2)-P(1)	55.4(1)

to the P_2Co_2 moiety. The reaction of $[(CO)_5M]_2P_2Co_2(CO)_5L$ ($L = CO$, PBu_3 or PPh_3) complexes with tertiary phosphines (L′) confirms this, since instead of a replacement of an additional carbonyl group, the species $M(CO)_5L'$, $[M(CO)_5]P_2Co_2(CO)_5L$ and $P_2Co_2(CO)_5L$ were obtained.

Another interesting feature of the structure is that the two end-on coordinated transition metal moieties cause a further lengthening of the P–P bond, indicating that further activation has taken place. In assessing the extent of this activation we note that the P–P distance in P_2 in the gas phase is 189.3 pm [27], while the value in $P_2Co_2(CO)_5PPh_3$ is 201.0 pm [6], that in $[(CO)_5Cr]_2P_2Co_2(CO)_6$ is 206.5(5) pm [20], and in $[(CO)_5Cr][(CO)_5W]P_2Co_2(CO)_6$ is 206.1(3) pm. This means that the two-fold side-on coordination ($P_2Co_2(CO)_6$) causes a lengthening of the P–P bond by about 12 pm with respect to that in free P_2, and the two further end-on coordinated metals cause a further 4 pm lengthening. In terms of Pauling's bond length/bond order relationship [9] in the first case the P–P bond order changes from 2.8 to 1.9 and in the second case from 1.9 to 1.7, which is not a large change but is by no means negligible.

The mass spectra of the new complexes (Table 3) show similar fragmentation behaviour. As usual for carbonyl metals [28] the loss of all CO ligands is observed first, and this is followed by the fragmentation of the MP_2Co_2 or $M_2P_2Co_2$ core. These features are in accord with the assumed structures.

TABLE 3

MASS SPECTRA OF SOME CARBONYLMETAL ADDUCTS OF $P_2Co_2(CO)_5L$ ($L = CO$, PBu_3) COMPOUNDS AT 75eV. (Intensities are in parentheses)

Compound	*m/e*
$Cr(CO)_5P_2Co_2(CO)_6$	540(27), 512(4), 484(< 1), 456(7), 428(14) 400(40), 372(62), 344(40), 316(27), 288(46) 260(44), 232(100), 180(3), 118(18), 80
$[Cr(CO)_5]_2P_2Co_2(CO)_6$	732(15), 704(1), 676(< 1), 648(1), 620(8) 592(8), 564(24), 536(30), 508(42), 480(22) 452(26), 424(32), 396(41), 368(22), 340(57) 312(46), 284(100), 232(67), 180(17)
$Cr(CO)_5W(CO)_5P_2Co_2(CO)_6$	864(19.5), 836(5), 808(< 1), 780(< 1), 752(17) 724(19.5), 696(29), 668(63), 640(61), 612(61) 584(51), 556(61), 528(63), 500(71), 472(67) 444(54), 416(100), 364(49), 232(73)
$Cr(CO)_5P_2Co_2(CO)_5(PBu_3)$	714(88), 686(5), 658(< 1), 630(< 1), 602(88) 574(100), 546(55), 518(50), 490(35), 462(58) 434(25), 382(98), 202(55), 180(20), 118(98)
$[Cr(CO)_5]_2P_2Co_2(CO)_5(PBu_3)$	906(41), 878(7), 850(< 1), 822(< 1), 794(7) 766(88), 738(29), 710(29), 682(81), 654(68) 626(59), 598(34), 570(71), 542(44), 514(100) 486(7), 434(12), 284(12)
$Fe(CO)_4P_2Co_2(CO)_5(PBu_3)$	690(4), 662(< 1), 634(6), 606(9), 578(9) 550(18), 522(57), 494(29), 466(51), 438(50) 382(100), 236(26), 180(27)
$Cr(CO)_5W(CO)_5P_2Co_2(CO)_5(PBu_3)$	1038(42), 1010(< 1), 982(< 1), 954(< 1) 926(4), 898(67), 870(54), 842(54), 814(100), 786(19), 758(22), 730(26), 702(15), 674(15), 646(19), 618(19), 566(44), 434(15)

Experimental

All operations were carried out under dry Ar or N_2, using carefully dried solvents. Reagents were of commercial origin except for $P_2Co_2(CO)_6$, $P_2Co_2(CO)_5(PBu_3)$ and $P_2Co_2(CO)_5(PPh_3)$, which were prepared as described previously [5,13].

