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Reactions of coordinated ligands

VII *. Preparation of $(CO)_5MR(H)PP(Cl)RM(CO)_5$ (M = Cr, Mo, W; R = Ph, NEt_2) by dehydrohalogenation of $(CO)_5MPRHCl$, and some of their reactions leading to complexes with bridging diphosphine ligands **,***

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Abstract

Removal of HCl from $(CO)_5MPRHCl$ (M = Cr, Mo, W; R = Ph, NEt_2) by treatment with NEt_3 has given the complexes $(CO)_5MPh(H)PP(Cl)PhM(CO)_5$ (M = Cr, Mo, W) (**1**) and $(CO)_5CrNEt_2(H)PP(Cl)NEt_2Cr(CO)_5$ (**2**) containing bridging diphosphine ligands. Surprisingly, $(CO)_5CrCl_2PPCl_2Cr(CO)_5$ (**3**) was formed from treatment of $(CO)_5CrPHCl_2$ with NEt_3. Reaction of **1** with tetrabutylammoniumfluoride, of **2** with gaseous HCl, and of **3** with MeOH gave $(CO)_5CrPh(H)PP(F)PhCr(CO)_5$ (**4**), $(CO)_5CrCl(H)PPCl_2Cr(CO)_5$ (**5**) and $(CO)_5Cr(MeO)_2PP(OMe)_2Cr(CO)_5$ (**6**) respectively. Except for Cl_2PPCl_2, the diphosphine ligands in **1**–**6** are unknown in the free state. Attempts to abstract HCl from **1** to give the diphosphene complex $(CO)_5CrPhP{=}PPhCr(CO)_5$ failed.

1. Introduction

Recently, we showed by using neutralisation-reionisation mass spectrometry (NRMS) that certain small molecules containing phosphorus, *e.g.* H_2PSH, H_3PCH_2, HSP, and its isomer HPS can exist in the rarefied gas phase in the mass spectrometer. They are kinetically unstable and so accessible only by methods which preclude intermolecular interactions [1].

An alternative route to such species used by our group involves their generation within the coordination sphere of a complex. Thus, by suitable reactions of coordinated ligands we obtained, for example, complexes containing diphosphine ligands like P_2Br_4 and $R(X)PP(X)R$ (R = aryl, X = H, Br, I) which are metastable or still unknown in the free state [2]. Coordination of the species via phosphorus to $M(CO)_5$ centres strongly reduces their nucleophilicity, presumably the main source of instability for many P^{III} compounds containing combinations of P–P/, P–halogen/ and P–H/bonds [3].

We describe below the preparation of complexes containing functionalized diphosphines that can be used as starting materials in the synthesis of further compounds containing diphosphines as bridging ligands.

2. Preparation of the complexes $(CO)_5MR(H)PP(Cl)RM(CO)_5$ (1,2)

We have found that compounds **1** and **2** can be easily prepared in good yields by reaction of coordinated phosphines RPHCl with triethylamine according to eqn. (1). The precursor complexes $(CO)_5MPRHCl$ can be readily made by various methods [4–10]. The preparation of $(CO)_5CrPHClNEt_2$ (see Experimental

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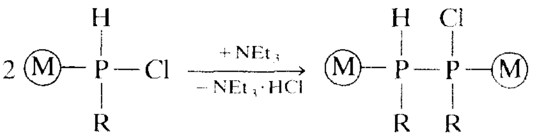
TABLE 1. $^{31}P\{^1H\}$ NMR spectroscopic data for crude $(CO)_5MR(Cl)P_AP_X(H)RM(CO)_5$ (**1a–1c**) and **2**, with **I** as the predominant isomer

	Isomer **I**			Isomer **II**		
	$\delta(P)_A$ (ppm)	$\delta(P)_X$ (ppm)	$^1J(PP)$ (Hz)	$\delta(P)_A$ (ppm)	$\delta(P)_X$ (ppm)	$^1J(PP)$ (Hz)
1a [a]	164.7 (d)	60.0 (d)	177	158.3 (d) [b]	64.1 (d) [c]	186 [d]
1b [a]	129.4 (d)	40.2 (d)	177	123.0 (d)	43.1 (d)	178
1c [a]	95.8 (d)	17.5 (d)	164	91.1 (d)	21.4 (d)	164
2 [e]	210.6 (d)	133.9 (d)	243	–	–	–

