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Journal of Organometallic Chemistry 593–594 (2000) 127–134

Journal of Organometallic Chemistry

Adducts of cyclotriphosphorus complexes: synthesis, solid state structure and solution behaviour of the bis-adducts $[\{(triphos)Co\}(P_3)\{M(CO)_5\}_2]$ [triphos = $MeC(CH_2PPh_2)_3$; M = Cr, Mo, W]

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Received 26 May 1999; accepted 29 June 1999

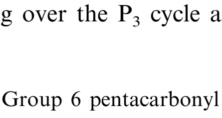
Abstract

Treatment of $[(triphos)CoP_3]$ (**1**) [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane] which has a pseudotetrahedral core formed by three unsubstituted phosphorus atoms and one cobalt, with an excess of Group 6 pentacarbonyl moieties affords the compounds $[\{(triphos)Co\}(\mu_3,\eta^{3:1:1}\text{-}P_3)\{M(CO)_5\}_2]$ [M = Cr (**2**), Mo (**3**), W (**4**)]. The notable features of the solid state structure of **4** are compared with those of the bischromium adduct **2**. The variable temperature NMR data of the compounds are suggestive of three fluxional processes in solution which may be interpreted as {(triphos)Co} rotation about its C_3 axis, $\{M(CO)_5\}$ scrambling over the P_3 cycle and a concerted motion of the two $\{M(CO)_5\}$ fragments. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Group 6 pentacarbonyl complexes; Unsubstituted phosphorus compounds; X-ray crystal structure; ^{31}P-NMR spectroscopy

1. Introduction

The field of coordinatively stabilized P_n fragments is currently under intense investigation. In the last 25 years a large number of complexes containing a variety of P_n ligands ($n = 1-14$) have been synthesized and in the main part have been characterized by X-ray structure analysis in the solid state as well as by ^{31}P-NMR spectroscopy in solution [1]. A series of neutral [2] and cationic [3] compounds (**1**) have been described in which the cyclic triatomic P_3 ligand is bound to one metal atom of the cobalt or of the nickel group which in turn bears the tripodal tridentate 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) as coligand.



M = Co, Rh, Ir ; n = 0

M = Ni, Pd, Pt ; n = 1

(I)

The unsubstituted phosphorus atoms are susceptible of addition reactions of metal moieties or of organic reagents having Lewis acidic properties. These reactions yield compounds in which the added fragment is bound in η^3 [4], η^2 [5] or η^1 [2a,6] fashion to the P_3 ring, depending on its binding properties. The compounds have been characterized in the solid state by X-ray analysis while their behaviour in solution, which was investigated by ^{31}P-NMR, was considered to a lesser extent. The scattered data have shown that the parent compounds $[(triphos)MP_3]$ (M = Co (**1**), Rh, Ir) [2] and $[(triphos)MP_3]BF_4$ (M = Ni, Pd, Pt) [3], as well as the diamagnetic triple decker derivatives $[\{(triphos)M\}(P_3)\{M(triphos)\}]^+$ (M = Ni, Rh, Pd) [4] are highly fluxional at room temperature, which has been interpreted in terms of free rotation of the {(triphos)M} moieties with respect to the *cyclo*-P_3 unit. All compounds formed by reaction of an unsaturated Lewis acidic metal fragment over one edge of the P_3 unit of the mononuclear complexes also present equivalence of the phosphorus atoms of the triphos ligand as well as of those of the P_3 unit at ambient temperature [5]. Although a lower limit form in the NMR spectra of

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PII: S0022-328X(99)00388-5

these compounds has never been reached, the results point to the occurrence of a process(es) involving migration of the metal fragment(s) over the P_3 unit which may be accompanied by the above mentioned rotation of the {(triphos)M} moiety. In contrast to the complexes bearing metal fragments on the *cyclo*-P_3 unit, the compound [(triphos)Co(P_3CH_3)]BF_4, which forms upon interaction of **1** with Me_3OBF_4, does not exhibit fluxionality at the *cyclo*-P_3 ligand [6c].

Although compounds presenting one organometallic 16 valence electron fragment bound per naked phosphorus atom have been described some time ago, their behaviour in solution has not yet been considered [2a,6a]. With the aim of obtaining information on the dynamic process(es) we have synthesized compounds which form upon the addition of two metal pentacarbonyls to **1** and investigated their behaviour in solution. In this paper we report the synthesis and characterization both in the solid state and in solution of the adducts [{(triphos)Co}(P_3){M(CO)$_5$}$_2$] [M = Cr (**2**), Mo (**3**), W (**4**)]. The crystal structure of **4** has been determined by X-ray analysis and its features are compared to those of the previously reported structure of the dichromium adduct **2** [2a].

