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REACTIONS OF COORDINATED LIGANDS

II *. METAL(0) CARBONYL COMPLEXES WITH DIPHOSPHANES R(X)PP(X)R (R = aryl; X = Br, I, H, C_4H_9) AS BRIDGING LIGANDS

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Summary

Complexes $(CO)_5MR(X)PP(X)RM(CO)_5$ (R = aryl; X = Br, I; M = Cr, W) (II) have been prepared by reaction of $(CO)_5M \cdot THF$ with the corresponding diphosphanes RXPPXR. The disproportionation, $R(X)PP(X)R \rightleftharpoons (RP)_n + RPX_2$, which is observed in solutions of the free diphosphanes, does not take place with the coordinated ligands. This is also the case for the diphosphane in $(CO)_5CrC_6H_5(H)PP(H)C_6H_5Cr(CO)_5$, which is obtained from IIa by reduction with $LiAlH_4$. These are additional examples of stabilization of oligophosphanes by complex formation. The complex $(CO)_5CrC_6H_5(C_4H_9)PP(C_4H_9)C_6H_5Cr(CO)_5$ has been synthesized from IIa and BuLi. The IR, NMR and mass spectra of the complexes are discussed.

Introduction

In solutions of 1,2-diaryl-1,2-dibromodiphosphanes Ia and Ib there is an equilibrium as represented in eq. 1 [2,3], which also applies to the analogous iodophosphanes [2,4]. In several reactions of the dissolved diphosphanes the products correspond to a reaction of the disproportionation products $(RP)_n$ and $RPBr_2$,

$$n\ R(X)PP(X)R \rightleftharpoons n\ RPX_2 + (RP)_n \qquad (1)$$

(Ia–Ic)

(Ia, R = C_6H_5; X = Br;
Ib, R = 4-$CH_3OC_6H_4$; X = Br;
Ic, R = C_6H_5; X = I)

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[*] For part I see ref. 1.

indicating the greater reactivity of the latter towards nucleophilic attack, whereas electrophilic agents mainly react with the cyclophosphanes. Under heterogeneous conditions, however, derivatives of the diphosphanes, e.g. $\mathrm{R(R')PP(R')R}$ ($\mathrm{R' = C_4H_9}$, $\mathrm{C_6H_5}$), were obtained [3].

Since disproportionation of $\mathrm{Br_2PPBr_2}$ was prevented by coordination [1,2] we hoped to stabilize compounds I by complex formation with metal(0) carbonyl moieties, and thus to be enabled to study some reactions of the P–X bond of coordinated I.

Very few coordination compounds containing diphosphanes with halogen substituents have yet been described. Apart from the compounds containing $\mathrm{Br_2PPBr_2}$, there is only one example, $\mathrm{(CO)_5CrC_6H_5(Cl)PP(Cl)C_6H_5Cr(CO)_5}$, which was isolated in low yield from the reaction between $\mathrm{Cr(CO)_6}$, $\mathrm{(CO)_5CrC_6H_5PH_2}$, $\mathrm{C_4H_9Li}$ and $\mathrm{C_6H_{11}NCl_2}$ [5,6].

Synthesis of $\mathrm{(CO)_5MR(X)PP(X)RM(CO)_5}$ ($\mathrm{R = C_6H_5}$, $\mathrm{4\text{-}CH_3OC_6H_4}$; X = Br, I; M = Cr, W) (II)

Because of the immediate disproportionation of Ia in THF solution several products are observed upon treatment with $\mathrm{(CO)_5M \cdot THF}$ in THF. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy shows that the resulting solutions contain IIa, $\mathrm{(CO)_5MRPBr_2}$ (III), and presumably $\mathrm{(CO)_5MR(Br)PP(Br)R}$ (IV), as well as unidentified products, in which cyclophosphanes $\mathrm{(RP)_n}$ are probably coordinated to metal carbonyl groups (eq. 2). Suitable work-up gives yellow crystals of IIa in 15–20% yield.