[a] In $CDCl_3$. [b] Lit. [11] 157.7 (d) (in CH_2Cl_2). [c] Lit. [11] 62.6 (d) (in CH_2Cl_2). [d] Lit. [11] 186 (in CH_2Cl_2). [e] In C_6D_6.

section) is described here for the first time. Complexes **1** and **2** form yellow crystals that are fairly stable in the solid state even when exposed to moist air. They are readily soluble in benzene, toluene, or chlorinated hydrocarbons.



$$2\,Ⓜ\!-\!\overset{H}{\underset{R}{P}}\!-\!Cl \xrightarrow[-NEt_3\cdot HCl]{+NEt_3} Ⓜ\!-\!\overset{H}{\underset{R}{P}}\!-\!\overset{Cl}{\underset{R}{P}}\!-\!Ⓜ \qquad (1)$$

(1,2)

Ⓜ = $M(CO)_5$
1: R = Ph; **a** M = Cr, **b** M = Mo, **c** M = W
2: R = NEt_2, M = Cr

Since **1** and **2** contain two chiral phosphorus centres, the products obtained are expected to be mixtures of the *threo-* and *erythro*-forms, giving rise to two groups of signals in the $^{31}P\{^1H\}$ NMR spectrum. In the case of the compounds **1a–1c**, the spectra of the crude products do indeed show two AX spin systems, in an approximate intensity ratio 4 : 1. After repeated recrystallization, the predominant diastereomers were obtained in the pure state. In contrast to **1**, solutions of crude **2** exhibit only one AX spin system, suggesting a stereospecific reaction (Table 1).

Huttner *et al.* [11] obtained **1a** by addition of HCl to $(CO)_5CrPhP{=}PPhCr(CO)_5$; they assumed *trans* addition, and hence a *threo* configuration of the diphosphine ligand. Comparison of their NMR data with ours shows that in the reaction shown in eqn. (1), the *erythro* isomers of **1** are preferentially formed. It is noteworthy that the predominating isomers of **1** gradually undergo isomerization (*erythro–threo* conversion?) when kept in $CDCl_3$ solution for days and weeks.

3. Preparation of $(CO)_5CrCl_2PPCl_2Cr(CO)_5$ (3)

Surprisingly, $(CO)_5CrPHCl_2$ (the preparation of which is described here for the first time) is treated with NEt_3 according to eqn. (1), complex **3** is the main product rather than the expected complex **5**. Complex **3** was previously prepared by electrochemical reduction of $(CO)_5CrPCl_3$ [12]. The route taken by this reaction is still unknown. However, we found that in the initial stage of the reaction (after addition of 0.5 mol of NEt_3) the solution contained mainly **5** and unchanged starting material. When all the NEt_3 had been added, the solution contained **3** and several phosphorus compounds that have not been identified. Later on in our investigations, we found (see below) a method of preparing pure **5**, and it should be possible to study its reaction with NEt_3 in the presence or absence of $(CO)_5CrPHCl_2$.

4. Reactions of complexes 1–3

Dehydrohalogenation of **1a** with NEt_3 or other bases under various conditions did not give the expected diphosphene complex $(CO)_5CrPhP{=}PPhCr(CO)_5$, but instead a complex mixture of products. However, a transient change in colour of the solution from yellow to deep purple during the reaction suggests the intermediate formation of low-coordinate phosphorus compounds.

When **1a** was treated with tetrabutylammonium fluoride in toluene at room temperature for 45 min, the Cl was completely replaced by F, to give **4**. The complex **4** obtained in this way turned out to be a mixture of two diastereoisomers in a 2 : 1 ratio. After repeated recrystallization from toluene, the predominant isomer was obtained in pure form as yellow crystals. The corresponding $^{31}P\{^1H\}$ NMR spectrum, data from which are given in Table 2, shows the expected resonance patterns and coupling constants.