The infrared spectra were run on a VEB Zeiss Jena SPECORD IR 75 type spectrophotometer. Calibration of the IR spectra was performed by simultaneous recording of a CO gas spectrum [29]. Mass spectra were recorded on a MAT-111 (Varian, Palo Alto, USA) instrument using direct sample introduction.

X-Ray structure determination of $[(CO)_5Cr][(CO)_5W]P_2Co_2(CO)_6$

Crystal dimensions: 0.25 × 0.25 × 0.18 mm, Syntex R3 four-circle diffractometer, Graphite monochromated Mo-K_α-radiation. Cell dimensions: a 979.8(1), b 1101.4(3), c 1258.5(3) pm, α 82.85(2), β 78.53(2), γ 78.38(2)°, V $1.2987(5) \times 10^9$ pm^3 refined from 25 reflections ($18° > 2\theta > 27°$). Triclinic, space group $P\bar{1}$; $Z = 2$; D_x 2.21 g/cm^3, $F(000) = 812$; μ 65.1 cm^{-1}. 2θ: ω scan data collection with variable scan speed of 2°/min ($I \le 150$ cps) to 30°/min ($I \le 2500$ cps) and a peak to background ratio of 1/1; 6006 independent intensities ($3° \le 2\theta \le 60°$), of which 4409 were treated as observed ($F_0 \le 4.5 \le \sigma(F)$).

Absorption corrections were applied with maximum transmission of 0.942 and minimum transmission of 0.503, which reduced the merging R-factor from 11.87 to 1.57%.

The chromium and tungsten atoms were disordered, each showing 50% occupancy of the metal sites. Positional and thermal parameters were refined to the same extents, with chromium and tungsten given the site occupation factor 0.5. No further disorder was detected in the last difference Fourier (maximum rest electron density 1.42 e/Å^3 with 0.8 Å from W, Cr(1)) or on taking account of the thermal parameters of the ligands. $R = 0.057$, $R_w = 0.066$, $w^{-1} = \sigma^2(F) + 145 \times 10^{-5} \times F^2$. Structure solution by Patterson methods, block cascade refinement, and display by SHELXTL-Program System [30] using a NOVA 3 computer (Data General) (Table 4). Tables of thermal parameters and structure factors are available from the authors.

Preparation of $[Cr(CO)_5]P_2Co_2(CO)_6$ and $[Cr(CO)_5]P_2Co_2(CO)_6$

A solution of $Cr(CO)_5(THF)$ was prepared from 0.3 mmol $Cr(CO)_6$ and 40 cm^3 THF as described by Strohmeier et al. [21]. Then $P_2Co_2(CO)_6$ (50 mg, 0.15 mmol) was added and the mixture was stirred for 30 min at room temperature. The solvent was evaporated off in vacuo, and the residue was dissolved in n-hexane (~ 20 cm^3). The n-hexane solution was chromatographed on a silica gel column (20 mm × 90 cm) with n-hexane as eluent. Three coloured fractions were collected; the first (orange-red) band was unchanged $P_2Co_2(CO)_6$, the second fraction was greenish violet and yielded brownish-black crystals of $[Cr(CO)_5]P_2Co_2(CO)_6$ (15%). The third was purple, and yielded black crystals of $[Cr(CO)_5]_2P_2Co_2(CO)_6$ (7%) after concentration (to 5–10 cm^3) and cooled in dry ice. (Found: Cr, 9.4; Co, 21.9; P, 11.2. $CrCo_2P_2C_{11}O_{11}$ calcd.: Cr, 9.26; Co, 21.85; P, 11.48%.) (Found: Cr, 6.95; Co, 16.05; P, 8.4. $Cr_2Co_2P_2C_{16}O_{16}$ calcd.: Cr, 7.0; Co, 16.12; P, 8.47%.)

