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Improved synthesis of $KHCr(CO)_5$ and comparative coordination chemistry from $KHCr(CO)_5$ and $KHFe(CO)_4$[1]

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Abstract

A practical procedure for the selective preparation of $KHCr(CO)_5$ is described. The use of a potassium cation in the coordination chemistry of the $[HFe(CO)_4]^-$ anion is completed and extended to the coordination chemistry of the $[HCr(CO)_5]^-$ anion: CO-substitution by phosphites, phosphines and phosphinites, and H-abstraction by aminophosphines. Most of the observed differences in reactivity between $KHFe(CO)_4$ and $KHCr(CO)_5$ can be rationalized by the stronger acidity of $KHFe(CO)_4$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Hydridocarbonylferrates; Hydridocarbonylchromates; CO-substitution; P-ligands

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1. Introduction

The relative reducing power of hydridocarbonylmetallates has been thoroughly studied versus both the transition metal (especially of Groups 6 and 8) and the nature and the number of σ-donor ligands [1]. Darensbourg et al. showed that CO-replacement by phosphane ligands enhances the hydridic character (two-electron transfer) more so than the single electron transfer (SET) ability of the $[M-H]^-$ unit [2]. With the aim of achieving asymmetric reduction of ketones by a 'chiral zwitterionic control' strategy, we recently disclosed the synthesis of chiral zwitterionic hydridotricarbonylferrate complexes by simultaneous CO-substitution and K^+-metathesis at $KHFe(CO)_4$ with chiral phosphinite ammonium ligands [3]. The poor reducing ability of these iron complexes prompted us to extend the strategy to the chromium series ([3]b): indeed, chromium hydrides derived from $[HCr(CO)_5]^-$ are generally better reducing agents than their iron counterparts derived from $[HFe(CO)_4]^-$ [2]. We were however surprised to find that, contrary to $[HFe(CO)_4]^-$, the $[HCr(CO)_5]^-$ anion was not readily available. We herein report an efficient synthesis of $KHCr(CO)_5$ and a general comparison of its coordination chemistry with the well-studied coordination chemistry of $KHFe(CO)_4$ [4].

2. Improved preparation of $KHCr(CO)_5$ 1b

Although ammonium salts of the $[HCr(CO)_5]^-$ anion can be selectively prepared by a cumbersome three-step procedure from $Cr(CO)_6$ [5], or under phase-transfer conditions (KOH/Et_4NHSO_4) [6], the coordination chemistry of $[HCr(CO)_5]^-$ has been severely limited by the lack of a routine method to prepare it. Alkali metal salts of $[HCr(CO)_5]^-$ were obtained by cation exchange from ammonium salts ([7]a). By contrast, $KHFe(CO)_4$ **1a** is easily prepared in a 90–95% yield by mixing $Fe(CO)_5$ with KOH in methanol or ethanol [4]. This difference holds to the fact that the dinuclear hydride $[HCr_2(CO)_{10}]^-$ acts as a thermodynamic sink for

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[1] Part of the thesis of P. Leglaye.

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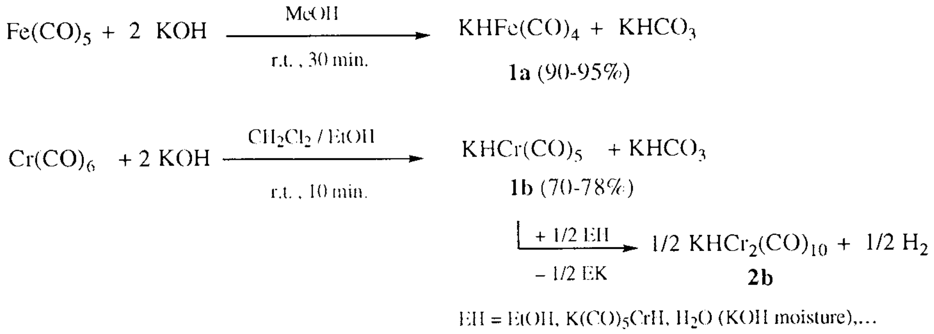


Scheme 1. Synthesis of mononuclear potassium hydridocarbonylmetallates.