TABLE 2. $^{31}P\{^1H\}$ NMR spectroscopic data in C_6D_6 of crude $(CO)_5CrPh(F)P_AP_X(H)PhCr(CO)_5$ (**4**); **I** is the predominating isomer

	$\delta(P)_A$ (ppm)	$\delta(P)_X$ (ppm)	$^1J(PP)$ (Hz)	$^1J(PF)$ (Hz)	$^2J(PF)$ (Hz)
Isomer **I**	237.8 (dd)	48.6 (dd)	179	899	68
Isomer **II**	230.7 (dd)	55.7 (dd)	183	898	76

When **1a–1c** was treated with gaseous HCl in pentane, no reaction was observed. Similarly, the P–P bond remains intact when **2** is treated with HCl under the same conditions. However, the NEt_2 groups in the latter are gradually replaced by Cl, with formation of **5**, the reaction being complete after 20 min when CH_2Cl_2 is used as a solvent.

$$\mathrm{(CO)_5CrCl(H)PPCl_2Cr(CO)_5}$$

(5)

By means of ^{31}P NMR spectroscopy it was shown that the first step in the reaction is the formation of the partially substituted complex $(CO)_5CrCl(H)PP(Cl)NEt_2Cr(CO)_5$. Subsequently it undergoes complete substitution to give **5**. The $^{31}P\{^1H\}$ NMR spectrum of $(CO)_5CrCl_2P_AP_X(H)ClCr(CO)_5$ (**5**) shows an AX pattern with chemical shifts $\delta(P)_A$ 201.3 ppm (d), $\delta(P)_X$ 144.2 ppm (d), and the coupling constant $^1J(PP) = 204$ Hz.

When we consider the range of tetraalkoxydiphosphines $(RO)_2PP(OR)_2$ that have been reported [13–16], we find it remarkable that the compound in which R is Me is still unknown. Perhaps this compound is unstable. Reaction of **3** with MeOH at room temperature for 3 days gave compound **6** as a white powder that gradually became beige upon exposure to moist air.

$$\mathrm{(CO)_5Cr(MeO)_2PP(OMe)_2Cr(CO)_5}$$

(6)

The $^{31}P\{^1H\}$ NMR spectrum of **6** exhibits a singlet at $\delta(P)$ 224.5 ppm.

5. Conclusions

It has been shown that complexes **1** and **2** containing functionalized diphosphines as bridging ligands are readily accessible. Because of the presence of reactive P–H, P–Cl or P–N bonds, they are versatile starting materials for the synthesis of further diphosphine complexes, *e.g.* **4–6**, which cannot be prepared by conventional methods because the corresponding free diphosphines are presumably kinetically unstable. The reactions are summarized in Scheme 1.

$$2\,\textcircled{M}\mathrm{PRHCl} \xrightarrow[-\mathrm{NEt_3\cdot HCl}]{+\mathrm{NEt_3}} \textcircled{M}\mathrm{R(H)PP(Cl)R}\textcircled{M}$$

$$\textcircled{M} = \mathrm{M(CO)_5};\ \mathrm{M = Cr, Mo, W};\ \mathrm{R = Ph, NEt_2}$$

$$\textcircled{Cr}\mathrm{Ph(H)PP(Cl)Ph}\textcircled{Cr} \xrightarrow{\mathrm{Cl/F\text{-}exchange}} \textcircled{Cr}\mathrm{Ph(H)PP(F)Ph}\textcircled{Cr}$$

$$\textcircled{Cr}\mathrm{NEt_2(H)PP(Cl)NEt_2}\textcircled{Cr} \xrightarrow{\mathrm{HCl_g}} \textcircled{Cr}\mathrm{Cl(H)PPCl_2}\textcircled{Cr}$$

$$2\,\textcircled{Cr}\mathrm{PHCl_2} \xrightarrow{\mathrm{NEt_3}} \textcircled{Cr}\mathrm{Cl_2PPCl_2}\textcircled{Cr} \xrightarrow{\mathrm{MeOH}} \textcircled{Cr}\mathrm{(MeO)_2PP(OMe)_2}\textcircled{Cr}$$

a.o.

Scheme 1.