Preparation of $[Cr(CO)_5]P_2Co_2(CO)_5(PR_3)$ and $[Cr(CO)_5]_2P_2Co_2(CO)_5(PR_3)$ (R = Bu or Ph)

The procedure was as described above but starting from $P_2Co_2(CO)_5(PR_3)$ (R = Bu or Ph) instead of $P_2Co_2(CO)_6$.

TABLE 4

ATOMIC COORDINATES FOR $[(CO)_5Cr][(CO)_5W]P_2Co_2(CO)_6$ (Standard deviations in parantheses)

Atom	x/a	y/b	z/c
W,Cr(1)	0.07781(6)	0.03775(6)	0.22142(5)
W,Cr(2)	0.32541(6)	0.31297(6)	0.48123(5)
Co(1)	0.42377(11)	0.25099(10)	0.14312(8)
Co(2)	0.18456(12)	0.40212(10)	0.16586(9)
P(1)	0.2871(2)	0.3006(2)	0.3041(2)
P(2)	0.2133(2)	0.1953(2)	0.2111(2)
C(1)	0.2222(11)	−0.0786(9)	0.2886(8)
C(2)	−0.0146(10)	0.0920(10)	0.3652(9)
C(3)	−0.0604(11)	0.1582(10)	0.1542(9)
C(4)	−0.0325(12)	−0.0889(11)	0.2298(11)
C(5)	0.1749(11)	−0.0073(10)	0.0807(9)
C(6)	0.3599(12)	0.3199(12)	0.6252(8)
C(7)	0.1209(10)	0.3464(9)	0.5336(8)
C(8)	0.5257(9)	0.2820(9)	0.4219(7)
C(9)	0.3249(10)	0.1360(10)	0.5093(7)
C(10)	0.3219(10)	0.4912(10)	0.4471(9)
C(11)	0.4449(10)	0.2076(10)	0.0045(7)
C(12)	0.5340(9)	0.1208(9)	0.2007(7)
C(13)	0.5321(10)	0.3691(10)	0.1275(8)
C(14)	0.1527(10)	0.3955(9)	0.0271(8)
C(15)	0.0053(11)	0.4339(9)	0.2414(8)
C(16)	0.2402(12)	0.5521(10)	0.1580(9)
O(1)	0.3087(10)	−0.1417(8)	0.3258(8)
O(2)	−0.0680(10)	0.1275(9)	0.4484(6)
O(3)	−0.1406(9)	0.2295(9)	0.1140(8)
O(4)	−0.0943(11)	−0.1678(9)	0.2318(9)
O(5)	0.2348(11)	−0.0338(10)	−0.0040(7)
O(6)	0.3755(10)	0.3270(10)	0.7106(7)
O(7)	0.0052(7)	0.3642(9)	0.5677(8)
O(8)	0.6425(8)	0.2655(9)	0.3827(7)
O(9)	0.3243(10)	0.0320(8)	0.5261(8)
O(10)	0.3181(11)	0.5953(7)	0.4248(9)
O(11)	0.4600(10)	0.1757(10)	−0.0793(7)
O(12)	0.5988(9)	0.0364(8)	0.2401(7)
O(13)	0.5960(9)	0.4475(8)	0.1165(9)
O(14)	0.1351(10)	0.3866(9)	−0.0550(6)
O(15)	−0.1064(8)	0.4495(9)	0.2893(8)
O(16)	0.2708(12)	0.6445(8)	0.1509(9)