2. Results and discussion

2.1. Syntheses of compounds and infrared properties

Compounds **2**, **3** and **4**, which may be considered as the bis-adducts of the Group 6 pentacarbonyl fragments {M(CO)$_5$} of the *cyclo*-P_3 ligand in **1**, are synthesized by adding the solvent-stabilized 16 valence electron fragment to the cobalt complex in THF. The immediate colour change of the solution from yellow to red upon addition of the metal pentacarbonyls indicates that formation of adducts occurs immediately. By monitoring the reaction (IR spectroscopy) it is observed that the mono-adduct forms within minutes ending subsequently in the final bis-adduct after ca. 4 h. After chromatographic work-up the complexes are isolated in moderate yields as orange to red crystalline solids, which are moderately soluble in toluene and very soluble in CH_2Cl_2 and THF. The solids, which may be handled in the air for a short time, show decomposition even under an inert atmosphere after a few weeks. With a threefold excess of the parent compound **1** in THF solution, the bis-adduct **2** commutates to the appropriate mono-adduct within 7 h at r.t.; however, no detachment reaction is observed with carbon monoxide. The highest yield of the bis-adducts **2**, **3** and **4** is obtained by applying a large excess of the complexing reagent [M(CO)$_5$(THF)]. Remarkably, the organometallic P_3 complexes [{Cp*(OC)$_2$W}(P_3)] and [{Cp*Ni}(P_3)] under similar conditions to those used in the present study form tetranuclear complexes of formulae [{M′}(P_3){Cr(CO)$_5$}$_3$] (M′ = Cp*(OC)$_2$W [7], Cp*Ni [8]). It is likely that the sterically demanding triphos ligand in **1** suppresses the formation of the tris-adducts; in fact, only in the presence of the less sterically demanding 16 valence electron fragment {Mn(CO)$_2$Cp} the tris-adduct [{(triphos)Co}(P_3){Mn(CO)$_2$Cp}$_3$] has been obtained [6b].

The IR absorptions of the compounds in solution (see Section 3.2) exhibit relative intensities and band shapes that are similar to those of the phosphine complexes [M(CO)$_5$(PR$_3$)] [e.g. M = W, R = Ph: 2072(m), 1980(w), 1938(vs), 1920(sh)]. Therefore the donor/acceptor properties of the naked phosphorus atoms in the 'ligand' {(triphos)CoP_3} towards the present carbonyl fragments may be regarded as comparable to those of a variety of phosphines. The two pentacarbonyl groups are non-independent as evidenced by the presence of more bands than the four ones expected for the [M(CO)$_5$L] complexes. Especially for the A_1 absorption in the high wavenumber region (ca. 2070 cm^{-1}) and for the very intense E one (ca. 1950 cm^{-1}) two separated bands are well distinguishable, with the higher energy one being slightly more intense.

2.2. X-ray crystal structure analysis of [{(triphos)Co}(P_3){W(CO)$_5$}$_2$] (4)

The structure of the compound **4** consists of trimetal molecules and interposed CH_2Cl_2 solvate molecules disorderly arranged in proximity to inversion centres. The overall arrangement within the molecule of the compound (Table 1, Fig. 1) is substantially similar to that reported for **2** [2a]. There are, however, differences which may be traced to the different effects of steric repulsion and should be ultimately due to the different lengths of the W–P and the Cr–P bonds. As far as the W–P bonds are concerned, their 2.554(7) Å mean value in **4** is slightly larger that the 2.516(2) Å value found for the W–P distance in the compound [W(CO)$_5$(PMe$_3$)] (**5**) [9], but is much smaller than the 2.686(4) Å value

Table 1
Selected bond lengths (Å) and angles (°) for [{(triphos)Co}(P_3){W(CO)$_5$}$_2$]·0.5CH_2Cl_2 (**4**)

Bond lengths (Å)			
Co–P(1)	2.226(4)	P(4)–P(5)	2.137(5)
Co–P(2)	2.199(4)	P(4)–P(6)	2.146(5)
Co–P(3)	2.216(4)	P(5)–P(6)	2.152(5)
Co–P(4)	2.280(4)	W(1)–P(4)	2.559(3)
Co–P(5)	2.291(4)	W(2)–P(5)	2.549(4)
Co–P(6)	2.350(4)		
Bond angles (°)			
Co–P(4)–W(1)	161.1(2)	Co–P(5)–W(2)	164.6(2)
P(5)–P(4)–W(1)	133.3(2)	P(4)–P(5)–W(2)	130.9(2)
P(6)–P(4)–W(1)	130.1(2)	P(6)–P(5)–W(2)	128.1(2)

