Pentacarbonylhydridochromates $M^+[HCr(CO)_5]^-$: Reactivity in Organic Synthesis and Homogeneous Catalysis

Jean-Jacques Brunet[a]

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As compared to the main group hydrides (boron, aluminum, ...) and their derivatives, which are very useful *stoichiometric* reagents for selective reductions in organic synthesis, hydrides of transition metals provide the chemist with potential *catalysts* or catalyst precursors. This interesting property is enhanced by the possibility of modifying the coordination sphere, which allows access to a wide variety of hydride complexes with tunable chemical reactivities. Among these, a great variety of carbonylhydridometallates is becoming available and studies of their reactivities continuously appear in the literature. This article reviews the current state of the art as regards the synthesis and reactivity of one of the more promising and versatile carbonylhydridometallates, $[HCr(CO)_5]^-$, the simplest anionic hydride derived from hexacarbonylchromium. Its reactivity in stoichiometric reactions is considered first, and then its generation and involvement as a reactive intermediate in catalytic reactions are reviewed.

1. Introduction

The first preparation of tetracarbonylnickel by Mond in 1890[1] and of pentacarbonyliron by Berthelot[2] and Mond[3] in 1891 are among the first historic landmarks in organotransition metal chemistry.[4] Soon after, extensive work led to the development of the Fischer−Tropsch process[5] and the cobalt-catalyzed oxo process,[6] while many homogeneously catalyzed processes were devised by Reppe's group.[7] Simultaneously, increasing interest in the field of carbonylmetal compounds resulted in the preparation of carbonyl complexes of a large number of transition metals.[8] Subsequently, some derivatives of these carbonylmetal compounds were generated and characterized, including the anionic complexes or "carbonylmetallates". The latter include dianionic carbonylmetallates $[M_x(CO)_z]^{2-}$ {e.g. $[Fe(CO)_4]^{2-}$, the sodium salt of which is commercially available as the Collman reagent[9]} and carbonylhydridometallates $[HM_x(CO)_y]^-$.

From a general point of view, several potential properties of carbonylhydridometallates $[HM_x(CO)_y]^-$ are noteworthy. Firstly, they exhibit reducing properties (as either H^-- or electron-transfer agents). Secondly, they can add to unsaturated carbon−carbon double bonds, generating organometallic derivatives prone to carbon monoxide insertions, thereby allowing access to carbonylated compounds.[10] Last but not least, a great variety of derivatives is a priori available owing to the number of carbonylmetal compounds available. This interest is further increased by the possibility of formally substituting one (or two) carbon monoxide ligand(s), e.g. with phosphanes, or even with chiral phosphanes, giving rise to a wide variety of reagents with tunable reactivities.

Ten years ago, the author published an exhaustive review on the properties and applications in organic synthesis and catalysis of the versatile tetracarbonylhydridoferrates, $M^+[HFe(CO)_4]^-$, which are easily prepared from $Fe(CO)_5$.[11] A further review concerned the coordination chemistry associated with ligand substitution processes in

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[a] Laboratoire de Chimie de Coordination du CNRS, UPR 8241,
205 route de Narbonne, 31077 Toulouse Cedex 4, France
E-mail: brunet@lcctoul.lcc-toulouse.fr
Fax: (internat.) + 33-5/61553003

Jean-Jacques Brunet was born in Clermont-Ferrand, France, in 1945. He attended the Faculté des Sciences and the Ecole Nationale Supérieure de Chimie de Clermont-Ferrand, where he received his Chemical Engineering degree in 1968. He obtained his PhD (These d'Etat) in 1972 at the University of Nancy under the supervision of Pr. P. Caubère. In 1985, he joined the Laboratoire de Chimie de Coordination of the CNRS (Toulouse) where he is one of the ten group leaders. His current research interests lie in organometallic chemistry and homogeneous catalysis directed towards organic synthesis, with some emphasis on both carbonylation reactions and on the functionalization of alkenes by hydroamination.

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$M^+[HFe(CO)_4]^-$.[12] The present review is devoted to the properties and applications in organic synthesis and homogeneous catalysis of the hitherto less well studied pentacarbonylhydridochromates $M^+[HCr(CO)_5]^-$, which are prepared from $Cr(CO)_6$. Some properties of these complexes have already been reported by Darensbourg et al. in 1987 in a more general review dealing with anionic transition metal hydrides.[13]

Hexacarbonylchromium, $Cr(CO)_6$, was first prepared by Job and Cassal in 1927.[14] It is a stable, nonvolatile colorless solid, and is less toxic and easier to handle than the liquid $Fe(CO)_5$.[15] Its synthesis has been improved throughout the years and it is now a commercial product.[8,16] It melts at 130 °C (dec.) and can be purified by sublimation in a static vacuum at 60−70 °C.[17] As in the carbonyliron series, several anionic carbonylchromium complexes are known, including monoanionic carbonylhydridometallates and dianionic carbonylmetallates (Scheme 1).[8]

$[HCr(CO)_5]^-$ $[Cr(CO)_5]^{2-}$

$[HCr_2(CO)_{10}]^-$ $[Cr_2(CO)_{10}]^{2-}$

$[Cr_3(CO)_{14}]^{2-}$

Scheme 1. Main carbonylchromates

The preparation procedures and structural and spectroscopic properties of $[HCr(CO)_5]^-$ salts are summarized below, and then their reactivity in stoichiometric reactions and their involvement in catalytic reactions is considered. The author is obliged to recall that the chemistry of pentacarbonylhydridochromates is largely based on the pioneering work of the groups of M. Y. and D. J. Darensbourg.

2. Preparation Procedures

2.1. Discovery

The first report of an $[HCr(CO)_5]^-$ salt was made by Behrens and Weber in 1957.[18] By protonation of $Na_2Cr(CO)_5$ with an aqueous solution of tris(*o*-phenanthroline)iron(II) sulfate, a crystalline complex could be isolated, which was formulated as $[Fe(o\text{-phen})_3][HCr(CO)_5]_2$ (elemental analysis) [Equation (1) and (2)].

$$Cr(CO)_6 + 2Na \xrightarrow{\text{liq. } NH_3} Na_2[Cr(CO)_5] + CO \tag{1}$$

$$Na_2[Cr(CO)_5] + H_2O \xrightarrow{Fe(phen)_3SO_4} [Fe(C_{12}H_8N_2)_3][HCr(CO)_5]_2 \tag{2}$$

The reaction of $[HCr(CO)_5]^-$ with water was also reported;[18,19] molecular hydrogen was liberated with formation of the hydride-bridged binuclear species $(\mu\text{-}H)[Cr_2(CO)_{10}]^-$, the structure of which was determined later.[20]

It was not until 1981 that salts of $[HCr(CO)_5]^-$ were spectroscopically characterized (IR and ^1H-NMR data, vide infra). Darensbourg and Deaton isolated the Et_4N^+ (26% yield) and Ph_4As^+ salts according to the above sequence [Equation (3) and (4)], followed by metathesis with Et_4NBr or Ph_4AsBr.[21]

$$Cr(CO)_6 + Na \xrightarrow{\text{liq. } NH_3} Na_2Cr(CO)_5 \xrightarrow[\text{THF}]{\text{recrist.}} [Na(THF)_x]_2Cr(CO)_5 \tag{3}$$

$$[Na(THF)_x]_2Cr(CO)_5 + MeOH \xrightarrow{CH_3CN} [Na][HCr(CO)_5] + MeONa \tag{4}$$

2.2. Preparation Procedures

Three methods have proven successful.