$$\mathrm{(CO)_5M \cdot THF + Ia\text{–}Ic \rightarrow \underset{(IIa\text{–}IId)}{(CO)_5MR(X)PP(X)RM(CO)_5} + \underset{(III)}{(CO)_5MRPX_2}}$$

$$\mathrm{+ \underset{(IV)}{(CO)_5MR(X)PP(X)R} + (RP)_n[M(CO)_x]_y} \qquad (2)$$

(a: $\mathrm{R = C_6H_5}$, X = Br, M = Cr;
b: $\mathrm{R = 4CH_3OC_6H_4}$, X = Br, M = Cr;
c: $\mathrm{R = C_6H_5}$, X = I, M = Cr;
d: $\mathrm{R = C_6H_5}$, X = Br, M = W)

TABLE 1

SYNTHESIS AND PROPERTIES OF $\mathrm{(CO)_5MR(X)PP(X)RM(CO)_5}$ (II)

Compound				Equilibr. time (d)	Yield (%)	Colour	M.p. (dec.) (°C)
	R	X	M				
IIa	$\mathrm{C_6H_5}$	Br	Cr	–	18	citron yellow	ca. 140
				10	36		
				12	42		
				20	57		
IIb	$\mathrm{4\text{-}CH_3OC_6H_4}$	Br	Cr	29	45	citron yellow	ca. 152
IIc	$\mathrm{C_6H_5}$	I	Cr	8	37	orange	ca. 130
IId	$\mathrm{C_6H_5}$	Br	W	20	34	citron yellow	ca. 140

When a solution of pure IIa in THF is kept for several hours the $^{31}P\{^1H\}$ NMR spectrum again shows most of the resonances assigned to the products mentioned above, indicating extensive disproportionation of complex IIa in this solvent. Assuming an equilibrium between all the products shown in eq. 2, we were able to increase the yield of IIa to 60% by suspending the mixture obtained by evaporation of the reaction product in a small volume of THF and keeping it at $-35°C$ for several days. During this time crystals of IIa, the least soluble component of the equilibrium mixture, separated progressively. Using this procedure we were also able to isolate the other compounds IIb–IId in quite good yields (Table 1).

It should be mentioned that small amounts of IIa are also formed in the reaction of $(CO)_5CrC_6H_5PBr_2$ (III) with magnesium in THF. In this case, however, it is difficult to isolate pure IIa [7].

Properties of II

Compounds II form citron yellow to orange crystals, which are quite stable in the solid state, even on exposure to moist air. They are moderately soluble in $CHCl_3$, less soluble in benzene or toluene and nearly insoluble in alkanes, the solutions being sensitive to oxygen and H_2O. On heating above 130–150°C the crystalline products decompose, with a change of colour and liberation of $M(CO)_6$.