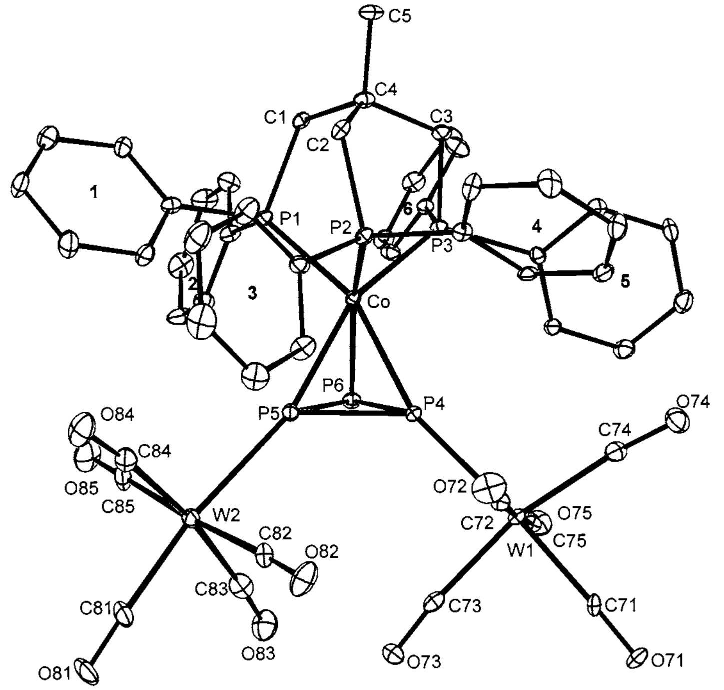

Fig. 1. A view of the [{(triphos)Co}(P_3){W(CO)$_5$}$_2$] molecule in the structure of **4**, with 20% probability thermal ellipsoids. The phenyl rings are identified by serial numbers for clarity.

exhibited by the more hindered [W(CO)$_5$(P^{t}Bu$_3$)] (**6**) [10]. Compared to the Cr–P distances in **2** the present W–P distances are longer, in the mean, by 0.13 Å. Such a difference is within the (wide) range of those found for distances formed by the two metals to phosphorus in related compounds [11]. In both the compounds **4** and **2** the two pentacarbonyl groups are oriented about their metal–phosphorus bonds in such a way as to minimize their interactions (Fig. 1). The W···W 5.561(2) Å and Cr···Cr 5.588(7) Å separations in the two compounds are comparable and may correspond to the closest possible approaches of the pentacarbonyl groups in the present arrangement [e.g. there is an O(73)···O(83) 2.99(2) Å contact in **4** and an O(8)···O(14) 3.09(2) Å contact in **2**]. However, in the case of the chromium derivative the double addition on the P_3 unit through shorter metal–phosphorus bonds is attained at the expense of some strains, as revealed by a less symmetrical mode of attack of the two pentacarbonyl groups compared to **4**. In particular, there is a larger difference (8.2°) between the two Co–P–Cr angles in **2** than between the Co–P–W angles (3.5°) in **4** and the spread of the P–P–Cr angles in **2** (14.8°) is larger than that (5.2°) of the P–P–W angles in **4**. Moreover, the angles formed by the direction of the W–P bonds with the normal to the plane of the P_3 group are closer together in **4**, 47.3(1) and 50.4(1)°, than are the corresponding angles, 46.3(1) and 53.7(1)°, formed by the Cr–P bonds in **2**.

The attack of the two pentacarbonyl groups to two phosphorus atoms of the CoP_3 core has a small but significant effect on its geometry. The Co–P bond formed by the unsubstituted phosphorus atom of the P_3 ring in **4**, Co–P(6) = 2.350(4) Å, is longer than the other two Co–P(P_3) bonds (2.285(8) Å, mean) the former value being definitely larger and the latter slightly smaller than the unique 2.301(1) Å value of the Co–P(P_3) bonds in the parent compound **1** [2a]. The P–P distance between the two substituted phosphorus atoms of the ring (P(4)–P(5) = 2.137(5) Å) is slightly shorter than the other two P–P distances, which average to 2.149(4) Å. Although the significance of the last comparison might be questioned, it should be noted that similar trends in the geometry of the CoP_3 core are found for **2**, with (i) a 2.340(4) Å Co–P distance formed by the unsubstituted phosphorus atom, which is longer than the other two Co–P(P_3) distances (average 2.286 Å) and (ii) with a 2.124(4) Å bond length between the substituted phosphorus atoms versus the 2.149(6) Å mean of the other two P–P bonds. The Co–P(triphos) distances in **4** do not seem to be notably affected by the addition to the P_3 atoms, although the slightly shorter bond formed by P(2), compared to the other two Co–P(triphos) bonds (Table 1), might be caused by the fact that the former lies almost *trans* to the longest Co–P(P_3) bond (P(2)–Co–P(6) = 156.1(1)°).