6. Experimental details

6.1. General procedures

All operations were carried out under nitrogen. Nitrogen and solvents were purified and dried by standard methods. Silica gel was silanized as reported in [17]. Melting points are uncorrected. $^{31}P\{^1H\}$ NMR, Bruker AM 200 (81 MHz); ^1H NMR, Bruker AM 200 (200 MHz); ^{19}F NMR, Bruker AM 200 (188 MHz); chemical shifts are relative to external 85% H_3PO_4 (^{31}P) and internal $(CH_3)_4Si$ (^1H), C_6F_6 (^{19}F) as reference compounds; positive shifts are to high frequency. Abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; c, centred. Values of coupling constants are in Hz. IR, Perkin-Elmer PE 283; IR spectra were recorded in the range 2200–1600 cm^{-1} in pentane solution. MS, Varian MAT 311 A; *m/z* data refer to the highest peak of a polyisotopic group.

6.2. Preparation of $(CO)_5CrPHClNEt_2$ and its precursors

6.2.1. $(CO)_5CrPCl(NEt_2)_2$

A solution of $(CO)_5Cr \cdot THF$, prepared from $Cr(CO)_6$ (10 mmol) and 130 ml of THF (ultraviolet irradiation for 45 min; Normag photoreactor, TQ 150 Hanau), was added to 10 mmol of $ClP(NEt_2)_2$ and the mixture was stirred for 2 h. The solvent and unchanged $Cr(CO)_6$ were then removed at 40°C *in vacuo*. The crude product was dissolved in pentane and chromatographed on silica gel (column size 4×2.5 cm^2). Elution with pentane gave a yellow fraction, and after removal of the solvent the pure complex was obtained in 80% yield as a yellow oil.

6.2.1.1. Pentacarbonyl-chloro-bis(diethylamino)phosphinechromium. Anal. Found: C, 38.94; H, 5.12; N, 6.91; Cl, 8.80. $C_{13}H_{20}ClCrN_2O_5P$ (402.7) calc.: C, 38.77; H, 5.01; N, 6.96; Cl, 8.81%. $^{31}P\{^1H\}$ NMR (in C_6D_6): δ(P) 202.2 (s) ppm. ^1H NMR (in C_6D_6): δ(H)(CH_3) 1.12 (t, ^3J(HCCH) = 7.0 Hz); δ(H)(NCH_2) 3.19 (mc, ^3J(PNCH) = 14.0 Hz) ppm. EI-MS: *m/z* 402 (20%) $[M]^{+\cdot}$; ν(CO) 2066m, 2021w, 1988s, 1960, 1947vs cm^{-1}.

6.2.2. $(CO)_5CrPH(NEt_2)_2$

In a previously described procedure [4], a solution of 10 mmol of $(CO)_5CrPCl(NEt_2)_2$ was added dropwise to 5 mmol of $LiAlH_4$ in 30 ml of diethyl ether at −80°C. The mixture was allowed to warm to room temperature and stirred for 6 h. After filtration, the solvent was removed *in vacuo* at room temperature. The residue was taken up in pentane and chromatographed on silica gel with pentane as eluent. The eluate was evaporated to dryness to give $(CO)_5CrPH(NEt_2)_2$ as a light yellow oil in 90% yield.

Pentacarbonyl-bis(diethylamino)phosphinechromium. Anal. Found: C, 42.15; H, 5.88; N, 7.43, $C_{13}H_{21}CrN_2O_5P$ (368.3) calc.: C, 42.40; H, 5.75; N, 7.61%. $^{31}P\{^1H\}$ NMR (in C_6D_6): δ(P) 126.9 (s) ppm. ^1H NMR (in C_6D_6): δ(H)(CH_3) 0.88 (t, ^3J(HCCH) = 7.1 Hz); δ(H)(NCH_2) 2.86 (mc, ^3J(PNCH) = 14.0 Hz); δ(H)(PH) 6.85 (d, ^1J(PH) = 386.9 Hz) ppm. EI-MS: *m/z* 368 (21%) $[M]^{+\cdot}$; ν(CO) 2057m, 1979m, 1943, 1936vs cm^{-1}.

6.2.3. $(CO)_5CrPHClNEt_2$

In a previously described procedure [4], a solution of 10 mmol of $(CO)_5CrPH(NEt_2)_2$ in 40 ml of pentane was treated with gaseous hydrogen chloride for 5 min at 0°C. After removal of the solvent *in vacuo* at room temperature, the residue was extracted with 25–50 ml of pentane. The extract was filtered and the filtrate evaporated to dryness. The residue was chromatographed on silica gel to give $(CO)_5CrPHClNEt_2$ as an orange oil in 85% yield.