Firstly, a general method based on hydride/labile ligand exchange in Group 6B carbonylmetal derivatives [Equation (5)] has been reported to be feasible for M = Cr (unreported yield).[22]

$$M(CO)_5(pip) + [PPN]^+[BH_4]^- \xrightarrow{THF} [PPN]^+[HM(CO)_5]^- + pip\text{->}BH_3 \tag{5}$$

Secondly, protonation of the mononuclear dianion $[Cr(CO)_5]^{2-}$ has also been developed as a synthetic method [Equation (6) and (7)].[23]

$$Cr(CO)_5(pip) + 2\,Na[C_{10}H_8] \xrightarrow[-78°C]{THF} Na_2[Cr(CO)_5] + pip + 2\,C_{10}H_8 \tag{6}$$

$$Na_2[Cr(CO)_5] + [PPN]^+[I]^- + CH_3OH \xrightarrow[-78°C]{THF} \underset{70\%}{[PPN]^+[HCr(CO)_5]^-} + NaI + NaOCH_3 \tag{7}$$

Thirdly, the synthesis of $[HCr(CO)_5]^-$ can be achieved by reaction of hexacarbonylchromium with hydroxide ions. Several preparations have been reported, which differ in the nature of the associated cation.

The reaction of $Cr(CO)_6$ with 2 equiv. of KOH, solubilized by cryptand 222 in THF or CH_3CN, at room temperature has been reported to quantitatively afford the $[HCr(CO)_5]^-$ derivative within minutes, as shown in a simplified manner in Equation (8).[24]

$$Cr(CO)_6 + [K(crypt\ 222)]^+[OH]^- \xrightarrow[\text{or } CH_3CN]{THF} [K(crypt\ 222)]^+[HCr(CO)_5]^- + CO_2 \tag{8}$$

Phase-transfer of hydroxide ions by a quaternary ammonium salt in a liquid−solid reaction also leads to a rapid synthesis of the $[HCr(CO)_5]^-$ derivative (75% yield), Equation (9).[25] Some amounts (≤ 20%) of the binuclear dianion $[Cr_2(CO)_{10}]^{2-}$ are also formed, which are easily separated by virtue of differences in solubility.

$$Cr(CO)_6 + [Et_4N]^+[HSO_4]^- + 15\,KOH \xrightarrow[60°C,\ 30\ min]{CH_3CN/H_2O} [Et_4N]^+[HCr(CO)_5]^- \tag{9}$$

The potassium salt $[K]^+[HCr(CO)_5]^-$ can be prepared by treatment of $Cr(CO)_6$ with KOH (7 equiv.) in a THF/$MeOH/H_2O$ solvent mixture. Yields are in the range

60−70%, but the selectivity $[HCr(CO)_5]^-/[HCr_2(CO)_{10}]^-$ is seemingly difficult to control. Both the water content and the temperature are important factors.[26]

More recently, a rapid and useful preparation of $[K]^+[HCr(CO)_5]^-$ has been reported, which is carried out in a CH_2Cl_2/EtOH solvent mixture at room temperature [Equation (10)].[27] The advantages of this procedure are its high reproducibility (70−78% yield from each of 30 runs) and the fact that only 2 equiv. of KOH are needed, in accordance with the stoichiometry.

$$Cr(CO)_6 + 2\ KOH \xrightarrow[\text{RT, 10 min; evaporation}]{CH_2Cl_2\text{-}EtOH} \underset{70\text{-}78\%}{[K]^+[HCr(CO)_5]^-} + KHCO_3 \qquad (10)$$

Some amounts of the bridged binuclear hydride $[K]^+[HCr_2(CO)_{10}]^-$ are also formed, which are easily eliminated (together with $KHCO_3$) by filtration of a THF solution. The purity of the thus formed potassium pentacarbonylhydridochromate can easily be verified by ^{1}H-NMR analysis since the chemical shifts of the monomeric and dimeric carbonylmetal hydrides are very different (vide infra, Table 2).

It must be noted that the chemistry of carbonylhydridochromates is characterized by the fact that the dimeric carbonylhydridochromate, $(\mu\text{-}H)[Cr_2(CO)_{10}]^-$, acts as a thermodynamic sink. The monomeric hydride, $[HCr(CO)_5]^-$, reacts readily with traces of H^+ to yield the binuclear hydride according to Equation (11)−(13).

$$[HCr(CO)_5]^- + H^+ \longrightarrow H_2Cr(CO)_5 \qquad (11)$$

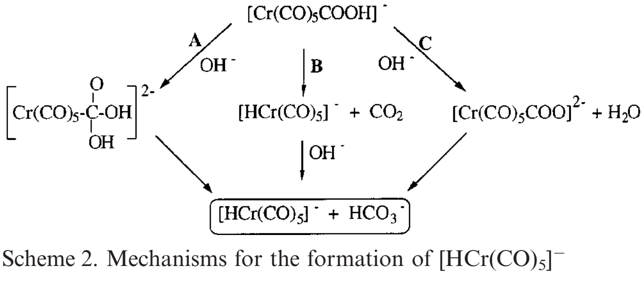
$$H_2Cr(CO)_5 \longrightarrow H_2 + Cr(CO)_5 \qquad (12)$$

$$Cr(CO)_5 + [HCr(CO)_5]^- \longrightarrow (\mu H)[Cr_2(CO)_{10}]^- \qquad (13)$$

As in the case of $Mo(CO)_6$ and $W(CO)_6$, the mechanism of the reaction of OH^- with $Cr(CO)_6$ is thought to involve a transient metallocarboxylic acid species [Equation (14)].[28]

$$Cr(CO)_6 + OH^- \longrightarrow [Cr(CO)_5COOH]^- \qquad (14)$$

Considering the stoichiometry (2 equiv. OH^-) necessary to obtain complete conversion of the hexacarbonylmetal compound, different reaction pathways have been proposed (Scheme 2).[29]



Scheme 2. Mechanisms for the formation of $[HCr(CO)_5]^-$

In aprotic media, pathway A is considered to be the most likely, whereas pathway C should become important in aqueous alcoholic systems.[29] A different mechanism has been proposed for the in situ generation of $[HCr(CO)_5]^-$ under thermal WGSR (water gas shift reaction) conditions, i.e. under CO pressure in basic $MeOH/H_2O$ solutions at elevated temperature, as well as under photocatalyzed WGSR conditions (vide infra).