Because of the presence of two chiral phosphorus atoms in II as well as in the free ligands I, these compounds are expected to exist in two diastereomeric forms, *meso* and *rac*. The $^{31}P\{^1H\}$ NMR spectra of the dissolved free ligands I show two singlets assignable to *meso*- and *rac*-I, and also the resonances for RPX_2 and $(RP)_n$ (see eq. 1) [3]. On the other hand solutions of II in C_6H_6 or $CHCl_3$ exhibit only the two singlets of the diastereomers (Table 2). Thus, as in the case of Br_2PPBr_2, disproportionation of diphosphanes I is prevented by coordination. Decomposition in THF, as mentioned above, is probably due to splitting of the M–P bonds by this strong donor solvent, followed by disproportionation of the liberated ligand I and subsequent recoordination of its disproportionation products to metal carbonyl moieties. The relative weakness of the M–P bonds in II may be attributed to steric crowding in this type of complex [5]. Comparison of the ^{31}P NMR spectra of I and II reveals two characteristic effects: First, in II the resonances of *meso* and *rac* compound are shifted to low field ($M = Cr$: $\Delta\delta(P) = \delta(P_{complex}) - \delta(P_{ligand}) = 80–90$ ppm; $M = W$: $\Delta\delta(P)$ ca. 30 ppm). These values are quite similar to those found for tetraorganodiphosphane complexes such as $(CO)_5M(CH_3)_2PP(CH_3)_2M(CO)_5$ ($M = Cr$: $\Delta\delta(P)$ 88 ppm; $M = W$: $\Delta\delta(P)$ 42 ppm) [8] or $(CO)_5M(C_6H_5)_2PP(C_6H_5)_2M(CO)_5$ ($M = Cr$: $\Delta\delta(P)$ 85 ppm; $M = W$: $\Delta\delta(P)$ 45 ppm) [9]. Anomalously low coordination shifts $\Delta\delta(P)$ were only observed with compounds, in which more than one halogen is bound to the donating phosphorus, e.g. $(CO)_5MBr_2PPBr_2M(CO)_5$ ($M = Cr$, W) [1,2], $(CO)_5MR_nPX_{3-n}$ ($M = Cr$, W; $X = Cl$, Br, I; $n = 0,1$) [4,7,10].

Second, the differences between the chemical shifts of the two diastereomers are decreased from ca. 10 ppm to 3–7 ppm in the case of II as a result of coordination. Such an effect was previously observed with complexes of the type $(CO)_5MR(R')PP(R')RM(CO)_5$ ($R,R' = CH_3$, C_2H_5, i-C_3H_7, n-C_4H_9, C_6H_5; $M = Cr$, W) [9].

It should be mentioned that measurement of the coupling constants of the tungsten compound IId, such as previously carried out with $(CO)_5WBr_2PPBr_2W(CO)_5$

TABLE 2

SPECTROSCOPIC AND ANALYTICAL DATA FOR II, V AND VIII

Compound	Formula (Molecular weight)	$\delta(^{31}P)$ (ppm)	$\nu(CO)$ (cm^{-1})	FD-MS $(M^{+\cdot})$	Analyses (Found (calcd.) (%))				
					C	H	P	metal	halogen
IIa	$C_{22}H_{10}Br_2Cr_2O_{10}P_2$ (760.1)	164.1 157.6 [a]	2080m, 2070s, 2008w, 1972vs [a]	758	34.25 (34.77)	1.34 (1.33)	7.96 (8.15)	13.69 (13.68)	
IIb	$C_{24}H_{14}Br_2Cr_2O_{12}P_2$ (820.1)	166.7 [a]	2068m, 1995w, 1980vs [a]	818	34.34 (35.15)	1.59 (1.72)	7.40 (7.55)		19.47 (19.49)
IIc	$C_{22}H_{10}Cr_2I_2O_{10}P_2$ (854.0)	126.1 122.7 [a]	2085m, 2070s, 2008w, 1971vs [a]	854	31.27 (30.94)		7.40 (7.25)	12.22 (12.18)	30.21 (29.72)
IId	$C_{22}H_{10}Br_2O_{10}P_2W_2$ (1023.8)	101.4 97.6 [a]	2088m, 2074s, 1975vs [a]	1022	25.72 (25.81)	0.96 (0.98)	6.30 (6.05)	36.08 (35.92)	15.36 (15.61)
V	$C_{22}H_{12}Cr_2O_{10}P_2$ (602.3)	25.6 24.4 [b]	2070m, 2062m, 1993w, 1960vs [c]	602 [d]	43.84 (43.88)	2.20 (2.01)	10.19 (10.29)	17.30 (17.27)	
VIII	$C_{30}H_{28}Cr_2O_{10}P_2$ (714.5)	51.5 50.8 [b]	2068m, 2058m, 1992w, 1983w, 1956vs, 1945s, 1932s [c]	714	50.25 (50.43)	3.99 (3.95)	8.52 (8.67)	14.35 (14.55)	

[a] In $CHCl_3$. [b] In toluene. [c] In pentane. [d] EI-MS (70 eV), rel. int. 15%.