The geometry of the pentacarbonyl tungsten groups is normal, with the W–C distances in the range 1.96–2.04 Å and all of the C–O distances in the range

1.13–1.16 Å (except for C(72)–O(72) = 1.22(2) Å), in agreement with the values found for the compounds **5** and **6**. Neither in the structure of **4**, nor in those of **5** or **6**, is a clear effect of shortening of the W–C bond *trans* to the phosphorus atom observed, whereas that type of shortening is found in **2** as well as for the chromium pentacarbonyl groups in some other compounds, where it has been attributed to a *trans* influence between groups competing for π bonding [12]. The largest deviations from the idealized 180° angles at the W and C atoms in the pentacarbonyl fragments [C(73)–W(1)–C(74) = 167.7(5)°, O(73)–C(73)–W(1) = 173.9(1.2)°, O(74)–C(74)–W(1) = 173.6(1.3)°] are presented by two carbonyls involved in short intramolecular contacts, such as the above mentioned O(73)···O(83) contact and a O(74)···H(43) 2.52(2) Å close approach. A possible indication of the significance of the latter interaction, as well as of hindrances between bulky groups in the molecule, may be provided by the fact that the phenyl group (n. 4) carrying H(43) approaches coplanarity with the plane through the triphos P atoms more than any other phenyl group of the ligand.

Extended-Hückel (EH) calculations [13,14] on undistorted model systems have provided a pattern of overlap population (op) values in agreement with the experimental geometries of the CoP_3 core in **2** and **4**, yielding slightly larger/smaller op values for the bonds of the core which are found to be shorter/longer than the other bonds of the same type. Such effects result from a relatively complex balance of differences in both bonding and antibonding interactions. However, it is clear that donation of electron density from two P_3 phosphorus atoms into the σ-type LUMO's of the $\{W(CO)_5\}$ groups allows a small fraction of antibonding interactions between those two P atoms to be released. The P–W interaction appears to be essentially of σ type, with only a small π contribution.

2.3. NMR properties

The ^{31}P-NMR spectra of the three compounds under investigation are very similar (Fig. 2, Table 2). At room temperature they exhibit two well separated resonances, one in the typical region for the triphos signals, the second in the characteristic high field region for *cyclo*-P_3 atoms. The shift of the signal due to the triphos coligand is substantially unchanged on going from the chromium to the tungsten derivative, whereas the resonances attributed to the P_3 ligand show a significant trend to higher field on moving down the periodic table. The difference in the shifts is more pronounced on going from chromium to molybdenum ($\Delta\delta = 43$

