Journal of Organometallic Chemistry, 476 (1994) 173–181

Reactions of coordinated ligands *

VIII **. Phosphinoformic acids RR'PCOOH (R, R' = organyl, H), the still unknown P-analogues of carbaminic acids, stabilized as ligands in complexes $(CO)_5MPRR'COOH$ (M = Cr, W) ***

K. Diemert, T. Hahn and W. Kuchen

Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität, Universitätsstrasse 1, D-40221 Düsseldorf (Germany)

(Received November 2, 1993)

Abstract

Metal carbonyl complexes containing phosphinoformic acids, including the parent compound H_2PCOOH, have been made by the following route: $(CO)_5MPRR'H \rightarrow (CO)_5MPRR'Li \rightarrow (CO)_5MPRR'COOLi \rightarrow (CO)_5MPRR'COOSiMe_3 \rightarrow (CO)_5MPRR'COOH$ (R = organyl, H; M = Cr, W).

While the uncoordinated silyl esters $RR'PCOOSiMe_3$ spontaneously decompose to RR'PH, CO_2 and Me_3SiOH in protic media the last step in the sequence above can be safely brought about by silica gel. So far only chromatography on silica gel has been found to provide the mild conditions necessary to avoid decarboxylation of the ligated esters during protolysis. Some reactions of $(CO)_5MPRR'COOLi$ are reported and compared with those of the free ligands RR'PCOOLi. The structures of the complexes have been confirmed by spectroscopic methods (IR, MS, ^1H-, ^{31}P-, ^{13}C-NMR).

Key words: Chromium; Tungsten; Phosphine; Carbonyl; Phosphinoformic acid

1. Introduction

Phosphinoformic acids RR'PCOOH (R, R' = organyl, H) are still unknown in the free state. Attempts to prepare them from their alkali salts or by hydrolysis of their esters resulted in spontaneous decarboxylation with formation of phosphines RR'PH [1,2]. *Ab initio* calculations for the system $H_2PCOOH/PH_3 + CO_2$ [2] showed the phosphinoformic acid to be less stable than its decomposition products. A possible intermediate in the decarboxylation reaction has the betain structure $H_3P^+CO_2^-$, for which a very weak P–C interaction and nearly the same geometry of its components was found as for PH_3 and CO_2. Thus, the betain may be perhaps better regarded as a weak adduct of these molecules. The betain is separated from the isomer H_2PCOOH by a high barrier that is probably considerably lower in protic media, as found for the decarboxylation of H_2NCOOH in the presence of H_2O [3].

In view of these findings we tried to generate RR'PCOOH within the coordination sphere of a complex by suitable reactions of coordinated ligands and to stabilize the acid by blocking the nucleophilic centre at the phosphorus atom by coordination to a $(CO)_5M$ group. The route shown in Scheme 1 proved to be successful.

Starting with **1a** we systematically varied the steric and electronic effects of R and R' until we finally obtained the still rather unstable complex **5g** containing coordinated H_2PCOOH, the parent compound of phosphinoformic acids.

Details of the procedures and properties of the

Correspondence to: Professor W. Kuchen.

[*] Dedicated to Prof. R. Schmutzler, Braunschweig, on occasion of his 60th birthday.

[**] For part VII, see: A. Bartmann, K. Diemert and W, Kuchen, *J. Organomet. Chem., 453* (1993) 65.

[***] Part of the Dissertation of T. Hahn, Heinrich-Heine-Universität Düsseldorf, 1992, partially presented at the XIIth ICPC Toulouse and the 29th ICCC Lausanne 1992.

0022-328X/94/$7.00
SSDI 0022-328X(93)24356-A

complexes **1**, **3**, **4** and **5** are reported below. The intermediates **2** were not isolated but treated *in situ* with CO_2.

2. Results and discussion

2.1. Complexes $(CO)_5MPRR'H$ (1)

Most of the compounds **1** were prepared in good yields (70–85%) from $(CO)_5MTHF$ and the corresponding phosphines RR'PH. In case of $(CO)_5CrPMeH_2$ (**1f**) we found it more convenient first to prepare the corresponding chlorphosphine complex from $(CO)_5CrTHF$ and $MePCl_2$ and then to reduce it *in situ* with $LiAlH_4$. By the same procedure $(CO)_5CrPH_3$ (**1g**) was obtained from $(CO)_5CrPCl_3$, which can also be prepared from $(CO)_5CrTHF$ and PH_4I, as reported by Mathey *et al.* [4].

Compounds **1** are yellow solids or oils that show good solubility in organic solvents such as pentane, toluene, benzene, ether or THF. They can be stored under nitrogen in the refrigerator for long periods of time without noticeable decomposition. If exposed to moist air they gradually turn green.

2.2. Complexes $(CO)_5MPRR'COOLi$ (3)

Preliminary experiments had shown that in some cases compounds **3** were formed by reaction of $(CO)_5CrTHF$ with lithium phosphinoformates RR'P-COOLi. However, it turned out to be difficult to separate them from some unidentified byproducts, and so we preferred the alternative route shown in Scheme 1 involving reaction of **2** with CO_2.

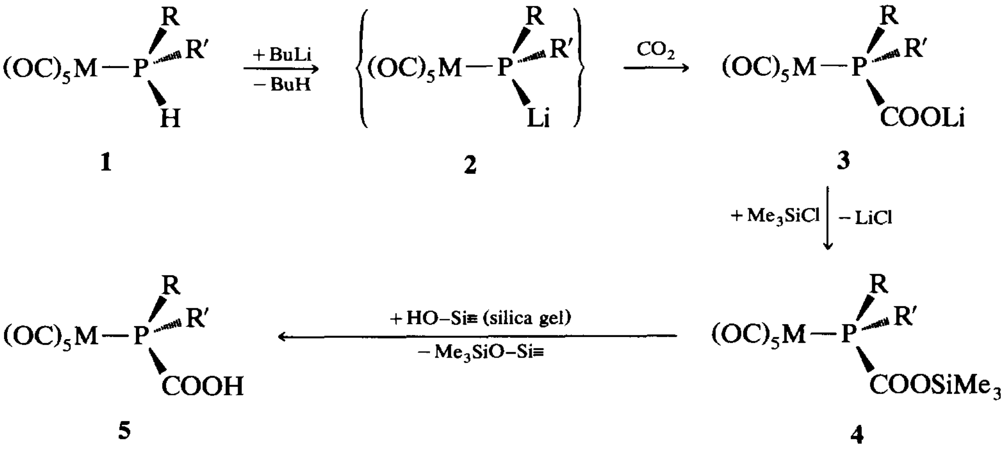
The procedure had to be modified depending on the nature of the coordinated phosphine in **1**. In case of complexes **1a–d** and **1h**, containing secondary phosphines as ligands, a slight excess of **1** in ether was treated with BuLi to give yellow solutions of **2**. The intense colour of **2** faded quickly with formation of **3** when these solutions were exposed to a stream of gaseous CO_2. After evaporation of the solvent traces of unchanged **1** were readily removed from the residue by washing with pentane in which the complexes **3** are only sparingly soluble. The yields were 80%–90%.

To avoid a side reaction according to eqn. (1):

$$\underset{\mathbf{2e}}{\textcircled{\small Cr}\text{P}^t\text{BuHLi}} \xrightarrow[\text{ether}]{\text{CO}_2} \underset{\mathbf{3e}}{\textcircled{\small Cr}\text{P}^t\text{BuHCOOLi}} \xrightarrow[-\textcircled{\small Cr}\text{P}^t\text{BuH}_2]{+\textcircled{\small Cr}\text{P}^t\text{BuHLi}} \textcircled{\small Cr}\text{P}^t\text{BuLi(COOLi)} \xrightarrow[\text{ether}]{\text{CO}_2} \textcircled{\small Cr}\text{P}^t\text{Bu(COOLi)}_2 \qquad (1)$$

$$\textcircled{\small Cr} = (\text{CO})_5\text{Cr}$$

compound **1e**, containing the primary phosphine $^tBuPH_2$, was metallated in pentane in which the resulting lemon yellow phosphide complex **2e** was insoluble. When the suspension was treated with gaseous CO_2 its colour faded within a few minutes. The solid was filtered off and dissolved in ether and the solution filtered and evaporated to give pure **3e**. In spite of variation of reaction conditions in the case of **1f**, the side reaction, which is analogous to that of the non-coordinated RPH_2 (R = Ph, ^{c}Hex) with BuLi and CO_2



	a	b	c	d	e	f	g	h
R	Ph	^{c}Hex	^{i}Pr	Et	^{t}Bu	Me	H	^{c}Hex
R'	Ph	^{c}Hex	^{i}Pr	Et	H	H	H	^{c}Hex
M	Cr	Cr	Cr	Cr	Cr	Cr	Cr	W

Scheme 1.