$[HCr(CO)_5]^-$ [8], while $[HFe_2(CO)_8]^-$ does not for $[HFe(CO)_4]^-$ [9]. Nonetheless, the sodium salt $NaHCr(CO)_5$ could be tediously prepared in a 50% yield by protonation of $Na_2Cr(CO)_5$, itself generated by Na/naphtalene reduction of $Cr(CO)_5$(piperidine) [5,10], and THF solutions of the potassium salt in the presence of cryptands have been used [11]. Although the reaction of hydroxide ions with $Cr(CO)_6$ is very slow and non selective in an aqueous alcohol as solvent [12]a), a simple procedure for preparing the potassium salt **1b** has been described provided that THF is used as a co-solvent ([12]b). However, the final ratio between **1b** and $K[HCr_2(CO)_{10}]$ **2b** appears quite variable and no rationale accounts for the need of five equivalents of KOH in a THF–H_2O mixture at 55°C, or seven equivalents of KOH in a MeOH–H_2O–THF mixture at 46–48°C ([12]b).

We observed that when an ethanol solution of slightly less than two equivalents of KOH is added to a dichloromethane solution of $Cr(CO)_6$, **1b** is repeatedly isolated in a 70–78% yield. Some amount of the dinuclear hydride **2b** also forms which is separated by simple filtration (see Section 5). This corresponds to the stoichiometry of Scheme 1, and as for the preparation of $KHFe(CO)_4$, no excess KOH is needed. The selectivity of the synthesis is measured from the ^{1}H-NMR spectrum (**1b**: $\delta_{CrH} = -7.05$ ppm. **2b**: $\delta_{CrH} = -19.56$ ppm). However, **1b** is more sensitive than **1a** to protic sources: the unstable protonated species $H_2Cr(CO)_5$ looses H_2 and the unsaturated '$Cr(CO)_5$' moiety is scavenged by another molecule of **1b** to give the dinuclear hydride **2b** ([8]a).

3. Coordination chemistry of $KHFe(CO)_4$ and $KHCr(CO)_5$ with phosphanes

By analogy with the synthetically useful CO-substitution process at $KHFe(CO)_4$ by phosphane ligands [4], the reactivity of $KHCr(CO)_5$ with phosphites, phosphines, phosphinites and aminophosphines has been considered (Scheme 2): to the best of our knowledge, the only reported phosphane-substituted derivatives of **1b** are the salts of $[HCr(CO)_4\{P(OMe)_3\}]^-$ and none of them was prepared by ligand exchange at $[HCr(CO)_5]^-$ [1].

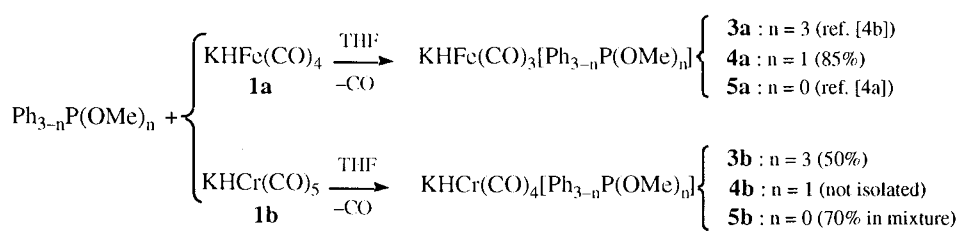
3.1. Phosphite ligands

It has been mentioned that CO-substitution on ammonium salts of $[HM(CO)_5]^-$ could not be an efficient route to phosphine or phosphite derivatives (M = Group 6 metal) [13]. The complex $[PPN]^+[cis\text{-}HCr(CO)_4\{P(OMe)_3\}]^-$ has thus been prepared by naphtalene/sodium reduction of $Cr(CO)_4[P(OMe)_3]$-(amine) and subsequent protonation with methanol ([7]a, [13,14]). Interestingly, we have now found that $P(OMe)_3$ does react with the potassium salt **1b** in THF to give K^+, $[cis\text{-}HCr(CO)_4\{P(OMe)_3\}]^-$ **3b** in a 50% yield. As in the case of the iron analogue K^+, $[trans\text{-}HFe(CO)_3[P(OMe)_3]]^-$ **3a**, the weak σ-donor versus π-acceptor character of trimethyl phosphite does not sufficiently enhance the basicity of the chromate anion of **3b** to trigger quantitative deprotonation of $[HCr(CO)_5]^-$ [15].