There were again three chromatographic fractions all deep red. The first was unchanged $P_2Co_2(CO)_5(PR_3)$, the second $[Cr(CO)_5]P_2Co_2(CO)_5(PR_3)$, and the third $[Cr(CO)_5]_2P_2Co_2(CO)_5(PR_3)$. The derivatives with $R = Bu$ were obtained only as amorphous solids upon evaporating the fractions to dryness. The derivatives with $R = Ph$ were obtained as black crystals by cooling the n-hexane solution to −40°C: $[Cr(CO)_5]P_2Co_2(CO)_5(PPh_3)$ (10% yield) and $[Cr(CO)_5]_2P_2Co_2(CO)_5(PPh_3)$ (13% yield). (Found: Cr, 6.1; Co, 15.05; P, 11.9. $CrCo_2P_3C_{28}H_{15}O_{10}$ calcd.: Cr, 6.55; Co, 14.86; P, 11.71%.) (Found: Cr, 11.0; Co, 12.1; P, 9.45. $Cr_2Co_2P_3C_{33}H_{15}O_{15}$ calcd.: Cr, 10.77; Co, 12.22; P, 9.63%.)

Preparation of $[W(CO)_5][Cr(CO)_5]P_2Co_2(CO)_6$ *and* $[W(CO)_5][Cr(CO)_5]$-$P_2Co_2(CO)_5(PBu_3)$

$W(CO)_6$ (0.05 mmol) was treated with THF (20 cm^3) as described by Strohmeier et al. [21] then $[Cr(CO)_5]P_2Co_2(CO)_6$ (15 mg, 0.03 mmol) or $[Cr(CO)_5]P_2Co_2(CO)_5(PBu_3)$ (25 mg 0.03 mmol) was added and the mixture was stirred for 1 h at room temperature. The solvent was evaporated off in vacuo, and the residue was extracted with n-hexane (40 cm^3). This solution was chromatographed on a silica gel column (20 mm × 120 cm) with n-hexane as eluent. The second (dark red) fraction was collected for both Cr–W containing compounds and, the solutions were concentrated in vacuo and cooled to ca. $-40°$. After 2–3 days $[W(CO)_5][Cr(CO)_5]P_2Co_2(CO)_6$ (30% yield), and $[W(CO)_5][Cr(CO)_5]$-$P_2Co_2(CO)_5(PBu_3)$ (10% yield) were obtained as black crystals. (Found: Cr, 6.2; W, 20.8; Co, 13.2; P, 7.1 $CrWCo_2P_2C_{16}O_{16}$ calcd.: Cr, 6.02; W, 21.29; Co, 13.66; P, 7.18%.) (Found: Cr, 4.9; W, 17.6; Co, 11.4; P, 8.8. $CrWCo_2P_3C_{27}H_{27}O_{15}$ calcd.: Cr, 5.00; W, 17.72; Co, 11.36; P, 8.96%.)

Preparation of $[Fe(CO)_4]P_2Co_2(CO)_5(PBu_3)$

Crystalline $Fe_2(CO)_9$ (50 mg, excess) was added to a solution of $P_2Co_2(CO)_5(PBu_3)$ (0.1 mmol, 50 mg) in 20 cm^3 dry THF. The heterogeneous mixture was stirred vigorously under argon at room temperature in darkness. After 30 min the dark solution was evaporated to dryness in vacuo, and the solid residue was extracted with n-pentane. The dark pentane solution was chromatographed on a silica gel column (20 mm × 60 cm) with pentane as eluent and the dilute second (purple) fraction was collected and concentrated in vacuo. The product $[Fe(CO)_4]P_2Co_2(CO)_5(PBu_3)$, was identified by IR and MS spectra. The solution of the complex was handled in darkness.