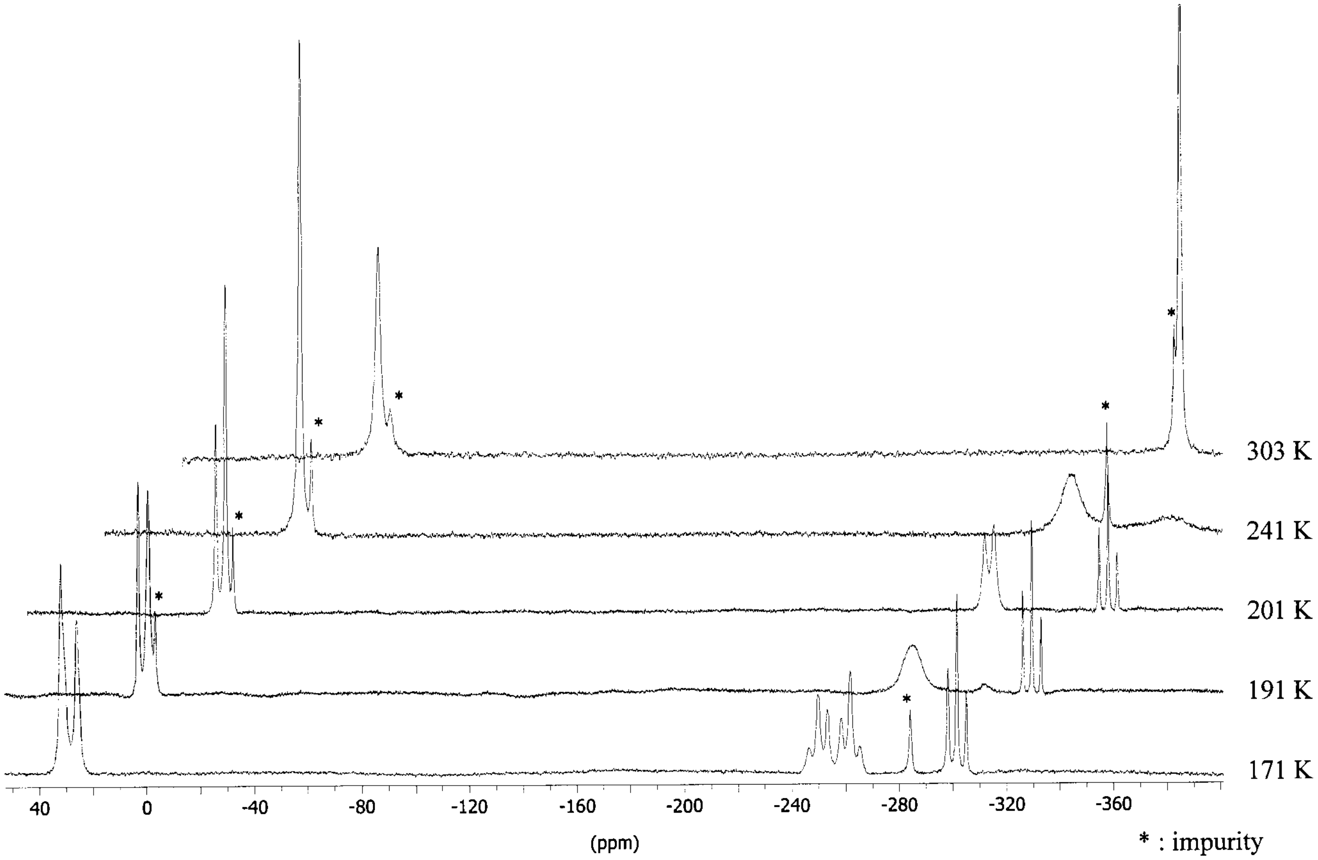

Fig. 2. $^{31}P\{^1H\}$-NMR spectra of $[\{(triphos)Co\}(P_3)\{W(CO)_5\}_2]$ (**4**) at different temperatures (CD_2Cl_2, 81.02 MHz).

Table 2
^{31}P-NMR data of the compounds [{(triphos)Co}(P_3){M(CO)$_5$}$_2$] (M = Cr (**2**), Mo (**3**), W (**4**)) at different temperatures [a]

Temperature (K)	**2**		**3**		**4**	
	Triphos	*Cyclo*-P_3	Triphos	*Cyclo*-P_3	Triphos	*Cyclo*-P_3
r.t.	31.0 (3P,s)	−210 (3P,s,br)	29.6 (3P,s)	−253.4 (3P,s)	29.6 (3P,s)	−269.4 (3P,s)
201	33.3 (1P,s,br)	−195.3 (2P,d,br,283)	34.0 (3P,m,br)	−230.3 (2P,d,br,250)	32 (1P,s,br)	−255.9 (2P,d,br,274)
	29.8 (2P,s,br)	−293.8 (1P,td,283,22)		−295.4 (1P,td,283,14)	28.4 (2P,s,br,)	−300.2 (1P,td,277,19)
170	31.4 (br)	−193.7 (1P,tr,280)	31.4 (3P,m,br)	−225.8 (1P,tr,290)	32.1 (s,br)	−250.1 (1P,tr,265)
	25.5 (br)	−200.0 (1P,tr,283)		−238.0 (1P,tr,280)	30.5 (s,br)	−261.8 (1P,tr,270)
		−297.2 (1P,tr,283)		−298.0 (1P,tr,280)	26.1 (s,br)	−301.8 (1P,tr,275)

[a] δ (ppm); J (Hz); in CD_2Cl_2; br = broad, m = multiplet, s = singlet, d = doublet, tr = triplet, td = triplet of doublets.