[2], could not be entirely suppressed, and so $(CO)_5CrPMeHCOOLi$ (**3f**) was always obtained as a mixture with about 10% $(CO)_5CrPMe(COOLi)_2$ (estimated from the intensity of the resonances in the ^{31}P-NMR spectrum). Since it was not possible to separate the two components the mixtures were used in the reactions of **3f** described below.

Attempts to prepare $(CO)_5CrPH_2COOLi$ (**3g**) from $(CO)_5CrPH_2Li$ [5] and CO_2 gave mixtures of $(CO)_5CrPH(COOLi)_2$ ($\approx 45\%$, $\delta_P = -16.8$ ppm (d), $^1J_{PH} = 342$ Hz, in THF), $(CO)_5CrP(COOLi)_3$ ($\approx 5\%$, $\delta_P = 6.9$ ppm (s), in THF) and $(CO)_5CrPH_3$ [5–7] ($\approx 50\%$, $\delta_P = -131.0$ ppm (q), $^1J_{PH} = 337$ Hz) in which no **3g** could be detected. As mentioned above, complexes **2** served only as intermediates in the preparation of **3**. The lithiation of coordinated phosphines was first reported by F.G.A. Stone *et al.* [8] and by P.M. Treichel *et al.* [9–11].

All the complexes **3** are light yellow solids, which are stable under nitrogen and turn to sticky pastes when exposed to moist air. They are easily soluble in ether or THF. In protic media, *e.g.* alcohols or THF/H_2O, they decompose within a few minutes with decarboxylation and regeneration of the corresponding starting complex **1**. We assume that in polar solvents the compounds **3** are dissociated to a small extent in the sense $(CO)_5M \cdots L$ so that electrophilic attack of protons on the P-atom is facilitated, followed by decarboxylation of the phosphine ligand. This view is supported by the finding that complexes $(CO)_5MPRR'COOH$ (**5**) are stable even in solvents such as ether but decompose, with evolution of CO_2, if water or alcohols are added to the solutions.

Some reactions of the coordinated phosphine ligands in **3** resemble those of non-coordinated $RR'PCOOLi$ [2], as shown by their reaction with MeI or dimethyl sulphate according to eqns. (2) and (3).

$$\textcircled{M}PRR'COOLi + MeI \xrightarrow{THF}$$

3a, d, h

$$\textcircled{M}PRR'Me + CO_2 + LiI \quad (2)$$

6a, d, h

$$2\,\textcircled{M}PRR'COOLi + (MeO)_2SO_2 \xrightarrow{THF}$$

3d, h

$$2\,\textcircled{M}PRR'COOMe + Li_2SO_4 \quad (3)$$

7d, h

$\textcircled{M} = (CO)_5M$

The reaction shown in eqn. (2) does not take place with suspensions of **3** in pentane or solutions in ether, but only in THF. This may be regarded as a further argument for dissociation of **3** in the latter solvent and for the mechanism of the reaction between the free ligands and MeI previously suggested [1,12].

Compounds **7** with phosphinoformic esters as a ligand are, like compounds **6**, light yellow oils or solids readily soluble in pentane, THF, ether, and alcohols.

While non-coordinated lithiumphosphinoformates $RR'PCOOLi$ readily give dithiophosphinoformates $RR'PCSSLi$ [2], solutions of **3** in THF did not react with CS_2. Even after several days' warming or stirring at room temperature the ^{31}P-NMR spectra of these solutions showed only the resonances of the starting complexes **3**.

2.3. Complexes $(CO)_5MPRR'COOSiMe_3$ (4)

When Me_3SiCl is added in excess to suspensions of **3** in pentane the complexes **4** are formed in good yields according to eqn. (4).

$$\textcircled{M}PRR'COOLi + ClSiMe_3 \xrightarrow{pentane}$$

3

$$\textcircled{M}PRR'COOSiMe_3 + LiCl \quad (4)$$

4

Although in the case of $(CO)_5CrPMeHCOOLi$ (**3f**) a mixture of this complex with *ca.* 10% of $(CO)_5CrPMe(COOLi)_2$ had to be used for this reaction, compound **4f** proved to be the sole product and no $(CO)_5CrPMe(COOSiMe_3)_2$ was detected. Analogous results were previously obtained when $RPHCOOSiMe_3$ was found to be the sole product of the reaction of a mixture of $RPHCOOLi$ and $RP(COOLi)_2$ ($R = Ph$, ^cHex) with Me_3SiCl. To account for this finding we suggested the reaction sequence shown in eqn. 5, in which the intermediately formed highly-reactive bis(silylester) is partly decarboxylated by protons from the glass wall of the reaction vessel [2].

$$RP(COOLi)_2 + 2\,ClSiMe_3 \xrightarrow{-2\,LiCl}$$

$$\{RP(COOSiMe_3)_2\} \xrightarrow[-Me_3SiO-Si\equiv]{+HO-Si\equiv}$$

$$RP(COOH)(COOSiMe_3) \xrightarrow{-CO_2}$$

$$RPHCOOSiMe_3 \quad (5)$$

$R = Ph, {}^cHex$

This reaction scheme may be similarly applied to the complexed ligand $MeP(COOLi)_2$ and to a mixture of $(CO)_5CrPH(COOLi)_2$ and $(CO)_5CrP(COOLi)_3$, the preparation of which had been described above. In the latter case reaction of this mixture with Me_3SiCl opens a route to complex $(CO)_5CrPH_2COOSiMe_3$ (**4g**) which was found to be the sole product.

Complexes **4** are yellow solids or oils that remain stable for weeks when stored under nitrogen in carefully silanized glass vessels. They are readily soluble in organic solvents. In protic solvents they slowly decompose with decarboxylation and formation of $(CO)_5MPRR'H$ (**1**).

2.4. *Complexes $(CO)_5MPRR'COOH$ (5)*

As mentioned above, complexes $(CO)_5MPRR'COOLi$ (**3**) and $(CO)_5MPRR'COOSiMe_3$ (**4**) are more or less rapidly decarboxylated in protic media. Thus initial attempts to prepare **5** by acidolysis of **3** or hydrolysis of **4** were unsuccessful even at low temperatures or in dilute alcoholic solutions.

Surprisingly we obtained **5** in good yields when we tried to purify **4** by chromatography on carefully dried silica gel. Obviously the protons of the silica gel had brought about protolysis according to Scheme 1, and column chromatography provided the mild conditions necessary to avoid decarboxylation of the phosphinoformic acid ligands in **5**. Attempts to prepare the non-coordinated acids $RR'PCOOH$ by the same method from $RR'PCOOSiMe_3$ gave only the corresponding phosphines $RR'PH$. This shows that stabilization of phosphinoformic acids can be achieved by ligation via phosphorus to a $(CO)_5M$ group.

Compounds **5** are yellow solids that remain stable for weeks under inert conditions. They are practically insoluble in pentane and sparingly soluble in toluene or ether. Only **5g**, the parent compound of this class of complexes, is rapidly decomposed in ether with formation of **1g**.

The postulated structure of complexes **5** is confirmed by their NMR- and IR-spectra. Characteristic data are listed in Tables 1 and 2.

3. Conclusions

Phosphinoformic acids $RR'PCOOH$ (R, R' = organyl, H) can be generated within the coordination sphere of complexes and stabilized as ligands in complexes $(CO)_5MPRR'COOH$ ($M = Cr, W$) according to Scheme 1. Protolysis of $(CO)_5MPRR'COOSiMe_3$ on silica gel provides the mild conditions necessary to avoid decarboxylation of the ligated acids.