3.2. Phosphine ligands

In the iron series, heating of **1a** is required for CO substitution by bulky phosphines such as PPh_3, but the high basicity of the intermediate triphenylphosphine hydride complex **5a** leads to the neutral complex *trans*-$Fe(CO)_3(PPh_3)_2$ ([4]a). $K_2Fe(CO)_4$ is also produced when the reaction is conducted in THF.

Under similar conditions (two equivalents of PPh_3, refluxing THF, 64 h), a slow reaction of $KHCr(CO)_5$ **1b** is evidenced by NMR monitoring. In the ^{1}H-NMR spectrum ([D_8]THF), the doublet of a hydride assigned to $KHCr(CO)_4(PPh_3)$ **5b** is observed at $\delta = -6.25$ ppm ($^2J_{PH} = 35.1$ Hz). In the ^{31}P-NMR spectrum, in addition to the major signal of **5b** (70%, $\delta = 81.3$ ppm), a minor signal (30%, $\delta = 77.8$ ppm) can be assigned, by analogy with the iron series, to the neutral complex



Scheme 2. CO-substitution by phosphines, phosphinites or phosphites at hydrido-carbonylmetallates.

trans-$Cr(CO)_4(PPh_3)_2$. This structure is also supported by a triplet for the four CO ligands in the ^{13}C-NMR spectrum ($\delta = 243.31$ ppm, $^2J_{PC} = 13.7$ Hz). The concommitant formation of an equimolar amount of $K_2Cr(CO)_5$ is indicated by the presence of a white air-sensitive precipitate in the final reaction medium. However, contrary to $KHFe(CO)_4$, $KHCr(CO)_5$ is not acidic enough to undergo complete deprotonation by $KHCr(CO)_4(PPh_3)$ **5b**.

3.3. Phosphinite ligands

Although PPh_3 does not selectively displace a single CO ligand from $KHFe(CO)_4$ **1a** (vide supra), replacing one of the phenyl rings at the phosphorus atom of PPh_3 by one methoxy group sufficiently lowers the σ-donor ability of the ligand to allow the new complex $KHFe(CO)_3[PPh_2(OMe)]$ **4a** to be stable in THF solution in the presence of $KHFe(CO)_4$, and finally isolated in an 85% yield. The *trans* stereochemistry is assigned on the basis of the low value of the $^2J_{PH}$ coupling constant (4.3 Hz, CD_3CN at 20°C), which is close to values reported for analogous *trans*-complexes with PPh_3 and $P(OMe)_3$ ligands (2.4 and 3.7 Hz, respectively, CD_3CN at 26°C) and very different from the value reported for the *cis* isomer of a salt of the $[HFe(CO)_3\{P(OPh)_3\}]^-$ anion (41.6 Hz, CD_3CN at ambient temperature) ([7]b).

In methanol, $KHFe(CO)_4$ reacts with two equivalents of $Ph_2P(OMe)$ much less selectively, beside the monosubstituted anionic complex **4a**, the disubstituted complexes $H_2Fe(CO)_2[PPh_2(OMe)]_2$ **7a** and $KHFe(CO)_2[PPh_2(OMe)]_2$ **8a** are identified. According to our previous studies on analogous phosphine and phosphite complexes [4], the bis(phosphinite) complex **7a** could form from **4a** via an elusive neutral monophosphinite dihydride intermediate $H_2Fe(CO)_3[PPh_2(OMe)]$ which would undergo a fast CO-substitution by a second equivalent of phosphinite. The conjugated base **8a**, resulting from a deprotonation of **7a** by MeOK, is also observed (Scheme 3) [16]. However, when the methanol solution is buffered with $KHCO_3$, the basic complex **8a** is no longer formed: the less basic complex **4a** is still present, and **7a** is produced in a 25% yield only, along with the long-known complex **6a** (7% yield) [17], further characterized by ^{31}P- and ^{13}C-NMR (see Section 5).