ppm) than between the heavier congeners ($\Delta\delta = 16$ ppm). The equivalence of the atoms within the two sets of phosphorus donors is not in accord with the solid state structures of **2** and **4**, in which the atoms of both sets fall into chemically different environments. These findings point to a dynamic behaviour which equalizes the different positions on the NMR time scale. Actually, on cooling the solutions down to ca. 200 K, the singlet at higher field, after running through coalescence (T_c (K) **2**, 265; **3**, 220; **4**, 250), transforms into a broad doublet and a triplet with relatively narrow lines, the latter additionally showing a doublet fine structure. The relative chemical shifts and the integral ratios of the A_2B spin system allow the assignment of the lower field doublet to the end-on coordinated P atoms. The separation of the multiplets decreases drastically with increasing atomic number ($\Delta\nu$ (Hz) **2**, 7980; **3**, 5275; **4**, 3590). On further cooling the solutions to ca. 170 K, the doublet, after further coalescence (T_c (K) **2**, 180; **3**, 195; **4**, 190), furnishes two triplets of similar chemical shift; whereas the high field triplet remains substantially unchanged (apart from line broadening due to the increased viscosity of the solution). The three pseudo-triplets of this ABC spin system have similar coupling constants which are in the range of other unsymmetrical *cyclo*-P_3 ligands (e.g. [{M′}(P_3){Mn(CO)$_2$Cp}$_3$]: 248Hz, [{M′}(P_3){Cr(CO)$_5$}$_3$]: 258Hz; [M′ = Cp*(OC)$_2$W] [7] and [(triphos)Co(P_3CH_3)]BF_4: 362Hz [6c]); such coupling constants are distinctly smaller than those found in complexes containing the larger P_5 cycle bearing organometallic fragments (ca. 410–510 Hz) [15]. In the low field region of the spectra, the single resonance of the triphos P atoms at ca. 200 K splits into two broad signals of 1:2 intensity ratio (T_c (K) **2**, 230; **3**, 200; **4**, 230) which is in accord with two different environments for the three phosphorus atoms of the polyphosphine. Further variations in the shapes of the signals appear below 200 K. Unfortunately, the line widths do not allow detection of fine structure partly because of the cobalt-quadrupolar broadening and partly because of the low homogenity.

The ^{1}H-NMR measurements qualitatively confirm the trend observed in the phosphorus spectra (Table 3). The three methylene groups of the triphos coligand at room temperature give rise to one signal, which splits into two broad peaks having an approximate integral ratio of 1:2 at ca. 200 K; such splitting confirms the existence of two different chemical environments for the tripodal arms.

A full line shape analysis of the ^{31}P-f and ^{1}H-NMR spectra could not be satisfactorily performed for the high line broadening due to low homogenity, overlap of signals and quadrupolar interactions (especially for the phosphine ^{31}P resonances).

The experimental data summarized above points to the presence of several dynamic processes. The chemical and magnetic equivalence of the P-triphos atoms may be achieved by rotation of the {(triphos)Co} fragment around its C_3 symmetry axis. However, this process cannot explain the equalization of the *cyclo*-P_3 positions; hence, also the exchange of the two pentacarbonyl fragments between the three phosphorus coordination sites has to be assumed. On lowering the temperature to 200 K these two dynamic processes are blocked as shown by the appearance of two signals having a 1:2 integral ratio in both regions of the ^{31}P spectra. A fixed mutual arrangement of the triphos and the P_3 ligand at this temperature is confirmed by the coupling (doublet fine structure) of the unsubstituted P atom of *cyclo*-P_3 with one of the phosphorus of triphos-probably the *trans* configured one. The blocking of the rotation in the substituted triphosphorus complexes in contrast to the free rotation in the parent compound **1** may be due to sterical interactions of the bulky (fixed) substituents at both ligands.

At 170 K the two η^1 coordinated P atoms are no longer equivalent. The small differences in the chemical shifts may stem from different environments of the {M(CO)$_5$}-bearing P_3 atoms. Orientations of the pentacarbonyl fragments similar to those found in the solid state structures of **2** and **4** (see Section 2.2) may be responsible for their inequivalence at low temperature in solution. A possible equalization process active between 170 and 200 K might consist in a concerted rotation around the M–P axes (M = Cr, Mo, W).

In the present study a lower limit NMR spectrum has been reached for the first time for addition products of $[(\text{triphos})MP_3]^{n+}$ complexes. Previously it has been observed that all cationic compounds featuring one metal fragment bound to two P atoms of the MP_3 [5] core in the solid state are fluxional at room temperature in solution, exhibiting one ^{31}P resonance for the triphos and P_3, respectively. The dynamic behaviour of these compounds is not blocked even at the lowest temperature reached (ca. −90°C). Furthermore, such behaviour does not appear to be affected by the extent of interaction between the metal fragment and the P–P bond to which the addition occurs [5].