References

1 e.g.: (a) A.E. Shilov, Usp. Khim., 43 (1974) 863; (b) J. Chatt, J.R. Dilworth and R.L. Richards, Chem. Rev., 78 (1978) 589.
2 (a) K. Jonas, Angew. Chem., 85 (1973) 1050; (b) C. Krüger and Y.H. Tsay, Angew. Chem., 85 (1973) 1051.
3 R.S. Dickson and P.J. Fraser, Advan. Organomet. Chem., 12 (1974) 323.
4 (a) M.I. Bán, G. Dömötör, A. Vizi-Orosz and G. Pályi, XIIth Internat. Conf. Coord. Chem., Budapest (Hungary), August 23–27, 1982, Abstr. Vol. 1., p. 139; (b) K.I. Goldberg, D.M. Hoffmann and R. Hoffmann, Inorg. Chem., 21 (1982) 3863.
5 A. Vizi-Orosz, G. Pályi and L. Markó, J. Organomet. Chem., 60 (1973) C25.
6 C.F. Campana, A. Vizi-Orosz, G. Pályi, L. Markó and L.F. Dahl, Inorg. Chem., 18 (1979) 3054.
7 P–P distance in $P_2Co_2(CO)_5PPh_3$: 201.9 pm [6], in P_2 molecule (gas phase): 189.3 pm [8], calculated P–P bond order [9] for the complex: 1.9.
8 A.E. Douglas and K.S. Rao, Can. J. Phys., 36 (1958) 565.
9 L. Pauling, The Chemical Bond. Cornell Univ. Press Ithaca (N.Y., USA), 1967, p. 136.
10 (a) D.A. Brown, J. Chem. Phys., 33 (1960) 1037; (b) F.A. Cotton, J.D. Jamerson and B.R. Stults, J. Am. Chem. Soc., 98 (1976) 1774.
11 A. Vizi-Orosz, J. Organomet. Chem., 111 (1976) 61.
12 A. Vizi-Orosz, V. Galamb, I. Ötvös, G. Pályi and L. Markó, Transition Met. Chem., 4 (1979) 294.
13 G. Váradi, A. Vizi-Orosz, S. Vastag and G. Pályi, J. Organomet. Chem., 108 (1976) 225.
14 L. Bencze, V. Galamb, A. Guttmann and G. Pályi, Atti Accad. Nazl. Lincei, Rend.Cl.Fis., Mat., Nat., 68 (1/5) (1980) 437.
15 A. Vizi-Orosz, V. Galamb, G. Pályi and L. Markó, J. Organomet. Chem., 216 (1981) 105.

16 It should be mentioned that recently Seyferth [17] and Nixon [18] succeeded to add $M(CO)_5$ (M = Cr, Mo, W) fragments to the phosporous atom in $(\mu_2\text{-}RCP)Co_2(CO)_6$ complexes.

17 D. Seyferth, J.S. Merola and R.S. Henderson, Organometallics, 1 (1982) 859.

18 J.C.T.R. Burckett-St. Laurent, P.B. Hitchock, H.W. Kroto, M.F. Meidine and J.F. Nixon, J. Organomet. Chem., 252 (1983) 95.

19 M. Müller and H. Vahrenkamp, J. Organomet. Chem., 252 (1983) 95.

20 N. Lang, L. Zsolnai and G. Huttner, Angew. Chem., 95 (1983) 1017.

21 (a) W. Strohmeier and H. Gerlach, Chem. Ber., 94 (1961) 398; (b) W. Strohmeier, J.F. Guttenberger and G. Popp, ibid., 98 (1965) 2248.

22 (a) G. Natile and G. Bor, J. Organomet. Chem., 35 (1972) 185; (b) F.A. Cotton and J.M. Troup, J. Am. Chem. Soc., 96 (1974) 3438.

23 J. Takâcs and L. Markó, Transition Met. Chem. 10 (1985) 23.

24 G. Bor, J. Organomet. Chem., 65 (1974) 81.

25 G.G. Sumner, H.P. Klug and L.E. Alexander, Acta Cryst., 17 (1964) 732.

26 A.S. Foust, M.S. Foster and L.F. Dahl, J. Am. Chem. Soc., 91 (1969) 5631.

27 A.E. Douglas and K.S. Rao, Can. J. Phys., 36 (1958) 565.

28 M.R. Litzow and T.R. Spalding, Mass Spectrometry of Inorganic and Organometallic Compounds. Elsevier, Amsterdam, 1973, p. 471–558.

29 G. Bor, Acta Chim. (Budapest), 39 (1962) 315.

30 G.M. Sheldrick, SHELXTL a complete system for solving, refining and displaying crystal structures from diffraction data (Rev. 4.1) (1983).