3. Main Structural and Spectroscopic Properties

3.1. Structure in the Solid State

The first solid-state characterization of a $[HCr(CO)_5]^-$ salt was performed on $[Ph_4P]^+[HCr(CO)_5]^-$.[30] The complex was found to exhibit a pseudooctahedral geometry (Figure 1), with a small *trans* effect of the hydride ligand being evident, the $Cr-C_{trans}$ distance being slightly shorter than the $Cr-C_{cis}$ distance [1.852(4) Å vs. 1.865(4) Å]. The hydride ion is located 1.66(5) Å from the chromium atom. The equatorial carbon monoxide ligands are at 90° angles to one another, but the $(CO)_{eq}-(CO)_{ax}$ bond angle is 95.4°, indicating a substantial bending of the equatorial CO ligands towards the hydride ligand. Nevertheless, this bending is less pronounced than that observed for the equatorial CO ligands in the distorted trigonal bipyramid of $[HFe(CO)_4]^-$, for which the $(CO)_{eq}-(CO)_{ax}$ bond angle is 99.1°.[31]

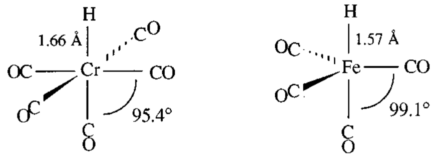


Figure 1. Comparison of solid-state geometries of $[HCr(CO)_5]^-$ and $[HFe(CO)_4]^-$

γ-Irradiated single crystals of $[PPN]^+[HCr(CO)_5]^-$ exhibit persistent anisotropic EPR spectra attributable to the free radical ($S = {}^1/_2$) anion $[Cr(CO)_5]^-$. Measurements of the *g* value and hyperfine interaction anisotropies in crystallographically aligned single crystals at 77 K are consistent with a square-pyramidal geometry for the radical.[32]

3.2. Spectroscopic Properties

3.2.1. Infrared Spectroscopy

It is well known that infrared spectroscopy is particularly useful for analyzing solutions of carbonylmetal compounds and their derivatives. The case of carbonylhydridometallates has been thoroughly studied by Darensbourg et al., whereby evidence for ion-pairing effects was found.[13]

As in the case of similar carbonylhydridometallates, e.g. $[HFe(CO)_4]^-$, no ν(M−H) band is observed. The IR spectrum of $Na^+[HCr(CO)_5]^-$ consists of one strong band (E vibration mode) at 1884 cm^{-1} (four equatorial CO ligands), one medium band ($A_1{}^1$) at 1854 cm^{-1} (CO *trans* to the hydride) with a shoulder at 1894 cm^{-1}, a weak band at 1814

cm^{-1}, and finally a very weak band at 2016 cm^{-1}.[33] Addition of HMPA to a THF solution leads to the disappearance of the band at 1814 cm^{-1} and of the shoulder at 1894 cm^{-1} (with a concomitant increase in the intensity of the 1884 cm^{-1} band), eventually giving the same spectrum as that of $PPN^+[HCr(CO)_5]^-$ (see Table 1).

Table 1. Infrared data for $[M]^+[HCr(CO)_5]^-$

M^+	Solvent	$\tilde{\nu}$(CO) [cm^{-1}] $A_1{}^2$ (vw)	E (s)	$A_1{}^1$ (m)	Ref.
Li^+	THF	2016	1885	1857	[33]
Na^+	THF	2016	1884 (1894 sh)	1854 (1814 w)	[33]
Na^+/HMPA	THF	2016	1884	1856	[33]
PPN^+	THF	2016	1884	1856	[22]
Et_4N^+	THF	2023	1892	1860	[21]
Ph_4As^+	THF	2020	1889	1860	[21]
[K-crypt]$^+$	CD_3CN	2023	1888	1857	[29]

These observations can be taken as evidence that reversible contact ion pair formation is responsible for the spectral changes. Furthermore, a change in the intensity of the $A_1{}^1$ band (CO *trans* to the hydride) has been interpreted in terms of site-specific interaction of the sodium cation with the *axial* CO oxygen atom. It must be noted that in the case of $Na^+[HFe(CO)_4]^-$ evidence has been found for a similar site-selective interaction with an *equatorial* CO oxygen atom (Figure 2).[13]

3.2.2. NMR Spectroscopy

The ^1H- (and ^2H-) NMR chemical shifts of $[HCr(CO)_5]^-$ salts invariably appear at $\delta \approx -7$ and differ considerably from those of the bridged binuclear hydride $[HCr_2(CO)_{10}]^-$ salts ($\delta \approx -20$) (Table 2). This difference is much larger than that between the corresponding mononuclear and binuclear carbonylhydridoferrates [e.g. $NaHFe(CO)_4$: $\delta_H = -8.74$; $NaHFe_2(CO)_8$: $\delta_H = -8.47$].[11]

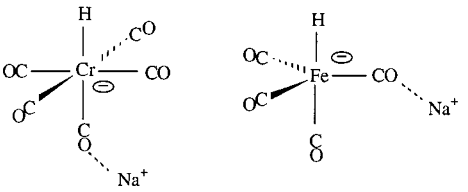


Figure 2. Comparison of Na^+ interactions in solution

Table 2. ^1H-NMR data for $[M]^+[HCr(CO)_5]^-$ and $[M]^+[HCr_2(CO)_{10}]^-$

Compound	Solvent	δ	Ref.
$[Li]^+[HCr(CO)_5]^-$	$[D_8]$THF	−6.80	[33]
$[Na]^+[HCr(CO)_5]^-$	$[D_8]$THF	−6.75	[33]
$[K]^+[HCr(CO)_5]^-$	$[D_8]$THF	−6.7	[26][27]
$[PPN]^+[HCr(CO)_5]^-$	$[D_8]$THF	−6.73	[13][33]
$[PPN]^+[HCr(CO)_5]^-$	CD_3CN	−6.92	[22]
$[Et_4N]^+[HCr(CO)_5]^-$	CD_3CN	−7.0	[21][25]
$[Ph_4As]^+[HCr(CO)_5]^-$	CD_3CN	−7.0	[21]
$[K(crypt)]^+[HCr(CO)_5]^-$	CD_3CN	−7.0	[29]
$[Na]^+[HCr_2(CO)_{10}]^-$	$[D_8]$THF	−19.17	[13][34]
$[K]^+[HCr_2(CO)_{10}]^-$	$(CD_3)CO$	−19.10	[35]
$[K]^+[HCr_2(CO)_{10}]^-$	$[D_8]$THF	−19.53	[27]
$[Et_4N]^+[HCr_2(CO)_{10}]^-$	$[D_8]$THF	−19.47	[13][34]
$[PPN]^+[HCr_2(CO)_{10}]^-$	$[D_8]$THF	−19.50	[36]

A theoretical study aimed at rationalizing the ^1H-NMR chemical shifts of these and other low-valent transition metal hydrides has recently been reported.[37] Calculations based on density functional theory and gauge-including atomic orbitals (DFT-GIAO) were in good agreement with experimental data. The negative "hydridic" shift observed for transition metal hydrides $H{-}ML_n$ was attributed to a paramagnetic current present in the adjacent ML_n fragment.

The ^{13}C-NMR spectrum of $[PPN]^+[HCr(CO)_5]^-$ under ambient conditions is indicative of a $CO_{cis}{-}CO_{trans}$ intramolecular exchange process.[22] Thus, at room temperature in CD_3CN, the five CO ligands are apparently equivalent, giving rise to just one signal (at $\delta = 228.7$), whereas at temperatures below 0 °C, two signals are observed, corresponding to four equatorial CO ligands ($\delta = 227.9$) and one axial CO ligand ($\delta = 235.1$). The same phenomenon has been observed for the $[K(crypt)]^+[HCr(CO)_5]^-$ derivative.[29]

4. Reactivity in Stoichiometric Reactions

4.1. Reactions with CO_2, CS_2, and COS

The reaction of $[HCr(CO)_5]^-$ with carbon dioxide has been studied in the context of the water gas shift reaction [Equation (15)].[38]