Rotation of the cyclic three-membered ligand against the metal-coligand moiety is well investigated and established for substituted *cyclo*-propenyl complexes. Examples include the cobalt complex $[\{(OC)_2(Me_3P)Co\}(\textit{cyclo}\text{-}C_3{}^tBu_3)]$ for which a rotation barrier of $\Delta G^{\neq}_{298} = (56.7 \pm 1.0)$ kJ mol^{-1} has been found [16] and $[\{(\text{triphos})Pd\}(\textit{cyclo}\text{-}C_3H_3)]^+$ with a similar barrier of 52 ± 4 kJ mol^{-1} [17]. The blocking of the rotation of *cyclo*-P_3 in mononuclear complexes has never been achieved pointing to a very low barrier which is expected in the range of those calculated for the hypothetical $[\{(OC)_3Fe\}(\textit{cyclo}\text{-}C_3H_3)]^-$ [18] and $[\{(OC)_3Co\}(\textit{cyclo}\text{-}C_3H_3)]$ [19] (24 kJ mol^{-1} and 28 kJ mol^{-1}, respectively) complexes. Only when strongly sterically demanding groups are introduced does it seem to increase the barrier sufficiently as to allow freezing of the process on the NMR time scale [7].

The exchange of coordinating metal fragments between different positions of end-on coordinated P atoms has scarcely been documented. In the diphosphorus complex $[\{Cp^*(OC)_2W\}_2(\mu_3,\eta^{2:2:1}\text{-}P_2)\{W(CO)_5\}]$ (W–W) [1] a barrier of ca. 50 kJ mol^{-1} has been estimated for the process which equilibrates the two P atoms [20]. In contrast to the P_3 and P_2 complexes mentioned here, no fluxional behaviour is reported along the P_5 perimeter of substituted pentaphosphaferrocene derivatives [15]. Probably, the tetrahedral core (MP_3 or M_2P_2) allows this kind of fluxionality due to the availability of appropriate sets of cluster orbitals.

To elucidate this mechanism, further studies are currently being carried out.

3. Experimental

3.1. General

All reactions and manipulations were performed under an atmosphere of dry oxygen-free argon. THF was freshly distilled from potassium; dichloromethane, hexane and Al_2O_3 (neutral, act. I) for chromatography were degassed and flushed with argon prior to use. The IR spectra were recorded on a Perkin–Elmer Spectrum BX spectrometer using a KBr cell. The $^{31}P\{^1H\}$- and ^1H-NMR spectra were measured on a Bruker AC 200 spectrometer at 81.02 MHz (200.13 MHz). ^{31}P (^1H) positive chemical shifts are to high frequency relative to 85% H_3PO_4 as external standard (relative to TMS as internal standard) at 0.0 ppm. Analytical data for carbon and hydrogen were obtained from the Microanalytical Laboratory of the Department of Chemistry. The hexacarbonyl complexes were used as purchased and $[(\text{triphos})CoP_3]$ (**1**) was synthesized according to the literature method [13].

3.2. Syntheses of $[\{(\text{triphos})Co\}(P_3)\{M(CO)_5\}_2]$ (M = Cr (**2**), Mo (**3**), W (**4**))

To a yellow solution of 0.10 g (0.13 mmol) $[(\text{triphos})CoP_3]$ (**1**) in 30 ml THF is added at r.t. under stirring the appropriate solvent stabilized $[M(CO)_5(THF)]$ complex in THF (freshly prepared via r.t. photolysis in a pyrex Schlenk tube $\{[Cr(CO)_6]$: 25, $[Mo(CO)_6]$: 30, $[W(CO)_6]$: 15 min.$\}$ of the hexacarbonyl (ca. 0.50 mmol in ca. 50 ml of THF)). The colour of the solution immediately changed to red. After about 4 h the reaction is completed (IR monitoring). The solvent is removed in a stream of inert gas and the residue

Table 3
^1H-NMR data of the compounds $[\{(\text{triphos})Co\}(P_3)\{M(CO)_5\}_2]$ (M = Cr (**2**), Mo (**3**), W (**4**)) at different temperatures [a]

Temperature (K)	**2**			**3**			**4**		
	Phenyl	CH_2	CH_3	Phenyl	CH_2	CH_3	Phenyl	CH_2	CH_3
r.t.	7.0–7.5 (30H,m,br)	2.36 (6H,br)	1.51 (3H,br)	6.9–7.8 (30H,m,br)	2.33 (6H,br)	1.45 (3H,br)	7.0–7.5 (30H,m,br)	2.37 (6H,br)	1.53 (3H,br)
201	6.6–7.6 (30H,m,br)	2.41 (4H,br) 2.10 (2H,br)	1.43 (3H,br)	6.8–7.9 (30H,m,br)	2.35 (4H,br) 2.21 (2H,br)	1.45 (3H,br)	6.5–7.6 (30H,m,br)	2.42 (4H,br) 2.07 (2H,br)	1.46 (3H,br)