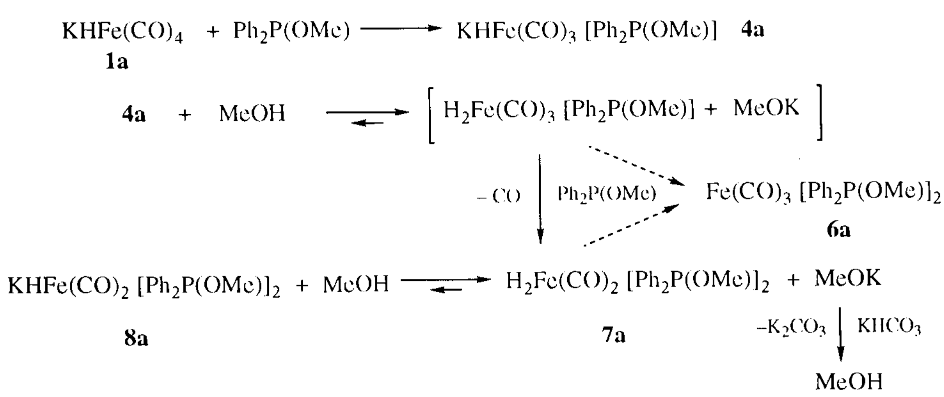
The *cis*-$(CO)_2$, *trans*-P_2 geometry of **7a** is assigned on the basis of solution IR and NMR spectra. The IR spectrum of **7a** in pentane exhibits two strong absorption bands of nearly equal intensity with a frequency difference of 39 cm^{-1}, thus implying a *cis*-$Fe(CO)_2$ arrangement [18]. The NMR data are in accordance with previous NMR studies on related diphosphine and diphosphite complexes [4]: the $^{31}P\{^1H\}$ and $^{13}C\{^1H, ^{31}P\}$ (carbonyl region) spectra give sharp singlet signals at 176.3 and 213.7 ppm, respectively. Therefore the phosphorus atoms are magnetically equivalent, as are the two carbon atoms of the carbonyl ligands. Furthermore, the ^{1}H (hydride region) and ^{31}P-NMR spectra exhibit well-resolved 1:2:1 triplets with a coupling constant $^2J_{PH} = 57.7$ Hz (CD_3CN), in agreement with a *cis*-H–P arrangement of two equivalent hydridic hydrogens with two equivalent phosphorus atoms ([7]b).

The *cis*-$(CO)_2$, *trans*-P_2 geometry of **7a** is confirmed, in the solid state, by a X-ray diffraction study of a monocrystal [19]. The octahedral bonding geometry is mainly characterized by the OC–Fe–CO angle [95(1)°] and a very bent P–Fe–P angle [151.6(3)°] (Fig. 1). However, the hydride ligands could not be located, and the structure is not discussed further owing to the poor refinement ($R = 0.17$) because of the poor quality of the crystal. Several attempts to improve the quality of the structure by collecting data at low temperature failed because of a phase transition occuring just below −15°C.

In the chromium series, $KHCr(CO)_5$ promotes the decomposition of $Ph_2P(OMe)$, leading to more than 20 unidentified ^{31}P-NMR signals [20]. An interpretation of the failure to isolate **4b** could reside in the higher nucleophilicity of the hydride brought by the stronger σ-donor ability of $Ph_2P(OMe)$ with respect to that of $P(OMe)_3$: unlike $[HFe(CO)_4]^-$, $[HCr(CO)_5]^-$ is not compatible with the lability of the Me–O–P moiety.

3.4. Tris(amino)phosphine ligands

The reaction of $KHFe(CO)_4$ with $P(NMe_2)_3$ does not proceed by CO-substitution at the iron atom: instead a formal Me_2N-substitution at the phosphorus atom takes place according to the stoichiometry depicted in Scheme 4 where the Collman anion $[Fe(CO)_4]^{2-}$ and the neutral complex $(CO)_4Fe[PH(NMe_2)_2]$ **9a** are formed [21,22].



Scheme 3. Reaction of $Ph_2P(OMe)$ with $KHFe(CO)_4$ in methanol.