Pentacarbonyl-chlorodiethylaminophosphinechromium. Anal. Found: C, 32.54; H, 3.31; N, 3.93; Cl, 10.61. $C_9H_{11}ClCrNO_5P$ (331.6) calc.: C, 32.60; H, 3.34; N, 4.22; Cl, 10.69%. $^{31}P\{^1H\}$ NMR (in C_6D_6): δ(P) 149.5 (s) ppm. ^1H NMR (in C_6D_6): δ(H)(CH_3) 0.93 (t, ^3J(HCCH) = 7.2 Hz); δ(H)(NCH_2) 2.98 (mc, ^3J(PNCH) = 14.3 Hz; δ(H)(PH) 7.61 (d, ^1J(PH) = 402.4 Hz ppm. EI-MS; *m/z* 331 (17%) $[M]^{+\cdot}$; ν(CO) 2078s, 2024w, 1989m, 1973, 1960vs cm^{-1}.

6.3. Preparation of $(CO)_5CrPHCl_2$

A solution of 10 mmol of $(CO)_5CrPH(NEt_2)_2$ in 40 ml of CH_2Cl_2 was treated with gaseous hydrogen chloride for 10 min at 0°C. The mixture was worked up as described above to give $(CO)_5CrPHCl_2$ as yellow crystals in 85% yield.

Pentacarbonyl-dichlorophosphinechromium. Anal. Found: C, 20.39; H, 0.40; Cl, 24.19. $C_5HCl_2CrO_5P$ (294.9) calc.: C, 20.36; H, 0.34; Cl, 24.04%. $^{31}P\{^1H\}$ NMR (in C_6D_6): δ(P) 155.5 (s) ppm. ^1H NMR (in C_6D_6); δ(H)(PH) 8.90 (d, ^1J(PH) = 391.1 Hz) ppm. EI-MS: *m/z* 294 (53%) $[M]^{+\cdot}$; ν(CO) 2081m, 1996vs, 1973vs cm^{-1}; m.p. 30–31°C (dec.).

6.4. General procedure for the preparation of $(CO)_5MPh(H)PP(Cl)PhM(CO)_5$ (1a–1c)

Triethylamine (5 mmol) was added dropwise to a solution of 10 mmol of $(CO)_5MPhPHCl$ in 30 ml of toluene at −35°C. The mixture was stirred for 30 min and then allowed to warm slowly to room temperature. After removal of the solvent *in vacuo*, the residue was washed with 30 ml of pentane (in which the diphosphine complex is only sparingly soluble) and then dissolved in toluene and chromatographed on silica gel (column size 5 × 2.5 cm^2; eluent toluene). The yellow fraction was reduced *in vacuo* to a volume of 20 ml, and kept at −4°C to give pure isomers of **1a–1c** as yellow crystals in 60–65% yield.

Decacarbonyl-μ-1-chloro-1,2-diphenyldiphosphinedichromium (**1a**). Anal. Found: C, 40.64; H, 1.85; Cl, 5.40. $C_{22}H_{11}ClCr_2O_{10}P_2$ (636.7) calc.: C, 41.50; H, 1.74; Cl, 5.57%. ^1H NMR (in $CDCl_3$): δ(H)(C_6H_5) 7.50 (mc); δ(H)(PH) 6.21 (dd, ^1J(PH) = 312.6 Hz; ^2J(PH) = 19.5 Hz) ppm. EI-MS: *m/z* 636 (12%) $[M]^{+\cdot}$; ν(CO) 2065m, 2027w, 1989m, 1970, 1964vs cm^{-1}; m.p. 138–138.5°C (dec.).

Decacarbonyl-μ-1-chloro-1,2-diphenyldiphosphinedimolybdenum (**1b**). Anal. Found: C, 36.47; H, 1.47; Cl, 4.99. $C_{22}H_{11}ClMo_2O_{10}P_2$ (724.6) calc.: C, 36.47; H, 1.53; Cl, 4.89%. ^1H NMR (in $CDCl_3$): δ(H)(C_6H_5) 7.62 (mc); δ(H)(PH) 6.19 (dd, ^1J(PH) = 312.1 Hz, ^2J(PH) = 16.6 Hz) ppm. EI-MS: *m/z* = 724 (71%) $[M]^{+\cdot}$; ν(CO) 2070m, 2024w, 1988m, 1973, 1963vs cm^{-1}; m.p.: 144–144.5°C (dec.).