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{15}$$

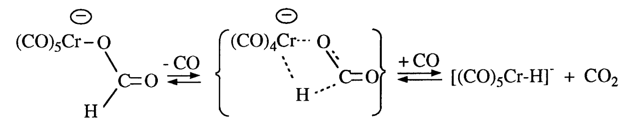
$[K(crypt\ 222)]^+[HCr(CO)_5]^-$ readily reacts with carbon dioxide or carbon disulfide in THF or CH_3CN to yield the corresponding pentacarbonylchromium formate or thioformate [Equation (16)].[24]

$$[HCr(CO)_5]^- + CX_2 \rightleftharpoons [HC(X)XCr(CO)_5]^- \tag{16}$$

The formato derivative (X = O) was shown to be identical to that prepared by the more conventional route [Equation (17)].[39]

$$[PPN]^+[Cr(CO)_5Cl]^- + TlOOCH \xrightarrow{CH_2Cl_2} [PPN^+[HC(O)OCr(CO)_5]^- + TlCl \tag{17}$$

As compared to the tungsten analogue, the pentacarbonylchromium formate exhibits two main characteristics. Firstly, it is readily decarboxylated (25−50 °C) with regeneration of $[HCr(CO)_5]^-$, and secondly, it undergoes rapid CO ligand exchange with free ^{13}CO in solution (80% incorporation within 10 min at room temp.). These observations suggest that CO lability is a requisite step for the rupture of the C−H bond of the formate ligand, leading to decarboxylation and regeneration of $[HCr(CO)_5]^-$ (Scheme 3).[24,29,40]



Scheme 3. Mechanism for the decarboxylation of $[HC(O)OCr(CO)_5]^-$

The reaction with COS proceeds instantaneously in CH_3CN, giving the addition product in which the thioformate ligand is bound to the $[Cr(CO)_6]$ moiety through its sulfur atom [Equation (18)]. This mode of binding has been established by X-ray diffraction analysis of the $[PPN][HC(O)SCr(CO)_5]$ derivative.[29,40]

$$[HCr(CO)_5]^- + COS \xrightarrow{CH_3CN} [HC(O)SCr(CO)_5]^- \qquad (18)$$

Alternatively, the pentacarbonylchromium thioformate may be obtained quantitatively by reaction of the formate derivative with COS, Equation (19).[40]

$$[HC(O)OCr(CO)_5]^- + COS \xrightarrow[12h]{CH_3CN} [HC(O)SCr(CO)_5]^- + CO_2 \qquad (19)$$

In contrast to its formate analogue, the thioformate complex shows no tendency for COS expulsion (owing to the greater strength of the Cr−S bond) and does not undergo ligand exchange with CO_2 or CS_2. Reaction according to Equation (19) is thus irreversible.

Ab initio calculations seem to indicate that the insertion of CO_2 into the H−Cr bond of $[HCr(CO)_5]^-$ involves an acid−base adduct (η^1-C coordination of CO_2 to the hydride), which is more stable than the reactants. The reaction pathway probably then involves a low-energy cost rearrangement into the η^2-O,H formate structure coupled with simultaneous CO dissociation.[41]

An extension of this facile insertion of CO_2 into $[HM(CO)_5]^-$ led to the catalytic synthesis of alkyl formates (vide infra, Part 5).

4.2. Reaction with Acyl Chlorides

Group 6B transition metal hydrides $[HM(CO)_4L]^-$ (M = Cr, W; L = CO or PR_3) exhibit the interesting property of reducing acyl chlorides to aldehydes without further reduction to the corresponding alcohols [Equation (20)].[42] Such selective reductions have previously been observed using $[HFe(CO)_4]^-$ [43] and $[CpV(CO)_3H]^-$.[44]

$$[PPN]^+[HCr(CO)_5]^- + RCOCl \xrightarrow[25°C]{THF} \underset{90\text{-}95\%}{RCHO} + [PPN]^+[ClCr(CO)_5]^- \qquad (20)$$

These reactions are almost quantitative for both aliphatic and aromatic acyl chlorides under mild conditions. Competitive experiments involving the reduction of $PhCH_2COCl$ indicated the reactivity order: $[HW(CO)_5]^- > [HCr(CO)_5]^- > [HFe(CO)_4]^-$, which parallels their hydride-transfer abilities, as established for the reduction of nonhindered alkyl halides (vide infra).[45] Furthermore, it is noteworthy that the reductions with $[HCr(CO)_5]^-$ can be performed in the presence of other reducible functional groups such as aryl bromides, alkyl bromides, or nitroaromatics. For example, 4-bromobutyraldehyde may be obtained in 95% yield from the corresponding acyl chloride. Reduction of the bromo group requires a second equivalent of $[HCr(CO)_5]^-$.

The reagent is also useful for the delivery of deuterium to the aldehydic carbon to give RCDO-type products. Indeed, taking advantage of the facile H/D exchange with CH_3OD of the $[PPN]^+$ salt, Equation (21), the reduction of benzoyl chloride with the reagent prepared in situ from $[PPN]^+[HCr(CO)_5]^-$ and CH_3OD (2-fold molar excess) in THF affords PhCDO [Equation (22)].[46]

$$[PPN]^+[HCr(CO)_5]^- + CH_3OD \xrightleftharpoons{THF} [PPN^+[CDCr(CO)_5]^- + CH_3OH \qquad (21)$$

$$PhCOCl + [PPN]^+[HCr(CO)_5]^- \xrightarrow[THF]{CH_3OD} PhCDO \qquad (22)$$

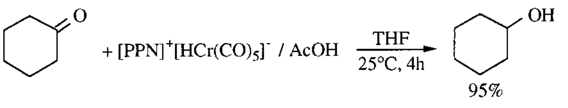
4.3. Reaction with Aldehydes and Ketones

In the course of their study on the selective reduction of acyl halides, Darensbourg et al. also discovered that $[HCr(CO)_5]^-$ is an effective reducing agent for aldehydes *under acidic conditions*.[42] Further studies allowed a determination of the scope and limitations of the stoichiometric reduction of aldehydes and ketones.[47]

$[PPN]^+[HCr(CO)_5]^-$ reacts rapidly with paraformaldehyde in THF (as shown by IR analysis) to yield methanol (98%, 0.5 h) after hydrolysis with a Brønsted acid (AcOH or H_2O). With propionaldehyde or benzaldehyde, only a sluggish reaction is observed. In contrast, rapid reductions to 1-propanol (98%, 1 h) and benzyl alcohol (90%, 1 h) are observed when the reactions are conducted in the presence of acetic acid [Equation (23)].[47]

$$RCHO + [PPN]^+[HCr(CO)_5]^- \xrightarrow[THF]{AcOH} RCH_2OH + [PPN]^+[AcOCr(CO)_4]^- \qquad (23)$$
$$R = C_2H_5,\ C_6H_6$$

Ketones show no reaction with $[PPN]^+[HCr(CO)_5]^-$. However, in the presence of acetic acid, a range of ketones do react at room temperature in THF, cyclohexanone being more easily reduced [95%, 4 h, Equation (24)] as compared to acetophenone (45%, 72 h) and norbornanone (50%, 8 h, *endo* alcohol).