[1], was not possible because of the low solubility of IId.

It was found that the isomeric composition of II depends on several factors, including the nature of R and X, the metal, and the reaction conditions. Thus, with IIa the formation of the isomer with a low field shift (isomer A) is only slightly favoured, whereas with IIc it is strongly favoured. In contrast, there is a clear preponderance of isomer B with IId. Only one resonance can be observed with IIb, indicating that the product is isomerically pure.

The solution IR spectra of II (Table 2) show the typical ν(CO) band pattern of $(CO)_5M$ moieties with pseudo-C_{4v} symmetry. Splitting of the sharp $A_1^{(1)}$ absorption is observed in most cases. The same phenomenon was found for a series of complexes of the type $(CO)_5MR(R')PP(R')RM(CO)_5$ ($R \neq R'$ = alkyl, aryl; M = Cr, W) [9], as well as for compound V (see below), but not for the non-chiral complexes $(CO)_5MR_2PPR_2M(CO)_5$ (R = Br, C_6H_5; M = Cr, W) [1,9].

Because of their low volatility mass spectra of II could only be obtained by the FD technique. They show intense peaks for the molecular ion as well as for fragments derived from it by loss of a $M(CO)_5$ moiety or one or two halogens.

Separation of the diastereomeric forms of II is easily achieved by thin layer chromatography on silica gel (e.g. with pentane/toluene). However, attempted chromatographic separation on a preparative scale was unsuccessful because of the low solubility of II.

Some studies of the chemical properties have shown that the compounds of type II are substantially less reactive than the free ligands or mononuclear halophosphane complexes. Thus IIa reacts only very reluctantly with H_2O or CH_3OH, even in the presence of base. Besides the substitution of the P–Br bond, side reactions including loss of one $Cr(CO)_5$ moiety occur. Further investigations of these reactions are in hand. Two reactions of IIa are described in detail below.

$(CO)_5CrC_6H_5(H)PP(H)C_6H_5Cr(CO)_5$ (V)

Free diphenyldiphosphane $C_6H_5(H)PP(H)C_6H_5$ (VI) was recently described as a metastable compound which quickly undergoes disproportionation at room temperature or under the influence of light, yielding a mixture of VI, $C_6H_5PH_2$, $(C_6H_5P)_5$ and several other oligophosphanes [11,12]. In $C_5H_5(CO)_2MnC_6H_5(H)PP(H)C_6H_5Mn(CO)_2C_5H_5$ (VII) [13,14], isolated in low yield from the products of the reaction between $C_5H_5(CO)_2MnC_6H_5PLi_2$ and $C_5H_5(CO)_2MnC_6H_5PCl_2$ in THF, VI is stabilized as a bridging ligand. We obtained complex V in ca. 70% yield by reducing IIa with $LiAlH_4$ in ether/benzene (eq. 3). This result is surprising in that

$$2\ IIa + LiAlH_4 \rightarrow$$

$$2\ \underset{(V)}{(CO)_5CrC_6H_5(H)PP(H)C_6H_5Cr(CO)_5} + LiBr + AlBr_3 \qquad (3)$$

the chlorophosphane substituted complex $(CO)_5Mo(C_6H_5)_2PCl$ does not react with this hydride [15]. Even when an excess of the reducing agent was employed there was no evidence of splitting of the P–P bond such as usually occurs in the case of free diphosphanes or cyclopolyphosphanes.

Complex V forms pale yellow crystals, which are stable at room temperature in an inert atmosphere. They are quite soluble in chloroform or toluene but only sparingly soluble in pentane. The $^{31}P\{^{1}H\}$ NMR spectrum of V in toluene exhibits two singlets at 25.6 (isomer A) and 24.4 ppm (isomer B), which again are assigned to the diastereomers, and does not indicate any disproportionation of V even when the solutions are kept at room temperature for several days. The relative intensities of these resonances reveal that B clearly predominates in the isomeric mixture (m.p. 129°C, dec.), from which pure B (m.p. 141°C, dec.) was obtained by recrystallisation from toluene/pentane.