TABLE 1. Some characteristic NMR data of $(CO)_5MPRR'COOH$ (**5**)

	δ_P [ppm] ($^1J_{PH}$ [Hz])	$\delta_C(COO)$ [ppm] ($^1J_{CP}$ [Hz])	$\delta_H(PH)$ [ppm] ($^1J_{HP}$ [Hz])	$\delta_H(OH)$ [ppm]
5a	56.7 (s) [a]	182.1 (d, 45)		12.0 (s, b)
5b	70.5 (s) [a]	180.3 (d, 31)		9.4 (s, b)
5c	87.1 (s) [b]	181.2 (d, 31)		10.9 (s, b)
5d	59.1 (s) [b]	181.9 (d, 42)		11.3 (s, b)
5e	56.9 (d, 340) [b]	181.3 (d, 40)	5.0 (d, 338)	10.3 (s, b)
5f	−5.8 (d, 342) [a]	181.4 (d, 51)	5.44 (d, 346)	10.7 (s, b)
5g	−37.7 (t, 342)		5.18 (d, 345)	9.1 (s, b)
5h	37.2 (s) [c]	180.2 (d, 43)		9.6 (s, b)

Solvent: $CDCl_3$, [a] ether, [b] toluene, [c] THF

TABLE 2. Wave numbers $\tilde{\nu}$ [cm^{-1}] of some characteristic absorption bands in the IR-spectra and relative intensity of the peaks for the molecular ion [$M^{+\bullet}$] in the EI-mass spectra of **5**

	$\nu_{A_1}^{(1)}$ (CO)	$\nu_{as,COO}$	ν_{P-H}	I_{rel} ($M^{+\bullet}$) [%]
5a	2068	1669		3
5b	2063	1668		3
5c	2062	1663		11
5d	2063	1664		15
5e	2065	1671	2357	20
5f	2069	1671	2384	28
5g	2064	1665	2385	17
5h	2069	1668		14

4. Experimental details

4.1. *General procedures*

All operations were performed under nitrogen. Nitrogen and solvents were purified and dried by standard methods. Melting points are uncorrected. ^{31}P-NMR, Bruker HX 90R (90 MHz); ^{13}C- and ^1H-NMR, Bruker AM 200 (200 MHz); chemical shifts are relative to external 85% H_3PO_4 (^{31}P) and internal Me_4Si (^{13}C, ^1H) as reference compounds; positive shifts are too high in frequency. Abbreviations are used as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; c, centred; b, broad. Values of the coupling constants are in Hz. IR, Perkin-Elmer 283. A complete list of the IR data of the complexes described here has been given [12]. Abbreviations: w, weak; m, medium; s, strong; vs, very strong. MS, Varian MAT 311 A; *m/z* data refer to the highest peak of a polyisotopic group and the intensities are relative to the base-peak (100%).

4.2. *Preparation of $(CO)_5MPRR'H$ (1)*

Method A. 9 mmol of the phosphine were added to a solution of 10 mmol of freshly prepared $(CO)_5MTHF$ [13] in 120 ml THF. After 2 h stirring at room temperature the solvent was evaporated and traces of unchanged $M(CO)_6$ were removed at room temperature under vacuum ($p < 0.1$ mm Hg).

Method B. A solution of 30 mmol of the chlorophosphine complex $(CO)_5CrPRCl_2$ (R = Me, Cl), prepared from $(CO)_5CrTHF$ and $PRCl_2$ as described above, in 150 ml ether was added dropwise during 2 h to an excess of $LiAlH_4$ (30–40 mmol) in 200 ml ether at −65°C. The suspension was then allowed to warm to room temperature and stirred for 15 h. Ethanol (20 ml) was then slowly added to destroy the excess of $LiAlH_4$ and the mixture refluxed for 1 h. After filtration the solvent was evaporated from the filtrate and the product dried under vacuum.

Method C. The procedure was as in method A but PH_4I was used instead of the phosphine, as described by F. Mathey *et al.* [4].

Purification (methods A–C). The products were dissolved in pentane and purified by chromatography on dry silica gel (Merck, 0.063–0.2 mm). Yields: 70%–85% (method A), 60%–65% (method B), 75%–80% (method C).

$(CO)_5CrPPh_2H$ (**1a**). Method A: light yellow solid; m.p. 55–56°C (Lit. [14] 55–65°C). ^{31}P-NMR (pentane): $\delta_P = 34.5$ ppm (d), $^1J_{PH} = 338$ Hz (Lit. [15] 32.1 ppm, 338.8 Hz). IR (pentane) ν_{CO}: 2069m, 1955vs, 1918w (Lit. [14] 2067w, 2024w, 1985w, 1953s, 1945s, 1916w).

$(CO)_5CrP^cHex_2H$ (**1b**). Method A: yellow solid; m.p. 60–62°C. ^{31}P-NMR (pentane): $\delta_P = 39.0$ ppm (d), $^1J_{PH} = 307$ Hz. IR (pentane) ν_{CO}: 2060s, 1945vs, 1910w, 1890w.

$(CO)_5CrP^iPr_2H$ (**1c**). Method A: yellow oil; $C_{11}H_{15}CrO_5P$ (310.2). Calc.: C 42.59, H 4.87, Cr 16.76. Found: C 42.24, H 4.67, Cr 16.43%. ^{31}P-NMR (pentane): $\delta_P = 51.4$ ppm (d), $^1J_{PH} = 307$ Hz. ^1H-NMR ($CDCl_3$): $\delta_H(CH_3) = 1.26$ ppm (dd), $^3J_{HCCP} = 16$ Hz, $^3J_{HCCH} = 7$ Hz; $\delta_H(CH) = 2.36$ ppm (mc); $\delta_H(HP) = 4.17$ ppm (td), $^1J_{HP} = 311$ Hz, $^3J_{HPCH} = 5$ Hz. IR (pentane) ν_{CO}: 2063m, 1942vs, 1913w, 1895w.

$(CO)_5CrPEt_2H$ (**1d**). Method A: yellow viscous oil; ^{31}P-NMR (pentane): $\delta_P = 20.3$ ppm (d), $^1J_{PH} = 315$ Hz (Lit. [16] 14.5 ppm (d), 322 Hz). IR (pentane) ν_{CO}: 2060s 1940vs, 1900m.

$(CO)_5CrP^tBuH_2$ (**1e**). Method A: yellow solid (Lit. [17] yellow oil); m.p. 32°C. ^{31}P-NMR (pentane): $\delta_P = 6.3$ ppm (t), $^1J_{PH} = 318$ Hz. IR (pentane) ν_{CO}: 2068s, 1948vs, 1918m (Lit. [17] 2065m, 1984vs, 1951sh, 1944vs, 1915s in c-hexane).

$(CO)_5CrPMeH_2$ (**1f**). Method B: yellow oil. ^{31}P-NMR (pentane): $\delta_P = -64.9$ ppm (t), $^1J_{PH} = 324$ Hz, $^2J_{PCH} = 10$ Hz. IR (pentane) ν_{CO}: 2063m, 1958vs, 1913m (Lit. [17] 2060m, 1982vs, 1955s, 1945vs, 1910s in c-hexane).

$(CO)_5CrPH_3$ (**1g**). Method C: yellow solid; m.p. 113–115°C (Lit. [6] 116°C). ^{31}P-NMR (THF): $\delta_P = -131.0$ ppm (q), $^1J_{PH} = 337$ Hz (Lit. [7] -129.6 ppm in benzene; Lit. [5] -131.0 ppm, 336 Hz in ether). IR (pentane) ν_{CO}: 2074m, 1960vs, 1925m (Lit. [6] 2075m, 1982sh, 1953vs, 1924m, 1910s in hexane).

$(CO)_5WP^cHex_2H$ (**1h**). Method A: yellow solid; m.p. 63–65°C. ^{31}P-NMR (pentane): $\delta_P = -1.4$ ppm (d), $^1J_{PH} = 314$ Hz. IR (THF) ν_{CO}: 2068m, 1974m, 1933vs.