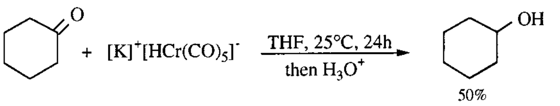
(24)

Where long reaction times are required, a drawback arises from decomposition of the reagent through H_2 elimination [Equation (25)].

$$[HCr(CO)_5]^- + AcOH \longrightarrow H_2 + [AcOCr(CO)_5]^- \qquad (25)$$

With regard to the reaction mechanism, it has been shown that the reductions are not affected by the presence of an excess of the CO ligand (saturated THF solution). It was thus proposed that the ketone carbonyl group must be activated (H^+ assistance) towards nucleophilic attack by $[HCr(CO)_5]^-$. Similar K^+ assistance has been demonstrated for the reduction of ketones by hydrido(phosphane)ruthenate complexes.[48]

These conclusions are relevant to the recent observation that, in contrast to the $[PPN]^+$ salt, the potassium salt $[K]^+[HCr(CO)_5]^-$ does react with cyclohexanone *in the absence* of acid.[49] The stoichiometric reaction of $[K]^+[HCr(CO)_5]^-$ with cyclohexanone at room temperature in THF leads, after hydrolysis, to cyclohexanol (50% yield, 24 h) [Equation (26)].



(26)

However, the yield could not be increased by using longer reaction times (120 h). Spectroscopic analysis of the reaction medium prior to hydrolysis indicated that free cyclohexanol was already present. These observations were rationalized in terms of the consumption of $[HCr(CO)_5]^-$ by in situ reaction with an intermediate alkoxochromate, $[RR'CHOCr(CO)_5]^-$,[50] yielding cyclohexanol and $[Cr_2(CO)_{10}]^{2-}$. As previously proposed by Marko et al. (vide infra),[51] $[HCr(CO)_5]^-$ is thus believed to act both as a hydride and a proton donor. These hypotheses have been used to design a system for the catalytic reduction of ketones in the presence of a hydrogen-transfer agent $[KHCr(CO)_5/HCO_2H/Et_3N]$ (vide infra, Part 5).[49]

4.4. Reaction with Organic Halides

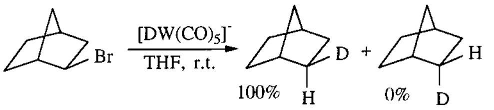
Darensbourg et al. reported a thorough study of the reactivities of anionic transition metal (Groups 6B and 8) hydrides.[52] They compared the reactivities of $[HM(CO)_4L]^-$ compounds (M = Cr, W; L = CO, PR_3) with those of $[HM(CO)_3L]^-$ analogues (M = Fe, Ru; L = CO, PR_3) in the reduction of primary, secondary, and tertiary alkyl halides. For the reaction with *n*BuBr, the following reactivity order was established [P = $P(OMe)_3$]:

$[HW(CO)_4P]^- > [HCr(CO)_4P]^- > [HW(CO)_5]^- > [CpV(CO)_3H]^- > [HCr(CO)_5]^- > [HRu(CO)_4]^- >$ *trans*-$[HFe(CO)_3P]^- >> [HFe(CO)_4]^-$ (no reaction)

This order compares well with the well-known nucleophilicity scale devised by Dessy, Pohl, and King for the series of simple transition metal carbonyl anions:[53]

$[CpFe(CO)_2]^- > [CpRu(CO)_2]^- > [CpNi(CO)]^- > [Re(CO)_5]^- > [CpW(CO)_3]^- > [Mn(CO)_5]^- > [CpMo(CO)_3]^- > [CpCr(CO)_3]^- > [Co(CO)_4]^-$

The Group 6B hydrides are efficient hydride-transfer agents towards a wide variety of C−X bonds, including tertiary centers and aromatic C−X bonds.[52] Interestingly, from a synthetic point of view, they tolerate the presence of functionalities such as nitro groups, ketones, and aldehydes. The convenient in situ method for H/D exchange allows deuterium labelling of the resulting alkane without isolation of the transition metal deuteride [Equation (27)].



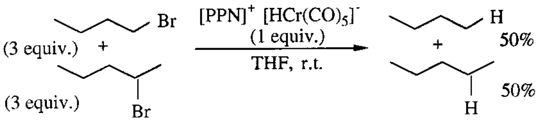
(27)

The propensity for H^- transfer (vs. the SET process) could also be correlated with the propensity for $Na^+\cdots HM^-$ interaction (vs. the tendency for $Na^+\cdots OC{-}M^-$ interaction), whereby a useful general scale was established:

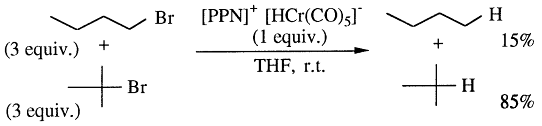
Increasing propensity for H^- transfer:
$[HFe(CO)_4]^- \rightarrow [HV(CO)_3]^- \rightarrow [HCr(CO)_5]^- \rightarrow [HW(CO)_5]^- \rightarrow [HCr(CO)_4P(OMe)_3]^- \rightarrow [HW(CO)_4P(OMe)_3]^-$.

Increasing propensity for SET processes:
$[HW(CO)_4P(OMe)_3]^- \rightarrow [HCr(CO)_4P(OMe)_3]^- \rightarrow [HW(CO)_5]^- \rightarrow [HCr(CO)_5]^- \rightarrow [HV(CO)_3]^- \rightarrow [HFe(CO)_4]^-$.

As can be seen, $[HCr(CO)_5]^-$ is placed in the middle of the scale. As a matter of fact, it reacts almost equally well with primary, secondary, and tertiary alkyl bromides. However, in competition experiments it exhibits a preference for tertiary alkyl bromides [Equation (28) and (29)]. No coupling (R−R) or elimination products could be detected.[52]

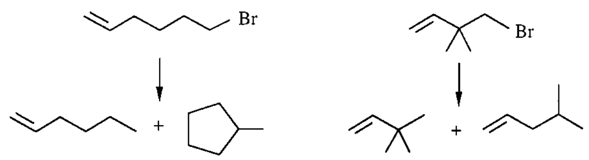


(28)



(29)

A still more interesting quantitative assessment of the competing pathways (ionic H^- transfer, S_N2, vs. radical chain mechanism, S_H2) was achieved by studying the reaction of $[HM(CO)_5]^-$ complexes with two mechanistic probes, namely 6-bromo-1-hexene and 4-bromo-3,3-dimethyl-1-butene (Scheme 4).[54]



Scheme 4. Possible reduction products from mechanistic probes

Computation of the results indicated the relative contributions of the S_N2 and S_H2 mechanisms given in Table 3.

Table 3. Relative contributions of S_N2 and S_H2 mechanisms to the reactivity of hydridometallates

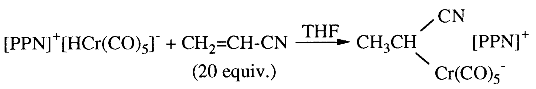
Hydridometallate	S_H2 vs. S_N2 participation
$[PPN]^+[HCr(CO)_5]^-$	10% S_H2, 90% S_N2
$[PPN]^+[HW(CO)_5]^-$	0.3% S_H2, 99.7% S_N2
$[PPN]^+[HW(CO)_4P(OMe)_3]^-$	0.03% S_H2, 99.97% S_N2

Interestingly, this work also pointed out that the unrearranged reduction products arise from *both* hydride displacement of Br^- (S_N2 path) and direct trapping of the unrearranged radical $R^\cdot$ (S_H2 path).