The separation of the two singlets of V is again smaller than in case of the free ligand (-67.4, -70.9 ppm [11]); $\Delta\delta(P)$ (94 ppm) is of the same order as with compounds II. The coupled ^{31}P NMR spectrum shows two symmetrical sets of lines centered on the shift values mentioned above. Both patterns approximately fit AA′ parts of AA′XX′ systems (H–P–P–H moiety). Because of low solubility and band broadening as a result of coupling to the phenyl protons it has not yet been possible to determine the coupling constants. However, $|N(PH)| = {}^{1}J(PH) + {}^{2}J(PH)$ is 342 for isomer A and 333 Hz for isomer B, values distinctly larger than those for the free ligand (218.6 and 218.2 Hz [12]). For the similar complex *meso*-VII a value of 335 Hz was observed [14], and was assigned, evidently erroneously, to $J(PH)$. In addition to a multiplet (ca. 7 ppm) for the aromatic proton resonance the ^{1}H NMR spectrum (in toluene-d_8) shows the corresponding two XX′ parts, which upon ^{31}P decoupling collapse to two singlets at 5.63 (isomer A) and 5.44 ppm (isomer B), the assignment being based on comparison of the relative intensities. Thus the PH protons, showing resonances at $\delta(H) = 4.37$ and 4.35 ppm in the free ligand VI, are strongly deshielded by coordination. The same effect was found for *meso*-VII (δ(H) 6.08 ppm) [14].

The IR spectrum of V in $CHCl_3$ shows the $\nu(CO)$ $A_1^{(1)}$ band at a significantly lower frequency than that for compounds II (Table 2), corresponding to a lower acceptor ability of ligand VI. Again the band is split as with compounds II. Two weak bands at 2340 and 2310 cm^{-1} (KBr) are assigned to $\nu(PH)$. This vibration is observed at 2294 cm^{-1} in VII [14] and at 2295 and 2287 cm^{-1} (Raman spectrum) in VI [11].

V was also formed when IIa was treated with magnesium in THF. During this reaction an intensely red coloured intermediate, most probably $(CO)_5CrC_6H_5$-$P{=}PC_6H_5Cr(CO)_5$, was observed, and this subsequently gave V, presumably by hydrogen abstraction from the solvent. In this context it should be added, that a temporary red colouration of the reaction mixture, indicating the same intermediate, was also observed during the preparation of V by reduction of IIa with $LiAlH_4$. Attempts to isolate complexes containing diphosphene RP=PR ligands are at present in progress [7].

$(CO)_5CrC_6H_5(C_4H_9)PP(C_4H_9)C_6H_5Cr(CO)_5$ (VIII)

Only a few reactions of coordinated halophosphanes with organometallic agents have yet been described, and these give rather low yields of the desired substitution products [16]. Though side reactions resulting from cleavage of the P–P bond are possible, we obtained VIII from IIa and n-butyllithium at low temperature accord-

$$\begin{aligned}&\mathrm{IIa} + 2\,C_4H_9Li \rightarrow\\ &(CO)_5CrC_6H_5(C_4H_9)PP(C_4H_9)C_6H_5Cr(CO)_5 + 2\,LiBr \qquad (4)\\ &\qquad\qquad\qquad\mathrm{(VIII)}\end{aligned}$$

ing to eq. 4. To our knowledge VIII is the first metal complex of a mixed-substituted tetraorganodiphosphane. $^{31}P\{^1H\}$ NMR monitoring of the reaction reveal that it proceeds via the intermediate $(CO)_5CrC_6H_5(Br)PP(C_4H_9)C_6H_5Cr(CO)_5$ (two resonance patterns of AX type).