The analogous reaction in the chromium series does not occur. However, if tris(dimethylamino)phosphine is first treated with a stoichiometric amount of acetic acid, the new neutral chromium complex $(CO)_5Cr[PH(NMe_2)_2]$ **9b** (^{31}P-NMR: $\delta = 132.5$ ppm; ^{1}H-NMR: $\delta = 7.70$ ppm; $^{1}J_{PH} = 315$ Hz) is formed and isolated in a 70% yield (Scheme 4). As proposed earlier [21], cleavage of the P–N bond proceeds via a protonation step $P(NMe_2)_3 + H^+ \rightarrow Me_2HN^+{-}P(NMe_2)_2$ which formally generates a $^+P(NMe_2)_2$ equivalent reacting further with anionic hydrides to give compounds **9a** and **9b**. The need of an auxiliary proton source in the case of chromium shows that given that the reference base $P(NMe_2)_3$, $KHCr(CO)_5$ is less acidic than $KHFe(CO)_4$, in agreement with the general trend stated for neutral transition metal hydrides, namely 'thermodynamic acidity and kinetic acidity generally increase from left to right across a transition series' [23].

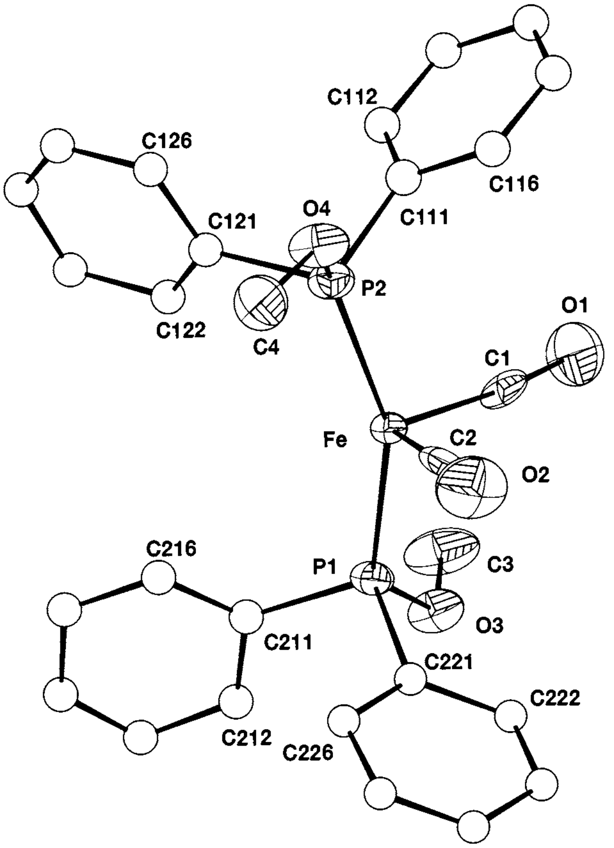


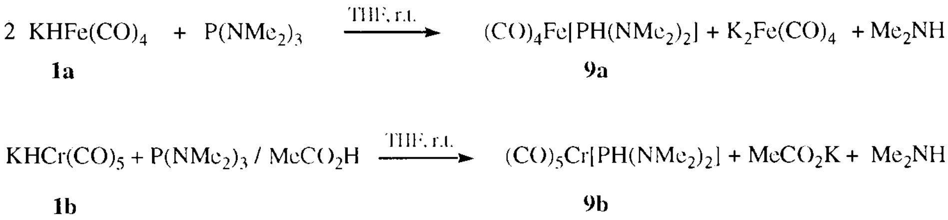
Fig. 1. CAMERON view of the X-ray crystal structure of the dihydride complex **7a** ($P\bar{1}$, $R = 0.17$), with thermal ellipsoids at 50% probability level. The hydrogen atoms were not located and the carbon atoms of the phenyl rings were isotropically refined.

4. Conclusion

The above results, driven by the search for an analogy with the coordination chemistry of $KHFe(CO)_4$, show that $KHCr(CO)_5$ is a versatile precursor for a coordination chemistry involving phosphanes. Although the iron and chromium hydrides behave similarly from a qualitative viewpoint, observed differences are accounted for by a lower acidity of $KHCr(CO)_5$ as compared with that of $KHFe(CO)_4$. Although acidity and hydridic character are not opposite properties, this fact is parallel to the well known increase of the hydridic character of transition metal hydrides going from the right to the left of periodic table [23,24]: beyond their relative reducing power toward ketones, this trend is more fundamentally illustrated by the established increasing 'dihydride' versus dihydrogen character of the congugated acids, $H_2Fe(CO)_4$ and $H_2Cr(CO)_5$ [25,26].