4.3. Preparation of $(CO)_5MPR_2COOLi$ 3a–3d, 3h

A 1.6 M solution of BuLi (6 ml, *ca.* 9.6 mmol) in hexane was added dropwise to 10 mmol of the phosphine complex **1a–1d**, **1h** in 100 ml of ether at −30°C. The yellow-orange solutions of **2** were subsequently stirred for 30 min at that temperature and a vigorous stream of dry gaseous CO_2 then passed through the solutions for about 2 min at −50°C until no further colour change was observed. After evaporation of the solvent traces of unchanged **1** were removed from the residue by washing with pentane. Yields: 80%–90%.

$(CO)_5CrPPh_2COOLi$ (**3a**). Yellow solid; m.p. 110–112°C (dec.); $C_{18}H_{10}CrLiO_7P$ (428.2). Calc.: C 50.49, H 2.35, Cr 12.14. Found: C 50.03, H 2.82, Cr 12.45%. $^{31}P\{^1H\}$-NMR (ether): $\delta_P = 47.6$ ppm (s). IR (ether) ν_{CO}: 2060s, 1980msh, 1938vs. IR (KBr): $\nu_{as,COO}$; 1608vs.

$(CO)_5CrP^cHex_2COOLi$ (**3b**). Yellow solid; m.p. 200–204°C (dec.); $C_{18}H_{22}CrLiO_7P$ (440.3). Calc.: C 49.10, H 5.03, Cr 11.81. Found: C 49.30, H 5.11, Cr 12.05%. $^{31}P\{^1H\}$-NMR (THF): $\delta_P = 58.1$ ppm (s). IR (THF) ν_{CO}: 2055s, 1974s, 1927vs. IR (KBr): $\nu_{as,COO}$; 1618vs.

$(CO)_5CrP^iPr_2COOLi$ (**3c**). Yellow solid; m.p. 159–161°C (dec.); $C_{12}H_{14}CrLiO_7P$ (360.1). Calc.: C 40.02, H 3.92, Cr 14.44. Found: C 40.22, H 4.19, Cr 14.15%. $^{31}P\{^1H\}$-NMR (THF): $\delta_P = 67.1$ ppm (s). IR (ether) ν_{CO}: 2056m, 1975msh, 1935vs. IR (KBr): $\nu_{as,COO}$; 1629s.

$(CO)_5CrPEt_2COOLi$ (**3d**). Yellow solid; m.p. *ca.* 210°C (dec.); $C_{10}H_{10}CrLiO_7P$ (332.1). Calc.: C 36.17, H 3.04, Cr 15.66. Found: C 36.28, H 3.12, Cr 16.13%. $^{31}P\{^1H\}$-NMR (ether): $\delta_P = 38.8$ ppm (s). IR (THF) ν_{CO}: 2055s, 1973msh, 1930vs. IR (KBr): $\nu_{as,COO}$; 1571vs.

$(CO)_5WP^cHex_2COOLi$ (**3h**). Beige solid; m.p. 195–200°C (dec.); $C_{18}H_{22}LiO_7PW$ (572.1). Calc.: C 37.79, H 3.88, W 32.13. Found: C 36.60, H 3.77, W 32.45%. $^{31}P\{^1H\}$-NMR (THF): $\delta_P = 27.7$ ppm (s), $^1J_{PW} = 110$ Hz. IR (THF) ν_{CO}: 2063m, 1973m, 1930vs. IR (KBr): $\nu_{as,COO}$; 1619vs.

4.4. Preparation of $(CO)_5CrPRHCOOLi$ (3e, f)

$(CO)_5CrP^tBuHCOOLi$ (**3e**). A 1.6 M solution of MeLi (5.6 ml, *ca.* 9 mmol) in ether was slowly added to a solution of 10 mmol of **1e** in 150 ml of pentane at −40°C. The resulting yellow suspension was stirred for 45 min at that temperature, then a vigorous stream of dry gaseous CO_2 was passed through it at −50°C until no further change of colour was observed. The resulting solid was filtered off and dissolved in ether, and the filtrate was filtered and the solvent evaporated under vacuum at room temperature. The excess of **1e** was removed by washing with pentane. Yield: 70–75%. Yellow solid; m.p. 178–180°C (dec.); $C_{10}H_{10}CrLiO_7P$ (332.1). Calc.: C 36.16, H 3.04, Cr 15.66. Found: C 35.61, H 3.47, Cr 15.13%. ^{31}P-NMR (THF): $\delta_P = 46.2$ ppm (d), $^1J_{PH} = 323$ Hz, $^3J_{PCCH} = 14$ Hz. IR (THF) ν_{CO}: 2060m, 1977msh, 1940vs. IR (KBr): $\nu_{as,COO}$; 1582vs.

$(CO)_5CrPMeHCOOLi$ (**3f**). The procedure was the same as for **3e** except that a 1.6 molar solution of BuLi in hexane was used for the lithiation. In spite of variation of reaction conditions **3f** was always obtained as a mixture with about 10% $(CO)_5CrPMe(COOLi)_2$. **3f** ^{31}P-NMR (THF): $\delta_P = -17.9$ ppm (d), $^1J_{PH} = 337$ Hz. In ether: $\delta_P = -12.7$ ppm (d), $^1J_{PH} = 322$ Hz; $(CO)_5CrPMe(COOLi)_2$. ^{31}P-NMR (THF): $\delta_P = 9.8$ ppm (s). In ether: $\delta_P = 17.9$ ppm (s).

*4.5. Reaction of $(CO)_5CrPH_2Li$ **2g** with CO_2*

A solution of 10 mmol of **1g** in pentane (200 ml) was treated with 5 ml of a 1.6 M solution of BuLi (8 mmol) in hexane as described above. The resulting ochre-coloured suspension of **2g** was treated with a vigorous stream of gaseous CO_2 for about 5 min at −50°C. The resulting beige solid was filtered off and washed with pentane to remove the excess of **1g**. The beige solid was a mixture of $(CO)_5CrPH(COOLi)_2$ ($\approx 95\%$, $\delta_P = -16.8$ ppm (d), $^1J_{PH} = 342$ Hz, in THF) and $(CO)_5CrP(COOLi)_3$ ($\approx 5\%$, $\delta_P = 6.9$ ppm (s), in THF). Characteristic bands in the IR-spectrum (KBr): $\nu_{as,COO}$ 1611sb; ν_{P-H} 2331m.

4.6. Preparation of $(CO)_5MPRR'COOSiMe_3$ (4)

Trimethylchlorsilane (2 g, 18.4 mmol) was added dropwise to a suspension of 5 mmol of the lithiumphosphinoformate complex **3** in 50 ml of pentane at −30°C. The mixture was allowed to warm to room temperature and stirred for 16 h. After filtration the solvent and the excess of Me_3SiCl were evaporated off under vacuum to leave **4** as a residue. Yield: 80%–90% (40% in case of **4g**).

$(CO)_5CrPPh_2COOSiMe_3$ (**4a**). Yellow solid; m.p. 73–76°C; $C_{21}H_{19}CrO_7PSi$ (494.4). Calc.: C 51.01, H 3.87, Cr 10.51. Found: C 50.57, H 3.61, Cr 10.48%. $^{31}P\{^1H\}$-NMR (pentane): $\delta_P = 59.7$ ppm (s). ^1H-NMR ($CDCl_3$): $\delta_H(SiMe_3) = 0.24$ ppm (s); $\delta_H(Ph) = 7.5$ ppm (mc). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(SiMe_3) = 0.1$ ppm (s); $\delta_C(Ph) = 129.1–133.5$ ppm (m); $\delta_C(COO) = 174.6$ ppm (d), $^1J_{CP} = 57$ Hz; $\delta_C(CO_{eq}) = 216.6$ ppm (d), $^2J_{CCrP} = 13$ Hz; $\delta_C(CO_{ax}) = 221.6$ ppm (d), $^2J_{CCrP} = 5.5$ Hz. IR (pentane) ν_{CO}: 2070m, 1957vs, 1949vs. IR (KBr) $\nu_{as,COO}$: 1692vs. EI-MS: $m/z = 494$ (9%) $[M^{+\bullet}]$.