4.5. Reactivity Towards C=C Double Bonds

No reaction was observed on stirring a THF solution of $[Et_4N]^+[HCr(CO)_5]^-$ at 50 °C under 1 atm of ethylene for 3−4 h.[21]

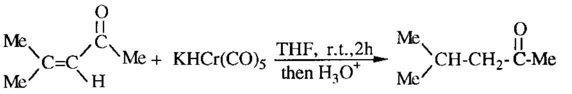
The reaction of $[PPN]^+[HCr(CO)_5]^-$ with a large excess of acrylonitrile results in quantitative formation of the stable insertion complex, together with large amounts of polymeric materials [Equation (30)]. The regioselectivity of the reaction was ascertained by IR, ^1H- and ^{13}C-NMR spectroscopy.[55]



$$[PPN]^+[HCr(CO)_5]^- + \underset{(20\ \text{equiv.})}{CH_2{=}CH\text{-}CN} \xrightarrow{THF} CH_3CH\begin{array}{l} CN \\ Cr(CO)_5^- \end{array} [PPN]^+ \qquad (30)$$

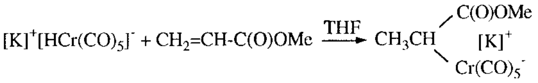
The course of this reaction is unaffected if it is performed under CO (1 atm). Furthermore, the observed second-order kinetics and activation parameters are consistent with an associative hydride-transfer process. For the above reaction, the reactivity order of comparable hydrides $\{[HCr(CO)_5]^- < [HW(CO)_5]^- < [HW(CO)_4P(OMe)_3]^-\}$ is the same as that found for the hydride/halide displacement reactions with organic halides (vide supra).[54]

The reaction of $KHCr(CO)_5$ with *stoichiometric* amounts of α,β-unsaturated ketones and esters has recently been studied.[56] The reaction with mesityl oxide was found to proceed rapidly (within 30 min) at room temperature to selectively afford the corresponding saturated ketone without significant formation of high molecular weight products [Equation (31)]. In this reaction, $KHCr(CO)_5$ proved to be much more reactive than $KHFe(CO)_4$ or $KHCr_2(CO)_{10}$.[49]



(31)

Methyl acrylate was also found to be rapidly reduced, yielding methyl propionate within 10 min (90% yield). However, in several cases the α,β-unsaturated ketones and esters were only partially reduced to the saturated ketones and high molecular weight products were generated. Interestingly, in the case of methyl acrylate, dimethyl fumarate, and dimethyl maleate, analysis of the reaction mixture prior to hydrolysis revealed the presence of the insertion product (^1H and ^{13}C NMR) [Equation (32)].[56]



$$[K]^+[HCr(CO)_5]^- + CH_2{=}CH\text{-}C(O)OMe \xrightarrow{THF} CH_3CH\begin{array}{l} C(O)OMe \\ Cr(CO)_5^- \end{array} [K]^+ \qquad (32)$$

4.6. Reactivity Towards C=N Bonds of Imines

Further to their study on the catalytic hydrogenation of imines in MeOH (vide infra, Part 5), Marko et al. reported the stoichiometric reactivity of $[Et_4N]^+[HCr(CO)_5]^-$ towards benzylideneaniline in aprotic solvents.[57]

In MeCN solution, $[Et_4N]^+[HCr(CO)_5]^-$ was found to react with *N*-benzylideneaniline at 75 °C under argon to yield the corresponding amine. Since the conversion did not exceed 50% and IR analysis indicated that the mononuclear hydride had been completely transformed into $[Cr_2(CO)_{10}]^{2-}$, the overall reaction was formulated as shown in Equation (33).[57] Under the same conditions, the binuclear hydride $[Et_4N]^+[HCr_2(CO)_{10}]^-$ proved to be practically inert.

$$PhCH{=}NPh + 2\,[HCr(CO)_5]^- \xrightarrow[75°C]{MeCN} PhCH_2NHPh + [Cr_2(CO)_{10}]^{2-} \qquad (33)$$

Although the intermediate addition complex could not be observed experimentally, it was formulated as $[PhCH_2N(Ph)Cr(CO)_5]^-$. In the second step, $[HCr(CO)_5]^-$ may act as a proton donor, affording benzylaniline and the dianionic complex $[Cr_2(CO)_{10}]^{2-}$ in situ.

4.7. Miscellaneous

4.7.1. Reaction with Diselenides

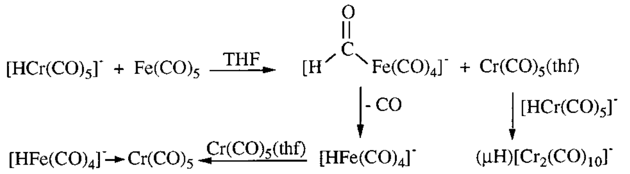
$[PPN]^+[HCr(CO)_5]^-$ reacts with dimethyl (or diphenyl) diselenide by nucleophilic cleavage of the Se−Se bond to yield the corresponding anionic chromium selenate complex [Equation (34)].[58]

$$[PPN]^+[HCr(CO)_5]^- + MeSeSeMe \xrightarrow[r.t.]{THF} \underset{96\%}{[PPN]^+[MeSeCr(CO)_5]^-} + MeSeH \qquad (34)$$

4.7.2. Reaction with Electrophilic Metal Carbonyls

As part of their studies on the hydride-transfer abilities of anionic transition metal hydrides, Darensbourg et al. reported the reaction of $[HCr(CO)_5]^-$ with $Fe(CO)_5$.[59]

Whereas no reaction occurs upon mixing $[HFe(CO)_4]^-$ with $Cr(CO)_6$ (THF, room temp.), the reaction of $[HCr(CO)_5]^-$ with $Fe(CO)_5$ yields products resulting from hydride transfer. The formation of the observed products was rationalized on the basis of an ionic mechanism (Scheme 5).

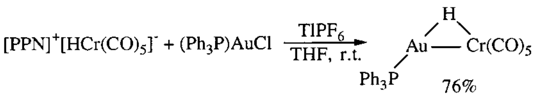


Scheme 5. Reaction of $[HCr(CO)_5]^-$ with $Fe(CO)_5$

The intermediate iron formyl complex, $[(CO)_4FeCHO]^-$, was identified on the basis of its IR and NMR characteristics.[60,61]

4.7.3. Reaction with Au^I and Ag^I Complexes

The reaction of $[HCr(CO)_5]^-$ with the gold(I) complex $(Ph_3P)AuCl$ leads to the formation of a hydrido-bridged heterobimetallic complex [Equation (35)], which has been subjected to single-crystal X-ray diffraction analysis. The three-center two-electron bond is characterized by the following distances: Au−H = 1.72(11) Å, Cr−H = 1.64(12) Å, Au−Cr = 2.770(2) Å.[62]

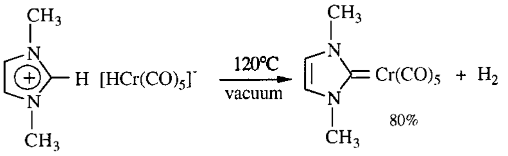


(35)

Similarly, reaction with $(Me_3P)AgI$ yields $(Me_3P)(\mu\text{-}H)AgCr(CO)_5$ in 65% yield.

4.7.4. Reaction with Imidazolium Cations

In 1968, Öfele et al. exploited the acidic nature of imidazolium salts to synthesize the first (diaminocarbene)chromium complex [Equation (36)].[63]



(36)

5. Reactivity in Catalytic Reactions

The pentacarbonylhydridochromate $[HCr(CO)_5]^-$ is involved as a key intermediate in several catalytic reactions, where it plays the role of a species active towards electrophiles. These are summarized below.