5. Experimental

All experiments were performed under an argon atmosphere using standard Schlenk techniques. THF and diethyl ether were distilled over Na/benzophenone before use. Commercial synthesis grade pentane, dichloromethane, methanol and ethanol were degassed by bubbling argon before use. Potassium hydroxide (Technical 86%, Prolabo), trimethyl phosphite



Scheme 4. Reaction of hydridocarbonylmetallates with $P(NMe_2)_3$ in the presence of a Brønstedt acid: $KHFe(CO)_4$ itself in the case of iron, acetic acid in the case of chromium.

(Aldrich), tris(dimethylamino)phosphine (Fluka), triphenylphosphine (Janssen), hexacarbonylchromium (Strem), pentacarbonyliron (Fluka) were commercially available. A sample of $Ph_2P(OMe)$ was purchased from Aldrich or prepared from distilled $ClPPh_2$ (Aldrich) and methanol in diethyl ether. A Sample of $KHFe(CO)_4$ was prepared as previously described [4]. Elemental analyses were performed on Perkin Elmer 2400 apparatus. IR spectra were recorded on a Perkin-Elmer 1725X FT-IR spectrometer using CaF_2 windows. NMR spectra were recorded on a Brucker AC 200 spectrometer at 200 for ^1H, 81 for ^{31}P and 50 MHz for ^{13}C, with positive chemical shifts at low field expressed in ppm by internal reference to TMS for ^1H and ^{13}C and by external reference to 85% H_3PO_4 in D_2O for ^{31}P.

5.1. Potassium hydridopentacarbonylchromate, $KHCr(CO)_5$ **1b**

A solution of KOH (0.290 g, 4.55 mmol) in 7.5 ml of absolute ethanol was added to 20 ml of a CH_2Cl_2 solution of $Cr(CO)_6$ (0.500 g, 2.27 mmol). After stirring for 10 min the solvent was evaporated to dryness. The yellow solid residue was treated with 10 ml of THF and evaporated to dryness: this procedure was repeated twice in order to eliminate any trace of ethanol and dichloromethane. The solid was finally extracted with 20 ml of THF and $KHCO_3$ was removed by filtration. The solvent was then evaporated to give a yellow solid (0.390 g, 1.68 mmol, 75% yield). Elemental analysis for C_5HCrKO_5 (232.2): calc.%: C 25.87, H 0.43; found%: C 25.79, H 0.32. IR (THF): $\nu = 2018$ (m), 1883 (s), 1852 (sh) cm^{-1}. ^1H-NMR (CD_3CN): $\delta = -7.05$ (CrH). $^{13}C\{^1H\}$-NMR (CD_3CN): $\delta = 229.06$ ($Cr(CO)_5$).

5.2. Potassium hydridotetracarbonyl(trimethyl phosphite)chromate **3b**

A total of 0.150 ml (1.20 mmol) of $P(OMe)_3$ was added to a solution of 0.267 g (1.15 mmol) of $KHCr(CO)_5$ in 10 ml of THF. The solution was stirred at 25°C for 24 h, then evaporated, and the yellow residue was washed with diethyl ether (3 × 15 ml) and dried. A total of 0.190 g (50%) of **3b** was obtained. ^1H-NMR ($[D_8]THF$): $\delta = -7.25$ (d, $^2J_{PH} = 52.7$ Hz, 1H; CrH); 3.68 (d, $^3J_{PH} = 10.0$ Hz, 9H; $POCH_3$); ^{31}P-NMR ($[D_8]THF$): $\delta = +215.3$ (dq, $^2J_{PH} = 52.7$ Hz). $^{13}C\{^1H\}$ ($[D_8]THF$): $\delta = 51.59$ (s, OCH_3); 230.37 and 231.48 (broad, $Cr(CO)_4$).