$(CO)_5CrP^cHex_2COOSiMe_3$ (**4b**). Light yellow solid; m.p. 94–96°C; $C_{21}H_{31}CrO_7PSi$ (506.5). Calc.: C 49.79, H 6.17, Cr 10.26. Found: C 49.27, H 6.11, Cr 10.22%. $^{31}P\{^1H\}$-NMR (pentane): $\delta_P = 74.7$ ppm (s). ^1H-NMR ($CDCl_3$): $\delta_H(SiMe_3) = 0.38$ ppm (s); $\delta_H(^cHex) = 1.6$ ppm (mc). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(SiMe_3) = 0.35$ ppm (s); $\delta_C(^cHex) = 26.6–36.7$ ppm (m); $\delta_C(COO) = 175.4$ ppm (d), $^2J_{CP} = 41$ Hz; $\delta_C(CO_{eq}) = 217.9$ ppm (d), $^2J_{CCrP} = 13$ Hz; $\delta_C(CO_{ax}) = 221.7$ ppm (d), $^2J_{CCrP} = 5.5$ Hz. IR (pentane) ν_{CO}: 2063m, 1990s, 1944vs. IR (KBr) $\nu_{as,COO}$: 1680vs; EI-MS: $m/z = 506$ (7%) $[M^{+\bullet}]$.

$(CO)_5CrP^iPr_2COOSiMe_3$ (**4c**). Yellow oil; $C_{15}H_{23}CrO_7PSi$ (426.4). Calc.: C 42.25, H 5.44, Cr 12.19. Found: C 42.03, H 5.28, Cr 11.82%. $^{31}P\{^1H\}$-NMR (pentane): $\delta_P = 83.8$ ppm (s). ^1H-NMR ($CDCl_3$): $\delta_H(SiMe_3) = 0.35$ ppm (s); $\delta_H(CH_3) = 1.28$ ppm (dd), $^3J_{HCCH} = 7$ Hz, $^3J_{HCCP} = 15$ Hz; $\delta_H(CH) = 2.42$ ppm (mc). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(SiMe_3) = 0.3$ ppm (s); $\delta_C(CH_3) = 18.4$ ppm (d), $^2J_{CCP} = 3.5$ Hz; $\delta_C(CH) = 27.3$ ppm (d), $^1J_{CP} = 17.5$ Hz; $\delta_C(COO) = 175.4$ ppm (d), $^1J_{CP} = 41.5$ Hz; $\delta_C(CO_{eq}) = 217.7$ ppm (d), $^2J_{CCrP} = 13$ Hz; $\delta_C(CO_{ax}) = 221.5$ ppm (d), $^2J_{CCrP} = 5$ Hz. IR (pentane) ν_{CO}: 2065m, 1953s, 1945vs. IR (film) $\nu_{as,COO}$: 1684vs; EI-MS: $m/z = 426$ (9%) $[M^{+\bullet}]$.

$(CO)_5CrPEt_2COOSiMe_3$ (**4d**). Light yellow solid; m.p. 34–37°C; $C_{13}H_{19}CrO_7PSi$ (398.3). Calc.: C 39.19, H 4.81, Cr 13.05. Found: C 38.66, H 4.40, Cr 13.14%. $^{13}P\{^1H\}$-NMR (pentane): $\delta_P = 56.0$ ppm (s). ^1H-NMR ($CDCl_3$): $\delta_H(SiMe_3) = 0.35$ ppm (s); $\delta_H(CH_3) = 1.2$ ppm (dt), $^3J_{HCCH} = 7.5$ Hz, $^3J_{HCCP} = 16$ Hz; $\delta_H(CH_2) = 2.1$ ppm (dq), $^3J_{HCCH} = 7.5$ Hz, $^2J_{HCP} = 42$ Hz. $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(SiMe_3) = 0.4$ ppm (s); $\delta_C(CH_3) = 8.9$ ppm (d), $^2J_{CCP} = 3$ Hz; $\delta_C(CH_2) = 20.3$ ppm (d), $^1J_{CP} = 22$ Hz; $\delta_C(COO) = 176.8$ ppm (d), $^1J_{CP} = 52$ Hz; $\delta_C(CO_{eq}) = 216.9$ ppm (d), $^2J_{CCrP} = 13$ Hz; $\delta_C(CO_{ax}) = 221.5$ ppm (d), $^2J_{CCrP} = 6$ Hz. IR (pentane) ν_{CO}: 2068m, 1955s, 1948vs. IR (KBr) $\nu_{as,COO}$: 1688vs. EI-MS: $m/z = 398$ (43%) $[M^{+\bullet}]$.

$(CO)_5CrP^tBuHCOOSiMe_3$ (**4e**). Light yellow solid; m.p. 47–49°C; $C_{13}H_{19}CrO_7PSi$ (398.3). Calc.: C 39.19, H 4.81, Cr 13.05. Found: C 38.53, H 4.46, Cr 12.87%. ^{31}P-NMR (pentane): $\delta_P = 59.9$ ppm (d), $^1J_{PH} = 340$ Hz. ^1H-NMR ($CDCl_3$): $\delta_H(SiMe_3) = 0.35$ ppm (s); $\delta_H(CH_3) = 1.36$ ppm (d), $^3J_{HCCP} = 16$ Hz; $\delta_H(HP) = 4.86$ ppm (d), $^1J_{HP} = 336$ Hz. $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(SiMe_3) = 0.3$ ppm (s); $\delta_C(CH_3) = 28.6$ ppm (d), $^2J_{CCP} = 2$ Hz; $\delta_C(CMe_3) = 33.2$ ppm (d), $^1J_{CP} = 19$ Hz; $\delta_C(COO) = 174.4$ ppm (d), $^1J_{CP} = 51$ Hz; $\delta_C(CO_{eq}) = 216.5$ ppm (d), $^2J_{CCrP} = 12$ Hz; $\delta_C(CO_{ax}) = 221.1$ ppm (d), $^2J_{CCrP} = 5$ Hz. IR (pentane) ν_{CO}: 2072m, 1952vs, 1920w. IR (KBr) $\nu_{as,COO}$: 1675vs; EI-MS: $m/z = 398$ (13%) $[M^{+\bullet}]$.

$(CO)_5CrPMeHCOOSiMe_3$(**4f**) (prepared with a mixture of **3f** containing about 10% $(CO)_5CrPMe(COOLi)_2$). Light yellow oil; $C_{10}H_{13}CrO_7PSi$ (356.3). Calc.: C 33.71, H 3.68, Cr 14.59. Found: C 34.26, H 3.81, Cr 14.51%. ^{31}P-NMR (pentane): $\delta_P = 0$ ppm (d), $^1J_{PH} = 340$ Hz. ^1H-NMR ($CDCl_3$): $\delta_H(SiMe_3) = 0.35$ ppm (s); $\delta_H(CH_3) = 1.67$ ppm (dd), $^2J_{HCP} = 8.5$ Hz, $^3J_{HCPH} = 6.5$ Hz; $\delta_H(HP) = 5.19$ ppm (qd), $^1J_{HP} = 342$ Hz, $^3J_{HPCH} = 6.5$ Hz. $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(SiMe_3) = 0.3$ ppm (s); $\delta_C(CH_3) = 9.2$ ppm (d), $^1J_{CP} = 27$ Hz; $\delta_C(COO) = 175.0$ ppm (d), $^1J_{CP} = 62$ Hz; $\delta_C(CO_{eq}) = 216.0$ ppm (d), $^2J_{CCrP} = 13$ Hz; $\delta_C(CO_{ax}) = 220.8$ ppm (d), $^2J_{CCrP} = 6.5$ Hz. IR (pentane) ν_{CO}:

2075m, 1990w, 1954vs, 1925w. IR (film) $\nu_{as,COO}$: 1694vs. EI-MS: $m/z = 356$ (7%) $[M^{+\bullet}]$.