5.1. Water Gas Shift Reaction

The water gas shift reaction (WGSR) [Equation (37)] finds extensive use in industry for hydrogen enrichment of synthesis gas (CO + H_2). Current processes involve the reaction of steam with synthesis gas over iron oxide/chromium oxide or zinc oxide/copper oxide catalyst beds at high temperatures (> 300 °C).[64,65]

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g) \quad (37)$$

Interestingly, it has been shown that the WGSR can be carried out at lower temperatures (< 200 °C) with water present in liquid form [Equation (38)] by using homogeneous catalysts.[66] The interest in carrying out the WGSR with liquid water rather than steam stems mainly from the considerable energy saving that this would represent.[67]

$$CO(g) + H_2O(l) \rightleftharpoons H_2(g) + CO_2(g) \quad (38)$$

The WGSR using $Fe(CO)_5$ as a catalyst precursor has been thoroughly studied.[68] Although it soon became apparent that this catalyst was unlikely to have any practical use, due to low turnover, studies of the elementary steps of the catalytic cycle provided very useful information on the reactivity of $[HFe(CO)_4]^-$.[69]

The hexacarbonyls of the Group 6B transition metals (Cr, Mo, W) have also been studied as catalyst precursors for the WGSR.[70] Indeed, it was soon recognized that, in contrast to $Fe(CO)_5$, these catalysts exhibit considerable tolerance to sulfur poisoning, an important attribute in the context of synthesis gas treatment.[71] The catalytic behavior of $Cr(CO)_6$ is representative of that of all three Group 6B hexacarbonylmetal compounds. Turnover numbers as high as 8530 mol H_2/mol $Cr(CO)_6$ per day can be achieved at 200 °C (initial CO pressure 20 bar).[67] These reactions exhibit considerably different kinetics as compared to the situation found in the case of $Fe(CO)_5$ (associative mechanism). Thus, the rate of hydrogen formation is found to be proportional to the amount of $Cr(CO)_6$ and inversely proportional to the CO pressure, and increases with base concentration. The overall kinetics led the authors to propose a dissociative mechanism based on formate decomposition [Equation (39)−(45)].[67]

$$CO + OH^- \xrightarrow{\text{fast}} HCO_2^- \quad (39)$$

$$Cr(CO)_6 \rightleftharpoons Cr(CO)_5 + CO \quad (40)$$

$$Cr(CO)_5 + HCO_2^- \longrightarrow HCO_2Cr(CO)_5^- \quad (41)$$

$$HCO_2Cr(CO)_5^- \longrightarrow HCr(CO)_5^- + CO_2 \quad (42)$$

$$HCr(CO)_5^- + H_2O \longrightarrow H_2Cr(CO)_5 + OH^- \quad (43)$$

$$H_2Cr(CO)_5 \longrightarrow Cr(CO)_5 + H_2 \quad (44)$$

$$CO_2 + OH^- \longrightarrow HCO_3^- \quad (45)$$

Most of these elementary steps have been studied independently.[72−76]

However, Darensbourg et al. presented compelling evidence that the *initial* mechanistic step in the *thermal* WGSR by Group 6B carbonylmetal compounds is in fact transition metal activation of CO towards attack by hydroxide ions [Equation (46)].[29][74]

$$Cr(CO)_6 + OH^- \rightleftharpoons [(CO)_5CrCOOH]^- \xrightarrow{OH^-} [(CO)_5CrH]^- + [HCO_3]^- \quad (46)$$

Once the active $[HCr(CO)_5]^-$ is formed, the formato complex $[HCO_2Cr(CO)_5]^-$ could then be generated according to Equation (43), (44), and (41).

The dissociative step [Equation (40)] is certainly involved in the photocatalyzed WGSR.[72][75] It has been shown that UV irradiation ($\lambda < 360$ nm) accelerates the conversion of $Cr(CO)_6$ into the formate complex $[HCO_2Cr(CO)_5]^-$, which is thermally activated, as evidenced by in situ IR and UV spectroscopy. The reaction is inhibited by increased CO pressure. An activation energy of 30 kJ/mol has been determined, as compared to 145 kJ/mol for the purely *thermal* WGSR.[75]

Confirmation of the dissociative mechanism [Equation (40) and (41)] is provided by the observation that $Cr(CO)_6$ is an efficient catalyst precursor for the photocatalytic decomposition of the formate ion into H_2 and CO_2 (or HCO_3^-) [Equation (47)].[76]

$$HCO_2^- + H_2O \xrightarrow[h\nu]{[Cr(CO)_6]} H_2 + HCO_3^- \quad (47)$$

5.2. Catalytic Synthesis of Alkyl Formates from Carbon Dioxide

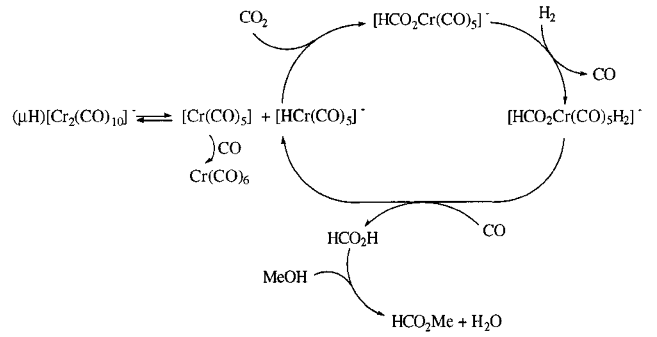
The observation that $[HCO_2M(CO)_5]^-$ complexes (M = Cr, W) undergo facile CO ligand dissociation (vide supra) led Darensbourg et al. to consider these complexes for dihydrogen binding.[77] Indeed, η^2-H_2 bonding has been evidenced (neutron diffraction studies) in some neutral Group 6B transition metal complexes such as $H_2W[P(OMe)_3]_5$.[78] Thus, $[HM(CO)_5]^-$ salts, which readily undergo insertion of CO_2 with generation of the corresponding $[HCO_2M(CO)_5]^-$ complexes, appeared to be good candidates for hydrocondensation reactions of carbon dioxide to yield alkyl formates.

Both $[PPN]^+[HCr(CO)_5]^-$ {generated in situ from $(\mu$-$H)[Cr_2(CO)_{10}]^-$} and the formato complex $[PPN]^+[HCO_2Cr(CO)_5]^-$ proved to be effective catalysts for the hydrogenation of CO_2 in methanol to provide methyl formate [Equation (48)]. Typical reaction conditions were a temperarure of 125 °C and loading pressures of CO_2 and H_2 of 250 psi each.

$$CO_2 + H_2 + MeOH \xrightarrow{[cat]} HCO_2Me + H_2O \quad (48)$$

Turnover numbers of 14−15 were achieved in reaction times of 24 h. These activities are higher than those reported for the same reaction using $[PPN]^+[HFe(CO)_4]^-$ or $[PPN]^+[HFe_3(CO)_{11}]^-$ as catalysts.[79]

At the end of catalytic runs, only $[HCO_2M(CO)_5]^-$ and $M(CO)_6$ could be detected by IR spectroscopy. The neutral hexacarbonylmetal compounds $M(CO)_6$ are catalytically inactive under the reaction conditions. One final point is that the catalytic activity was greatly diminished when the reactions were performed in the presence of added CO (100 psi loading pressure). On the basis of these observations, a catalytic cycle was proposed (Scheme 6). The possible formation of methyl formate through carbonylation of methanol (CO originating from the reverse of the WGSR) has been ruled out on the basis of labelling experiments. Methyl formate is formed by a rapid reaction of HCO_2H with methanol.