Decacarbonyl-μ-1-chloro-1,2-diphenyldiphosphineditungsten (**1c**). Anal. Found: C, 29.15; H, 1.15; Cl, 3.78. $C_{22}H_{11}ClO_{10}P_2W_2$ (900.4) calc.: C, 29.35; H, 1.23; Cl, 3.94%. ^1H NMR (in $CDCl_3$): δ(H)(C_6H_5) 7.62 (mc); δ(H)(PH) = 6.74 (dd, ^1J(PH) = 324.7 Hz, ^2J(PH) = 17.4 Hz) ppm. EI-MS: *m/z* 900 (47%) $[M]^{+\cdot}$; ν(CO) 2072m, 2025w, 1968s, 1959vs cm^{-1}; m.p. 168–168.5°C (dec.).

6.5. $(CO)_5CrNEt_2(H)PP(Cl)NEt_2Cr(CO)_5$ (2)

A solution of 25 mmol of NEt_3 in 5 ml of pentane was added dropwise at 0°C to 10 mmol of $(CO)_5CrPHClNEt_2$ in 60 ml of pentane. The reaction was completed by stirring for 15 min, the precipitate then filtered off and the filtrate evaporated *in vacuo* at room temperature. The residue was taken up in pentane and the solution mixed with 20 ml of silica gel. After removal of the solvent, a powder-like product remained and this was placed on the top of a silica gel in a column (size 20×2.5 cm^2). Elution at -30°C with pentane gave a yellow fraction, what was evaporated *in vacuo* at room tempeature to small volume then kept at -4°C to give yellow rhomb-shaped crystals in 40% yield.

Decacarbonyl-μ-1-chloro-1,2-bis(diethylamino)diphosphinedichromium (**2**). Anal. Found: C, 34.33; H, 3.29; N, 4.49; Cl, 5.49. $C_{18}H_{21}ClCr_2N_2O_{10}P_2$ (626.7) calc.: C, 34.49; H, 3.38; N, 4.47; Cl, 5.66%. ^1H NMR (in C_6D_6): $\delta(H)(PH)$ 6.96 (dd, $^1J(PH) = 357.8$ Hz, $^2J(PH) = 53.8$ Hz); $\delta(H)_A(NCH_2)$ 3.30 (mc, $^3J(PNCH)$ = 11.6 Hz); $\delta(H)_X(NCH_2)$ 3.10 (mc, $^3J(PNCH) = 11.6$ Hz); $\delta(H)_A(CH_3)$ 1.01 (t, $^3J(HCCH) = 7.1$ Hz); $\delta(H)_X(CH_3)$ 0.88 (t, $^3J(HCCH) = 7.1$ Hz) ppm. EI-MS: m/z 626 (4%) $[M]^{+\cdot}$; ν(CO) 2059m, 1989s, 1962, 1956vs cm^{-1}; m.p. 84.5–85°C (dec.).

6.6. $(CO)_5CrCl_2PPCl_2Cr(CO)_5$ (3) [12]

A solution of 5 mmol of NEt_3 in 5 ml of pentane was added dropwise with stirring to a solution of 10 mmol of $(CO)_5CrPHCl_2$ in 50 ml pentane at 0°C. When the addition was complete, the yellow mixture was stirred for a further 15 min, the solvent was removed *in vacuo* at room temperature and the residue treated with 20 ml of diethyl ether. The undissolved material was filtered off. When the filtrate was kept for several days at -4°C further product separated. For purification, the solid product was chromatographed (column size 5×2.5 cm^2; eluent toluene), and the yellow fraction evaporated *in vacuo* to a small volume and kept at -4°C to give yellow crystals in 50% yield.

Decacarbonyl-μ-tetrachlorodiphosphinedichromium (**3**). $C_{10}Cl_4Cr_2O_{10}P_2$ (587.8) $^{31}P\{^1H\}$ NMR (in C_6D_6): $\delta(P)$ 208.5 (s) ppm. EI-MS: m/z 588 (62%) $[M]^{+\cdot}$; ν(CO): 2076m, 2000s, 1988vs cm^{-1}; m.p. 153–153.5°C (dec.).