$(CO)_5CrPH_2COOSiMe_3$ (**4g**) (prepared with mixture of $(CO)_5CrPH(COOLi)_2$ containing about 5% $(CO)_5CrP(COOLi)_3$). Light yellow oil; $C_9H_{11}CrO_7PSi$ (342.2). Calc.: C 31.58, H 3.24, Cr 15.19. Found: C 31.08, H 3.04, Cr 15.41%. $^{31}P\{^1H\}$-NMR (pentane): $\delta_P = -38.3$ ppm (t), $^1J_{PH} = 339$ Hz. ^1H-NMR ($CDCl_3$): $\delta_H(SiMe_3) = 0.29$ ppm (s); $\delta_H(H_2P) = 4.9$ ppm (d), $^1J_{HP} = 342$ Hz. $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(SiMe_3) = 0.3$ ppm (s); $\delta_C(COO) = 170.9$ ppm (d), $^1J_{CP} = 66$ Hz; $\delta_C(CO_{eq}) = 215.5$ ppm (d), $^2J_{CCrP} = 13$ Hz; $\delta_C(CO_{ax}) = 220.4$ ppm (d), $^2J_{CCrP} = 6$ Hz. IR (pentane) ν_{CO}: 2075m, 1960vs, 1927w. IR (film) $\nu_{as,COO}$: 1695sb. EI-MS: $m/z = 342$ (10%) $[M^{+\bullet}]$.

$(CO)_5WP^cHex_2COOSiMe_3$ (**4h**). Beige solid; m.p. 86–89°C; $C_{21}H_{31}O_7PSiW$ (638.4). Calc.: C 39.51, H 4.89, W 28.80. Found: C 38.67, H 4.74, W. 28.56%. $^{31}P\{^1H\}$-NMR (pentane): $\delta_P = 39.8$ ppm (s), $^1J_{PW} = 116$ Hz. ^1H-NMR ($CDCl_3$): $\delta_H(SiMe_3) = 0.28$ ppm (s); $\delta_H(^cHex) = 1.6$ ppm (mc). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(SiMe_3) = 0.3$ ppm (s); $\delta_C(^cHex) = 23.1$–36.6 ppm (m); $\delta_C(COO) = 174.7$ ppm (d), $^2J_{CP} = 47$ Hz; $\delta_C(CO_{ax}) = 197.4$ ppm (d), $^2J_{CWP} = 7$ Hz; $\delta_C(CO_{eq}) = 199.0$ ppm (d), $^2J_{CWP} = 22.5$ Hz. IR (pentane) ν_{CO}: 2072m, 1949ssh, 1942vs. IR (KBr) $\nu_{as,COO}$: 1681vs. EI-MS: $m/z = 638$ (12%) $[M^{+\bullet}]$.

4.7. Preparation of $(CO)_5MPRR'COOH$ (5)

A solution of 2–3 mmol of complex **4** in 20–25 ml of pentane was chromatographed, with pentane as eluent, on carefully dried silica gel (Merck, size: 0.063–0.2 mm) in a small column (40 × 15 mm) until the eluate was colourless. Subsequent elution with 50 ml of toluene gave an intense yellow fraction, which was evaporated under vacuum to leave **5** as a solid residue. Yield: 70%–80% (in case of **5g** 40%).

$(CO)_5CrPPh_2COOH$ (**5a**). Yellow solid; m.p. 79–81°C (dec.); $C_{18}H_{11}CrO_7P$ (422.3). Calc.: C 51.20, H 2.63, Cr 12.31. Found: C 51.32, H 2.56, Cr 12.16%. $^{31}P\{^1H\}$-NMR (ether): $\delta_P = 56.7$ ppm (s). ^1H-NMR ($CDCl_3$): $\delta_H(Ph) = 7.6$ ppm (mc); $\delta_H(OH) = 12.0$ ppm (s, b); $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(Ph) = 129.4$–133.7 ppm (m); $\delta_C(COO) = 182.1$ ppm (d), $^1J_{CP} = 45$ Hz; $\delta_C(CO_{eq}) = 216.1$ ppm (d), $^2J_{CCrP} = 12.5$ Hz; $\delta_C(CO_{ax}) = 221.1$ ppm (d), $^1J_{CCrP} = 5.5$ Hz. IR (THF) ν_{CO}: 2068m, 1970msh, 1947vs. IR (KBr) $\nu_{as,COO}$: 1669vs. EI-MS: $m/z = 422$ (3%) $[M^{+\bullet}]$.

$(CO)_5CrP^cHex_2COOH$ (**5b**). Light yellow solid; m.p. 137–140°C (dec.); $C_{18}H_{23}CrO_7P$ (434.3). Calc.: C 49.78, H. 5.34, Cr 11.97. Found: C 49.59, H 5.23, Cr 11.90%. $^{31}P\{^1H\}$-NMR (ether): $\delta_P = 70.5$ ppm (s). ^1H-NMR ($CDCl_3$): $\delta_H(^cHex) = 1.6$ ppm (mc); $\delta_H(OH) = 9.4$ ppm (s, b). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(^cHex) = 26.4$–36.9 ppm (m); $\delta_C(COO) = 180.3$ ppm (d), $^1J_{CP} = 30.5$ Hz; $\delta_C(CO_{eq}) = 217.3$ ppm (d), $^2J_{CCrP} = 12.5$ Hz; $\delta_C(CO_{ax}) = 221.5$ ppm (d), $^2J_{CCrP} = 5$ Hz. IR (THF) ν_{CO}: 2063m, 1987m, 1942vs. IR (KBr) $\nu_{as,COO}$: 1668vs. EI-MS: $m/z = 434$ (3%) $[M^{+\bullet}]$.

$(CO)_5CrP^iPr_2COOH$ (**5c**). Yellow solid; m.p. 78–80°C (dec.); $C_{12}H_{15}CrO_7P$ (354.2). Calc.: C 40.69, H 4.27, Cr 14.67. Found: C 40.63, H 4.30, Cr 14.76%. $^{31}P\{^1H\}$-NMR (toluene): $\delta_P = 87.1$ ppm (s). ^1H-NMR ($CDCl_3$): $\delta_H(CH_3) = 1.32$ ppm (dd), $^3J_{HCCH} = 7$ Hz, $^3J_{HCCP} = 16$ Hz; $\delta_H(CH) = 2.49$ ppm (mc); $\delta_H(OH) = 10.9$ ppm (s, b). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(CH_3) = 17.8$ ppm (d), $^2J_{CCP} = 3$ Hz; $\delta_C(CH) = 26.9$ ppm (d), $^1J_{CP} = 17$ Hz; $\delta_C(COO) = 181.2$ ppm (d), $^1J_{CP} = 31$ Hz; $\delta_C(CO_{eq}) = 216.4$ ppm (d), $^2J_{CCrP} = 12$ Hz; $\delta_C(CO_{ax}) = 220.9$ ppm (d), $^2J_{CCrP} = 5$ Hz. IR (pentane) ν_{CO}: 2062m, 1985msh, 1938vs. IR (KBr) $\nu_{as,COO}$: 1663vs. EI-MS: $m/z = 354$ (11%) $[M^{+\bullet}]$.

$(CO)_5CrPEt_2COOH$ (**5d**). Light yellow solid; m.p. 85–86°C (dec.); $C_{10}H_{11}CrO_7P$ (326.2). Calc.: C 36.82, H 3.40, Cr 15.94. Found: C 36.90, H 3.40, Cr 15.79%. $^{31}P\{^1H\}$-NMR (toluene): $\delta_P = 59.1$ ppm (s). ^1H-NMR ($CDCl_3$): $\delta_H(CH_3) = 1.24$ ppm (dt), $^3J_{HCCH} = 7.5$ Hz, $^3J_{HCCP} = 17$ Hz; $\delta_H(CH_2) = 2.1$ ppm (dq), $^3J_{HCCH} = 7.5$ Hz, $^2J_{HCP} = 33$ Hz; $\delta_H(OH) = 11.3$ ppm (s, b). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(CH_3) = 8.3$ ppm (d), $^2J_{CCP} = 3$ Hz; $\delta_C(CH_2) = 19.4$ ppm (d), $^1J_{CP} = 22$ Hz; $\delta_C(COO) = 181.9$ ppm (d), $^1J_{CP} = 42$ Hz; $\delta_C(CO_{eq}) = 216.2$ ppm (d), $^2J_{CCrP} = 12$ Hz; $\delta_C(CO_{ax}) = 220.7$ ppm (d), $^2J_{CCrP} = 5$ Hz. IR (THF) ν_{CO}: 2063m, 1985wsh, 1940vs. IR (KBr) $\nu_{as,COO}$: 1664vs. EI-MS: $m/z = 326$ (15%) $[M^{+\bullet}]$.