5.3. Potassium hydridotetracarbonyl(triphenylphosphine)chromate **5b**

A total of 0.363 g (1.56 mmol) of $KHCr(CO)_5$ **1b** and 0.840 g (3.2 mmol) of PPh_3 were stirred for 45 min at room temperature (r.t.) and then for 64 h at reflux. The final reaction mixture was filtered and the remaining solid was washed with 2 × 5 ml of THF. The combined THF phases are evaporated to dryness. The resulting brown solid was washed with 3 × 10 ml of Et_2O, dried, and analyzed by NMR: **5b** corresponds to 70% of the ^{31}P-NMR signal. ^1H-NMR ($[D_8]THF$): $\delta = -6.25$ (d, $^2J_{PH} = 35.1$ Hz, 1H; FeH); 7.23–7.60 (15H, m, aromatic H); ^{31}P-NMR: δ (ppm) $= +81.3$ (d, $^2J_{PH} = 35.1$ Hz). $^{13}C\{^1H\}$ ($[D_8]THF$): $\delta = 128.41$ (d, $J_{PC} = 8.3$ Hz); 129.18; 135.14 (d, $J_{PC} = 11.8$ Hz) (-*o*, -*m*, -*p*-aromatic C); 142.69 (d, $^1J_{PC} = 27.1$ Hz, C_{ipso}); 244.22 (broad, $Cr(CO)_4$).

5.4. Reactions of $KHFe(CO)_4$ with $Ph_2P(OMe)$ in the absence of $KHCO_3$

5.4.1. In THF: potassium hydridotricarbonyl(methyl diphenylphosphinite)ferrate **4a**

A total of 2.0 ml (10.0 mmol) of $PPh_2(OMe)$ was added to a solution of 1.04 g of $KHFe(CO)_4$ (5.0 mmol) in 20 ml of THF. The solution was stirred at 25°C for 16 h, then evaporated. The residue was washed with pentane giving 1.68 g (85%) of **4a** as a yellow solid. ^1H-NMR (CD_3CN): $\delta = -8.87$ (1H, d, $^2J_{PH} = 4.3$ Hz, FeH); 3.53 (3H, d, $^3J_{PH} = 13.5$ Hz, MeO); 7.24–7.46 (6H, m, Ph); 7.66–7.81 (4H, m, Ph). $^{31}P\{^1H\}$-NMR (CD_3CN): $\delta = +191.1$. $^{13}C\{^1H\}$-NMR (CD_3CN): $\delta = 52.39$ (s, OCH_3); 128.39 (d, $J_{PC} = 7.6$ Hz); 129.39; 131.40 (d, $J_{PC} = 12.2$ Hz); 146.90 (d, $J_{PC} = 37.4$ Hz); 223.36 (d, $^2J_{PC} = 14.0$ Hz, $Fe(CO)_3$).

5.4.2. In methanol: complexes **7a** and **8a**

Dihydridodicarbonylbis(methyl diphenylphosphinite)iron **7a**. ^1H-NMR (CD_3CN): $\delta = -9.85$ (t,

$^2J_{PH} = 57.7$ Hz, 2 H; FeH$_2$); 3.63 (dd, $^3J_{PH} = {}^5J_{PH} = 6.7$ Hz, 6 H; OCH$_3$); 6.78–7.79 (20 H, m, Ph). ^{1}H-NMR (CDCl$_3$): $\delta = -9.91$ (t, $^2J_{PH} = 57.7$ Hz, 2 H; FeH$_2$); 3.64 (dd, $^3J_{PH} = {}^5J_{PH} = 6.5$ Hz, 6 H; OCH$_3$); 7.39–7.85 (20 H, m, Ph). ^{31}P-NMR (CDCl$_3$): $\delta = +176.3$ (t, $^2J_{PH} = 57.7$ Hz). ^{13}C-NMR (CDCl$_3$): $\delta = 52.86$ (q, $^1J_{CH} = 145$ Hz, O*C*H$_3$); 127.97 (d, $^1J_{CH} = 162$ Hz, *Cmeta*); 129.83 (d, $^1J_{CH} = 160$ Hz, *Cpara*); 130.70 (m, $^1J_{CH} = 162$ Hz, $^2J_{PC} = 26$ Hz, *Cortho*); 142.36 (dd, $^1J_{CP} = {}^3J_{CP} = 26$ Hz, *Cipso*); 213.67 (t, $^2J_{CP} = 13$ Hz, $^1J_{CP} < 5$ Hz, Fe(*C*O)$_2$). IR (pentane): $\nu = 2001$ (s), 1962 (s) cm^{-1}.