6.7. $(CO)_5CrPh(H)PP(F)PhCr(CO)_5$ (4)

A solution of 1 mmol of **1a** in 40 ml of toluene was added dropwise with stirring to a suspension of an equimolar amount of tetrabutylammonium fluoride (TBAF) in 10 ml of toluene at room temperature. (The TBAF trihydrate used was dried for 5 h at 35°C *in vacuo* as described by Cox [18].) When the addition was complete, the mixture was stirred for 45 min, the solvent then evaporated *in vacuo* at room temperature, and the residue treated with 30 ml of diethyl ether then filtered off and dried *in vacuo*. The product was purified by chromatography on silica gel (eluent toluene; column size 5×2.5 cm^2). The eluate was evaporated to small volume and kept at -4°C to give the pure isomer as yellow crystals in 70% yield.

Decacarbonyl-μ-1-fluoro-1,2-diphenyldiphosphinedichromium (**4**). Anal. Found: C, 42.16; H, 1.77; F, 3.20. $C_{22}H_{11}Cr_2FO_{10}P_2$ (620.2) calc.: C, 42.60; H, 1.79; F, 3.06%. ^1H NMR (in $CDCl_3$): $\delta(H)(C_6H_5)$ 7.24 (mc); $\delta(H)(PH)$ 5.54 (ddd, $^1J(PH) = 322.0$ Hz, $^2J(PH) = 17.5$ Hz) ppm. ^{19}F NMR (in C_6D_6): $\delta(F)$ 11.2 (ddd, $^3J(FH)$ = 19.4 Hz) ppm. EI-MS: m/z 620 (32%) $[M]^{+\cdot}$; ν(CO) 2064m, 2027w, 1981m, 1969, 1963vs cm^{-1}; m.p. 147°C (dec.).

6.8. $(CO)_5CrCl(H)PPCl_2Cr(CO)_5$ (5)

A solution of 2 mmol of **2** in 30 ml of Cl_2CH_2 was treated with gaseous hydrogen chloride for 20 min at -30°C. Removal of the solvent *in vacuo* at room temperature left a yellow powder which was treated with 20 ml of pentane and the precipitate removed by filtration. The filtrate was evaporated *in vacuo* at room temperature, and the crude product chromatographed on silica gel (eluent toluene; column size 5×2.5 cm^2). The yellow fraction was reduced to a small volume then kept for several days at -30°C to allow complete crystallization. Compound **5** was obtained in 85% yield as yellow crystals.

Decacarbonyl-μ-1,2,2-trichlorodiphosphinedichromium (**5**). Anal. Found: C, 21.60; H, 0.18; Cl, 19.15. $C_{10}HCl_3Cr_2O_{10}P_2$ (553.4) calc.: C, 21.70; H, 0.18; Cl, 19.22%. ^1H NMR (in C_6D_6): $\delta(H)(PH)$ 6.75 (dd, $^1J(PH) = 345.6$ Hz, $^2J(PH) = 23.1$ Hz) ppm. EI-MS: m/z 553 (70%) $[M]^{+\cdot}$; ν(CO) 2075m, 2000s, 1990, 1987vs cm^{-1}; m.p. 95–96°C (dec.).

6.9. $(CO)_5Cr(MeO)_2PP(OMe)_2Cr(CO)_5$ (6)

A solution of 2 mmol of **3** in 60 ml of methanol was stirred at room temperature for 3 days. The mixture was then reduced to a volume of 20 ml and kept for several days at -30°C to give **6** as a white solid in 90% yield.

Decacarbonyl-μ-tetramethoxydiphosphinedichromium (**6**). Anal. Found: C, 29.27; H, 1.89; Cr, 18.14. $C_{14}H_{12}Cr_2O_{14}P_2$ (570.1) calc.: C, 29.49; H, 2.12; Cr, 18.24%. ^1H NMR (in C_6D_6): $\delta(H)(CH_3)$ 3.55 (mc, $^3J(POCH) = 11.2$ Hz) ppm. EI-MS; m/z 568 (25%) $[M]^{+\cdot}$; ν(CO) 2060m, 2026w, 1988m, 1968, 1958vs cm^{-1}; m.p. 160–161°C (dec.).

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