$(CO)_5CrP^tBuHCOOH$ (**5e**). Light yellow solid; m.p. 107–108°C (dec.); $C_{10}H_{11}CrO_7P$ (326.2). Calc.: C 36.82, H 3.40, Cr 15.94. Found: C 36.34, H 3.44, Cr 15.48%. ^{31}P-NMR (toluene): $\delta_P = 56.9$ ppm (qd), $^1J_{PH} = 340$ Hz, $^3J_{PCCH} = 18$ Hz. ^1H-NMR ($CDCl_3$): $\delta_H(CH_3) = 1.40$ ppm (d), $^3J_{HCCP} = 17$ Hz; $\delta_H(HP) = 5.00$ ppm (d), $^1J_{HP} = 338$ Hz; $\delta_H(OH) = 10.3$ ppm (s, b). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(CH_3) = 28.8$ ppm (d), $^2J_{CCP} = 5$ Hz; $\delta_C(CMe_3) = 33.7$ ppm (d), $^1J_{CP} = 19.5$ Hz; $\delta_C(COO) = 181.3$ ppm (d), $^1J_{CP} = 40$ Hz; $\delta_C(CO_{eq}) = 216.0$ ppm (d), $^2J_{CCrP} = 12$ Hz; $\delta_C(CO_{ax}) = 220.5$ ppm (d), $^2J_{CCrP} = 5.5$ Hz. IR (THF): ν_{CO}: 2065m, 1980msh, 1943vs. IR (KBr) $\nu_{as,COO}$: 1671vs. EI-MS: $m/z = 326$ (20%) $[M^{+\bullet}]$.

$(CO)_5CrPMeHCOOH$ (**5f**). Light yellow solid; m.p. 95–96°C (dec.); $C_7H_5CrO_7P$ (284.1). Calc.: C 29.59, H 1.77, Cr 18.30. Found: C 29.59, H 1.82, Cr 18.45%. ^{31}P-NMR (ether): $\delta_P = -5.8$ ppm (d), $^1J_{PH} = 342$ Hz. ^1H-NMR ($CDCl_3$): $\delta_H(CH_3) = 1.80$ ppm (dd), $^2J_{HCP} = 8$ Hz, $^3J_{HCPH} = 6.5$ Hz; $\delta_H(HP) = 5.44$ ppm (qd), $^1J_{HP} = 346$ Hz, $^3J_{HPCH} = 6.5$ Hz; $\delta_H(OH) = 10.7$ ppm (s, b). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta_C(CH_3) = 9.1$ ppm (d), $^1J_{CP} = 27$ Hz; $\delta_C(COO) = 181.4$ ppm (d), $^1J_{CP} = 51$ Hz; $\delta_C(CO_{eq}) = 215.5$ ppm (d), $^2J_{CCrP} = 13$ Hz; $\delta_C(CO_{ax}) =$

220.3 ppm (d), $^2J_{\mathrm{CCrP}} = 6$ Hz. IR (pentane): ν_{CO}: 2069w, 1987wsh, 1954vs. IR (KBr) $\nu_{\mathrm{as,COO}}$: 1671vs. EI-MS: $m/z = 284$ (28%) [$\mathrm{M}^{+\bullet}$].

$(\mathrm{CO})_5\mathrm{CrPH_2COOH}$ (**5g**). Light yellow solid; m.p. 99–102°C (dec.); $\mathrm{C_6H_3CrO_7P}$ (270.1). Calc.: C 26.68, H 1.12, Cr 19.25. Found: C 26.50, H 1.18, Cr 19.51%. $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR: $\delta_\mathrm{P} = -45.2$ ppm (t), $^1J_{\mathrm{PH}} = 351$ Hz in toluene (-37.7 ppm (t), 342 Hz in $\mathrm{CDCl_3}$). ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta_\mathrm{H}(\mathrm{H_2P}) = 5.18$ ppm (d), $^1J_{\mathrm{HP}} = 345$ Hz; $\delta_\mathrm{H}(\mathrm{OH}) = 9.1$ ppm (s, b). IR (benzene) ν_{CO}: 2064m, 1980w, 1947vs. IR (KBr) $\nu_{\mathrm{as,COO}}$: 1665vs. EI-MS: $m/z = 270$ (17%) [$\mathrm{M}^{+\bullet}$].

$(\mathrm{CO})_5\mathrm{WP^cHex_2COOH}$ (**5h**). Beige solid; m.p. 159–160°C (dec.); $\mathrm{C_{18}H_{23}O_7PW}$ (566.2). Calc.: C 38.19, H 4.09, W. 32.47. Found: C 38.65, H 4.37, W. 32.57%. $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR (THF): $\delta_\mathrm{P} = 37.2$ ppm (s), $^1J_{\mathrm{PW}} = 115$ Hz. ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta_\mathrm{H}(^c\mathrm{Hex}) = 1.6$ ppm (mc); $\delta_\mathrm{H}(\mathrm{OH}) = 9.6$ ppm (s, b). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($\mathrm{CDCl_3}$): $\delta_\mathrm{C}(^c\mathrm{Hex}) = 26.6$–$37.1$ ppm (m); $\delta_\mathrm{C}(\mathrm{COO}) = 180.2$ ppm (d), $^1J_{\mathrm{CP}} = 43$ Hz; $\delta_\mathrm{C}(\mathrm{CO_{ax}}) = 197.2$ ppm (d), $^2J_{\mathrm{CWP}} = 7$ Hz; $\delta_\mathrm{C}(\mathrm{CO_{eq}}) = 198.4$ ppm (d), $^2J_{\mathrm{CWP}} = 22$ Hz. IR (THF): ν_{CO}: 2069m, 1980msh, 1937vs. IR (KBr) $\nu_{\mathrm{as,COO}}$: 1668vs. EI-MS: $m/z = 566$ (14%) [$\mathrm{M}^{+\bullet}$].

4.8. Preparation of $(CO)_5MPRR'Me$ (6)

Methyl iodide (2.8 g, 0.02 mol) was added to 5 mmol of complex **3** in 50 ml of THF at -30°C. The mixture was allowed to warm to room temperature and stirred for 12 h. After evaporation of the solvent the residue was extracted with in 30 ml of pentane and the LiCl filtered off from the extract. The solutions were subjected to column chromatography on silica gel with pentane as eluent. Yield: 60%–70%.

$(\mathrm{CO})_5\mathrm{CrPPh_2Me}$ (**6a**). Light yellow solid; m.p. 84–85°C (Lit. [18] 75°C, Lit. [19]: 90–92°C). $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR (THF): $\delta_\mathrm{P} = 34.1$ ppm (s) (Lit. [15] -104 ppm (ref. $\mathrm{P(OMe)_3}$) corresp. to 36 ppm (ref. 85% $\mathrm{H_3PO_4}$)). ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta_\mathrm{H}(\mathrm{CH_3}) = 2.05$ ppm (d), $^2J_{\mathrm{HCP}} = 6.5$ Hz; $\delta_\mathrm{H}(\mathrm{Ph}) = 7.4$ ppm (mc). IR (THF) ν_{CO}: 2065m, 1949msh, 1937vs. EI-MS: $m/z = 392$ (8%) [$\mathrm{M}^{+\bullet}$].

$(\mathrm{CO})_5\mathrm{CrPEt_2Me}$ (**6d**). Yellow oil; $\mathrm{C_{10}H_{13}CrO_5P}$ (296.2). Calc.: C 40.55, H 4.42, Cr 17.55. Found: C 40.27, H 4.59, Cr 17.02%. $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR (pentane): $\delta_\mathrm{P} = 28.6$ ppm (s). ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta_\mathrm{H}(CH_3\mathrm{P}) = 1.39$ ppm (d), $^2J_{\mathrm{HCP}} = 7$ Hz; $\delta_\mathrm{H}(CH_3\mathrm{CH_2}) = 1.16$ ppm (dt), $^3J_{\mathrm{HCCH}} = 7.5$ Hz, $^3J_{\mathrm{HCCP}} = 16$ Hz; $\delta_\mathrm{H}(\mathrm{CH_2}) = 1.9$ ppm (mc). IR (pentane) ν_{CO}: 2064m, 1950msh, 1942vs. EI-MS: $m/z = 296$ (15%) [$\mathrm{M}^{+\bullet}$].