Potassium hydridodicarbonylbis(methyl diphenylphosphinite)ferrate **8a.** ^{1}H-NMR ([D$_6$] acetone): $\delta = -9.65$ (t, $^2J_{PH} = 64.3$ Hz, 1 H, FeH); 3.39 (t, $^3J_{PH} = {}^5J_{PH} = 6.7$ Hz, 6 H; OCH$_3$); 6.78–7.79 (m, 20 H, Ph); ^{31}P-NMR (CD$_3$CN): $\delta = +182.2$ (d, $^2J_{PH} = 64.3$ Hz).

5.5. Reactions of KHFe(CO)$_4$ with Ph$_2$P(OMe) in the presence of KHCO$_3$ in methanol

A total of 0.220 ml of Fe(CO)$_5$ (1.6 mmol) was syringed into a solution of 0.218 g of 86% KOH (3.2 mmol) in 10 ml of methanol. The solution was stirred at r.t. for 30 min. The IR spectrum of the solution confirms the presence of KHFe(CO)$_4$ and KHCO$_3$. After cooling to 0°C, 0.645 ml of Ph$_2$P(OMe) (3.3 mmol) was syringed. The solution was stirred for 24 h at 0°C, and then evaporated to dryness. The residue was washed with 3×20 ml of pentane, and 0.270 g of a light brown solid was obtained, consisting in a mixture of complexes **6a**:**7a** = 30:70 (^{31}P-NMR analysis): **7a** is thus obtained in c.a. 25% yield and **6a** in c.a. 7% yield. Green–yellow crystals of complex **7a** deposit from a diluted pentane solution at -10°C, and have been analyzed by X-ray diffraction.

Tricarbonylbis(methyl diphenylphosphinite)iron **6a.** ^{31}P-NMR (CD$_3$CN): $\delta = +184.4$. ^{13}C{^{1}H}-NMR (CD$_3$CN): $\delta = 53.96$ (s, O*C*H$_3$); 129.29, 131.69, 133.13 (broad overlaping signals: *C-ortho-*, *meta*, *para*); 140.76 (d, $^1J_{PC} = 27.5$ Hz, *C-ipso*); 231.79 (t, $^2J_{PC} = 30.6$ Hz, Fe(*C*O)$_3$). IR (pentane): ν(CO) = 1902 (s) cm^{-1} [17].

*5.6. [Bis(dimethylamino)phosphine]pentacarbonylchromium **9b***

A solution of tris(dimethylamino)phosphine (0.410 ml, 2.25 mmol) and acetic acid (0.130 ml, 2.25 mmol) in 10 ml of THF was added to 5 ml of a THF solution of KHCr(CO)$_5$ (0.522 g, 2.25 mmol). After stirring for 15 min at 25°C the solvent was evaporated under vacuum to afford a yellow residue. This residue was extracted with pentane (3×15 ml), leaving a pale yellow–white solid. The pentane solution was evaporated to dryness, leaving 0.491 g (70%) of spectroscopically pure solid **9b**.

Elemental analysis for C$_9$H$_{13}$N$_2$O$_5$PCr (312.18): calc.%: C 34.63, H 4.20, N 8.97. Found%: C 35.13, H 4.15, N 8.81. ^{1}H-NMR (CD$_3$CN): $\delta = 2.79$ (d, $^3J_{PH} = 10.5$ Hz, 12 H; N(CH$_3$)$_2$); 6.77 (d, $^1J_{PH} = 400$ Hz, 1 H; PH). ^{31}P-NMR (CD$_3$CN): $\delta = +142.2$ (d, $^1J_{PH} = 400$ Hz). ^{13}C{^{1}H}-NMR (CD$_3$CN): $\delta = 42.46$ (s, NMe$_2$); 217.68 (d, $^2J_{PC} = 16.3$ Hz, Cr(*C*O)$_5$). IR (THF): $\nu = 2066$ (s); 2031 (w); 1981 (w); 1949–1941 (s); 1919 (w) cm^{-1}; ν(PH) = 2403 (w) cm^{-1}.

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