[a] δ (ppm); in CD_2Cl_2; br = broad.

resolved in a small amount of CH_2Cl_2 (ca. 3 ml) and transferred onto a column (water-cooled; 1 × 20 cm; Al_2O_3, in *n*-hexane). The products were eluted with 2/1 hexane/CH_2Cl_2 as red bands, giving red crystalline solids on evaporating the solvents. They may be recrystallized from hexane/CH_2Cl_2 by reducing the volume of the solution in a light stream of inert gas. Yields: 59% (**2**); 31% (**3**); 49% (**4**). Anal. Calc.: for $C_{51}H_{39}CoCr_2O_{10}P_6$ (**2**): C: 52.77; H: 3.39. Found: C: 53.83; H: 3.80. Anal. Calc. for $C_{51}H_{39}CoMo_2O_{10}P_6$ (**3**): C: 49.06; H: 3.15. Found: C: 49.22; H: 3.58. Anal. Calc. for $C_{51.5}H_{40}ClCoO_{10}P_6W_2$ (**4**) 0.5 CH_2Cl_2: C: 42.17; H: 2.75. Found: C: 42.25; H: 2.84.

IR (ν (cm^{-1}); CH_2Cl_2): **2**, 2065(m), 2056(m), 1988(w), 1950(vs), 1929(vs), 1915(sh); **3**, 2074(m), 2068(m), 1995(w), 1955(vs), 1936(vs), 1917(sh); **4**, 2073(m), 2066(m), 1986(w), 1948(vs), 1926(vs), 1911(sh).

4. X-ray data collection, structure determination and refinement

X-ray diffraction data were collected for the CH_2Cl_2 solvate of **4** at r.t. with an Enraf–Nonius CAD4 diffractometer using Mo–K$_\alpha$ radiation. Crystal data and details about data collection and structure refinement are given in Table 4. Unit-cell parameters were obtained from the settings of 25 reflections with $13 < \theta < 15°$. No crystal decay was observed during data collection. An empirical correction for absorption was applied (ψ scans, min/max transmission factors 0.554/0.999). The main programs used in the crystallographic calculations are listed in Refs. [21–24].

The structure was solved by direct and heavy-atom methods, with SIR [21] and SHELXL 93 [22], and was refined by full-matrix least-squares on F_o^2. In addition to one molecule of the compound the asymmetric unit contains half of a dichloromethane solvate molecule, since there is one such molecule in the triclinic cell, disorderly arranged about an inversion centre. In the final refinement cycles all the non-hydrogen atoms, including the fractional atoms of the solvent, were assigned anisotropic temperature factors (with restraints for the solvent). Hydrogen atoms were in calculated positions, riding on the carrier atoms, with $U_H = 1.2U_C^{eq}$ (methyls were treated as rigid groups with $U_H = 1.5U_C^{eq}$). Soft restraints were imposed on the C–C distances of the phenyl groups as well as on the geometry of the solvent molecule.

5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 121764. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax. +44(1223) 336033 or e-mail: deposit@ccdc.cam.ac.uk, www: http://www.ccdc.cam.ac.uk).

Table 4
Crystallographic data for $[\{(triphos)Co\}(P_3)\{W(CO)_5\}_2]\cdot 0.5CH_2Cl_2$ (**4**)

Formula	$C_{51.5}H_{40}ClCoO_{10}P_6W_2$
M	1466.73
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a(Å)	11.185(3)
b(Å)	12.302(8)
c(Å)	22.008(5)
α (°)	75.71(4)
β (°)	81.59(2)
γ (°)	69.40(4)
U(Å^3)	2741(2)
Z	2
D_{calc} (g cm^{-3})	1.777
Crystal size (mm)	0.03 × 0.17 × 0.70
μ (mm^{-1})	4.76
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)
Data collected	$\pm h, \pm k, +l$
Scan type	$\omega - 2\theta$
2θ range (°)	5–46
Reflections collected	7401
Unique reflections	7120
Unique observed reflections, with $I > 2\sigma(I)$	4986
Absorption correction	ψ scan method
No. of parameters	655
R_1 (observed reflections)	0.051
R_1 (all unique reflections)	0.093
wR_2	0.117
Goodness of fit	1.036
Largest features (max, min) in final ΔF map (e Å^{-3})	1.08, −0.87

Acknowledgements

We acknowledge financial support by the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica. The work has been enabled by support with a post-doctoral grant (M.P.E.) of the 'Gemeinsamen Hochschulsonderprogramm III von Bund und Ländern' by the DAAD (German Academic Exchange Service). This work was supported by the European Commission (INCO ERB-IC15CT960746).

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