$(\mathrm{CO})_5\mathrm{WP^cHex_2Me}$ (**6h**). Beige solid; m.p. 90–92°C; $\mathrm{C_{18}H_{25}O_5PW}$ (536.2). Calc.: C 40.31, H 4.70, W. 34.29. Found: C 40.03, H 4.66, W 34.17%. $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR (THF): $\delta_\mathrm{P} = 7.1$ ppm (s). ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta_\mathrm{H}(\mathrm{CH_3}) = 1.5$ ppm (d), $^2J_{\mathrm{HCP}} = 7$ Hz; $\delta_\mathrm{H}(^c\mathrm{Hex}) = 1.6$ ppm (mc). IR (pentane) ν_{CO}: 2068m, 1943ssh, 1938vs. EI-MS: $m/z = 536$ (50%) [$\mathrm{M}^{+\bullet}$].

4.9. Preparation of $(CO)_5MPRR'COOMe$ (7)

Dimethyl sulphate (0.63 g, 5 mmol) was added to 5 mmol of complex **3** in 50 ml of THF at -30°C. The mixture was warmed to room temperature and stirred for 16 h. The solvent and the excess of dimethyl sulfate were removed by warming under vacuum. The oily residue was dissolved in pentane and the $\mathrm{Li_2SO_4}$ was filtered off. The complexes **7** were purified by column chromatography (silica gel, pentane). Yield: 70%–80%.

$(\mathrm{CO})_5\mathrm{CrPEt_2COOMe}$ (**7d**). Light yellow oil; $\mathrm{C_{11}H_{13}CrO_7P}$ (340.2). Calc.: C 38.84, H 3.85, Cr 15.28. Found: C 38.60, H 4.07, Cr 15.45%. $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR (pentane): $\delta_\mathrm{P} = 57.0$ ppm (s). ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta_\mathrm{H}(\mathrm{CH_3}) = 1.20$ ppm (dt), $^3J_{\mathrm{HCCH}} = 7.5$ Hz, $^3J_{\mathrm{HCCP}} = 16.5$ Hz; $\delta_\mathrm{H}(\mathrm{CH_2}) = 2.1$ ppm (mc); $\delta_\mathrm{H}(\mathrm{CH_3O}) = 3.85$ ppm (s). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($\mathrm{CDCl_3}$): $\delta_\mathrm{C}(\mathrm{CH_3}) = 9.0$ ppm (d), $^2J_{\mathrm{CCP}} = 3$ Hz; $\delta_\mathrm{C}(\mathrm{CH_2}) = 20.3$ ppm (d), $^1J_{\mathrm{CP}} = 22$ Hz; $\delta_\mathrm{C}(\mathrm{OCH_3}) = 53.0$ ppm (s); $\delta_\mathrm{C}(\mathrm{COO}) = 178.0$ ppm (d), $^1J_{\mathrm{CP}} = 52$ Hz; $\delta_\mathrm{C}(\mathrm{CO_{eq}}) = 216.7$ ppm (d), $^2J_{\mathrm{CCrP}} = 13$ Hz; $\delta_\mathrm{C}(\mathrm{CO_{ax}}) = 220.9$ ppm (d), $^2J_{\mathrm{CCrP}} = 7$ Hz. IR (pentane) ν_{CO}: 2070s, 1950vs, 1923msh. IR (film) $\nu_{\mathrm{as,COO}}$: 1708vs. EI-MS: $m/z = 340$ (22%) [$\mathrm{M}^{+\bullet}$].

$(\mathrm{CO})_5\mathrm{WP^cHex_2COOMe}$ (**7h**). Beige solid; m.p. 55–58°C; $\mathrm{C_{19}H_{25}O_7PW}$ (580.2). Calc.: C 39.33, H 4.34, W 31.67. Found: C 39.04, H 4.40, W. 31.60%. $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR (THF): $\delta_\mathrm{P} = 40.8$ ppm (s). ^{1}H-NMR ($\mathrm{CDCl_3}$): $\delta_\mathrm{H}(^c\mathrm{Hex}) = 1.6$ ppm (mc); $\delta_\mathrm{H}(\mathrm{CH_3O}) = 3.84$ ppm (s). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($\mathrm{CDCl_3}$): $\delta_\mathrm{C}(^c\mathrm{Hex}) = 25.9$–$36.4$ ppm (m); $\delta_\mathrm{C}(\mathrm{OCH_3}) = 52.5$ ppm (s); $\delta_\mathrm{C}(\mathrm{COO}) = 174.0$ ppm (d), $^1J_{\mathrm{CP}} = 49$ Hz; $\delta_\mathrm{C}(\mathrm{CO_{ax}}) = 196.8$ ppm (d), $^2J_{\mathrm{CWP}} = 8$ Hz; $\delta_\mathrm{C}(\mathrm{CO_{eq}}) = 198.3$ ppm (d), $^2J_{\mathrm{CWP}} = 23$ Hz. IR (pentane) ν_{CO}: 2067m, 1980msh, 1936vs. IR (KBr) $\nu_{\mathrm{as,COO}}$: 1706vs. EI-MS: $m/z = 580$ (6%) [$\mathrm{M}^{+\bullet}$].

Acknowledgments

We thank the Fonds der chemischen Industrie for support of this work and Bayer and Hoechst for gifts of chemicals.

Literature

1 K. Diemert, T. Hahn and W. Kuchen, *Phosphorus Sulfur Silicon Relat. Elem., 60* (1991) 287.

2 K. Diemert, T. Hahn, W. Kuchen and P. Tommes, *Phosphorus Sulfur Silicon Relat. Elem., 83* (1993) 65.

3 P. Ruelle, U.W. Kesselring and Ho Nam-Tran, *J. Mol. Struct. (Theochem) 124* (1985) 41.

4 F. Nief, F. Mercier and F. Mathey, *J. Organomet. Chem., 328* (1987) 349.

5 H. Schäfer and W. Leske, *Z. anorg. allg. Chem., 552* (1987) 50.

6 E.O. Fischer, E. Louis, W. Bathelt and J. Müller, *Chem. Ber., 102* (1969) 2547.

7 E. Moser, E.O. Fischer, W. Bathelt, W. Gretner, L. Knaus and E. Louis, *J. Organomet. Chem., 19* (1969) 377.

8 M. Green, A. Taunton-Rigby and F.G.A. Stone, *J. Chem. Soc. (A)*, (1969) 1875.

9 P.M. Treichel, W.K. Dean and W.M. Douglas, *Inorg. Chem., 11* (1972) 1609.

10 P.M. Treichel, W.K. Dean and W.M. Douglas, *Inorg. Chem., 11* (1972) 1615.

11 P.M. Treichel, W.K. Dean and W.M. Douglas, *J. Organomet. Chem., 42* (1972) 145.

12 T. Hahn, Dissertation, Düsseldorf 1992.

13 W. Strohmeier and F.J. Müller, *Chem. Ber., 102* (1969) 3608.

14 J.G. Smith and D.T. Thompson, *J. Chem. Soc. (A)*, (1967) 1694.

15 E. Vincent, L. Verdonck and G.P. van der Kelen, *Spectrochim. Acta, 36A* (1980) 699.

16 P. Peringer and D. Obendorf, *J. Organomet. Chem., 320* (1987) 47.

17 R. Lal De and H. Vahrenkamp, *Z. Naturforsch., 40b* (1985) 1250.

18 E. Vincent, L. Verdonck and G.P. van der Kelen, *J. Mol. Struc., 69* (1980) 33.

19 S.O. Grim, D.A. Wheatland and W. McFarlane, *J. Am. Chem. Soc., 89* (1967) 5573.