VIII forms fairly air stable pale yellow crystals, which are slightly soluble in pentane but readily soluble in most other organic solvents. Its $^{31}P\{^1H\}$ NMR spectrum exhibits two close singlets at 51.5 and 50.8 ppm (toluene). The separation of the resonances corresponding to *meso* and *rac* forms is thus reduced from 6.5 ppm in the free ligand [17] to less than 1 ppm in the complex, $\Delta\delta(P)$ being ca. 80 ppm. The position of the $\nu(CO)A_1^{(1)}$ band (Table 2) confirms the expected lower acceptor ability of ligand $C_6H_5(C_4H_9)PP(C_4H_9)C_6H_5$ compared with I and VI.

We also obtained complex VIII from the reaction of $Cr(CO)_5 \cdot THF$ with $C_6H_5(C_4H_9)PP(C_4H_9)C_6H_5$ [9]. The products from the two methods show identical physical and spectroscopic properties.

Experimental

All operations were performed under nitrogen. Nitrogen, solvents and silica gel were purified and dried by standard procedures.

Photolyses: Normag photoreactor, TQ 150 Hanau; photochemical lamp located in the water-jacketed inner tube. IR: Perkin–Elmer IR 283. ^1H, ^{31}P NMR: Bruker Physik HX 90 R. MS: Varian MAT 311A.

Starting materials: The synthesis of Ia and b is described elsewhere [3]. Ic was prepared by a published method [18].

$(CO)_5MR(X)PP(X)RM(CO)_5$ ($R = C_6H_5$, $4\text{-}CH_3OC_6H_4$; $X = Br$, I; $M = Cr$, W) (IIa–IId)

A solution of $(CO)_5M \cdot THF$, prepared from $M(CO)_6$ (25 mmol) and 360 ml THF (UV irradiation, 5.5 h) is added quickly to 12.5 mmol of the corresponding diphosphane I and the mixture is stirred for 2 h. The solvent and unreacted $Cr(CO)_6$ are then removed during 6 h in vacuo at room temperature. The residue is suspended in 6 ml THF and kept at −35°C for the time indicated in Table 1. After removal of the solvent 60 ml of toluene are added. Cooling to −35°C for 12 h yields complexes II, which are filtered off at 0°C (in case of IId at room temperature), washed with a small amount of cold toluene, and dried in vacuo.

Decacarbonyl-μ-1,2-diphenyldiphosphanedichromium(V)

A solution of 0.2 g $LiAlH_4$ (5.3 mmol) in 50 ml ether is added dropwise to 2.45 g IIa (3.2 mmol) in 110 ml benzene at 40°C. The mixture soon becomes turbid, and the colour changes first to red and then back to yellow. After 1 h stirring the solvent is removed and the residue purified by chromatography (column 50 × 25 mm, pentane/toluene (1/1, v/v), SiO_2 70–235 mesh ASTM). The yellow fraction is evaporated, the residue is suspended in pentane and the yellow crystals are filtered off. Yield 1.4 g V (71.5%).

Decacarbonyl-μ-1,2-dibutyl-1,2-diphenyldiphosphanedichromium (VIII)

A solution of 0.34 g n-butyllithium (5.26 mmol) in n-hexane is added dropwise to a suspension of 2.0 g IIa (2.63 mmol) in 30 ml toluene at −40°C. The mixture is allowed to warm to room temperature and stirred for 12 h. After addition of ca. 2 g silica gel the solution is evaporated to dryness. The solid residue obtained is chromatographed on silica gel (30 × 20 mm) using pentane/toluene (1/1, v/v). After the eluate has been evaporated to a small volume, 40 ml pentane are added and the resulting suspension is cooled to −30°C for 12 h. Filtration at −30°C gives 850 mg VIII (45%), pale yellow crystals, m.p. ca. 145°C (dec.).

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