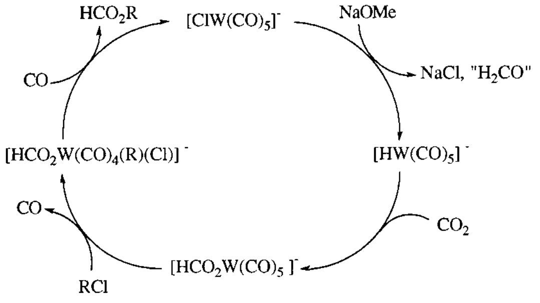


Scheme 6. Catalytic cycle for the formation of methyl formate

The catalytic synthesis of higher alkyl formates can also be performed by the reaction of alkyl halides, CO_2, and H_2 in the presence of anionic Group 6B carbonyl catalyst precursors {$[M(CO)_5Cl]^-$ or $(\mu$-$H)[M_2(CO)_{10}]^-$; M = Cr, W} and sodium alkoxides [Equation (49)].[80]

$$RX + CO_2 + H_2 \xrightarrow[NaY]{[cat]} HCO_2R + NaX + HY \quad (49)$$

In these reactions, terminal hydrides $[HM(CO)_5]^-$ are also involved as key intermediates in the generation of formato complexes $[HCO_2M(CO)_5]^-$. In Scheme 7, the proposed catalytic cycle is represented in the case of the tungsten complex.



Scheme 7. Catalytic cycle for the formation of alkyl formates

The intriguing steps of this catalytic cycle are the regeneration of the hydrides from the anionic carbonyl halides [activation of dihydrogen, Equation (50)], the kinetics of which have been studied, and the reaction of the formato complexes with RX. The latter reaction has been proposed to proceed according to Equation (51)−(53).

$$[ClW(CO)_5]^- + H_2 + NaHCO_3 \longrightarrow [HW(CO)_5]^- + NaCl + H_2CO_3 \qquad (50)$$

$$[HCO_2W(CO)_5]^- \rightleftharpoons [HCO_2W(CO)_4]^- + CO \qquad (51)$$

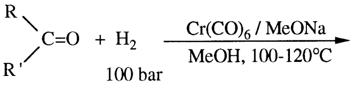
$$[HCO_2W(CO)_4]^- + nBuCl \longrightarrow HCO_2W(CO)_4(nBu)(Cl)]^- \qquad (52)$$

$$HCO_2W(CO)_4(nBu)(Cl)]^- \xrightarrow{CO} [Cl(W(CO)_5]^- + HCO_2nBu \qquad (53)$$

It must be noted that such an oxidative addition of alkyl halides to $[W(CO)_5X]^-$ species [Equation (52)] is without precedent. Nevertheless, this mechanism [Equation (51)−(53)] is consistent with the experimental results.

5.3. Catalytic Hydrogenations of Aldehydes and Ketones

The first report on the use of carbonylchromium derivatives as catalysts for the hydrogenation of ketones was that of Marko et al. in 1985.[51] The hydrogenation of ketones was found to be catalyzed by $Cr(CO)_6$ in the presence of NaOMe in methanol under 100 bar H_2 at 100−120 °C [Equation (54)].

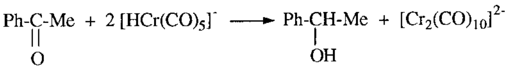


$$\underset{R'}{\overset{R}{>}}C{=}O + \underset{100\ bar}{H_2} \xrightarrow[MeOH,\ 100\text{-}120°C]{Cr(CO)_6\ /\ MeONa} \underset{R'}{\overset{R}{>}}CH\text{-}OH \qquad (54)$$

Both aliphatic and aromatic ketones could be hydrogenated in > 98% yield within 3 h (Table 4). Aromatic aldehydes were also hydrogenated, whereas aliphatic ones proved to be prone to secondary reactions.

In these reactions, $Cr(CO)_6$ is a more active catalyst precursor than $W(CO)_6$, but less active than $Mo(CO)_6$, which can be used at lower temperatures.

The mechanism of this catalytic reaction has been studied.[51] The stoichiometric reaction of $[Et_4N]^+$-$[HCr(CO)_5]^-$ with acetophenone (no solvent) was monitored by GC and IR analysis. The results were interpreted in terms of Equation (55), where both H atoms involved in the reduction originate from $[HCr(CO)_5]^-$, a proposal that has been criticized,[81] but also seems to be valid for the reduction of cyclohexanone with $[K]^+[HCr(CO)_5]^-$.[49]



$$Ph\text{-}\underset{\underset{O}{\|}}{C}\text{-}Me + 2\,[HCr(CO)_5]^- \longrightarrow Ph\text{-}\underset{\underset{OH}{|}}{CH}\text{-}Me + [Cr_2(CO)_{10}]^{2-} \qquad (55)$$

Table 4. Hydrogenation of carbonyl compounds in the presence of $Cr(CO)_6$/NaOMe catalyst under H_2 pressure

Carbonyl compound	Conv. to alcohol (%)[a]
acetophenone	99.8
cyclohexanone	100
acetone	100
isobutyl methyl ketone	98.8
benzaldehyde	99.6
methyl benzoate	0
4-*tert*-butylcyclohexanone	99.4[b]

[a] Ketone/$Cr(CO)_6$/NaOMe = 10:0.5:1 mmol in 4 mL MeOH, 100 bar H_2 at 20 °C, 120 °C, 3 h. − [b] *cis*/*trans* = 0.34:1.

On the basis of these results, it has been proposed that the intermediate is an alkoxocarbonylchromate.[51] Evidence supporting this hypothesis is provided by the stereochemical outcome of the hydrogenation of 4-*tert*-butylcyclohexanone (Table 4). With the catalytic system $Cr(CO)_6$/MeONa, the hydrogenation of 4-*tert*-butylcyclohexanone leads preferentially to the *trans* alcohol (75%). This observation led the authors to suggest that the primary intermediate formed from $[HCr(CO)_5]^-$ and the ketone is an alkoxocarbonylchromate $[RR'CHOCr(CO)_5]^-$. In such a complex, the bulky "$OCr(CO)_5$" group would tend to occupy the less crowded equatorial position of the 4-*tert*-butylcyclohexane ring. Reaction with a second equivalent of $[HCr(CO)_5]^-$ would then liberate the *trans* 4-*tert*-butylcyclohexanol.

In contrast, the analogous $Fe(CO)_5/Et_3N$ system furnishes only 38% *trans* 4-*tert*-butylcyclohexanol. The difference in behavior between $[HCr(CO)_5]^-$ and $[HFe(CO)_4]^-$ in the reactions with ketones stems from the fact that the former is hexacoordinate whereas the latter is only pentacoordinate. The reaction with $[HCr(CO)_5]^-$ may be regarded as a hydride transfer to the carbon atom of the ketone carbonyl group, leading to an alkoxocarbonylchromate $[RR'CHOCr(CO)_5]^-$. In contrast, the reaction with $[HFe(CO)_4]^-$ involves nucleophilic attack of the iron center, leading to an alkyliron hydride $[HFe(CO)_4(RR'CO)]^-$ with an Fe−C bond. These differences in the natures of the catalytic intermediates account for the different stereochemical outcomes in the hydrogenation of 4-*tert*-butylcyclohexanone with the chromium- and iron-based systems.

It has been proposed that in catalytic reactions, $[HCr(CO)_5]^-$ is generated through H_2 activation by the unsaturated species "$[Cr(CO)_5]$" [Equation (56)−(58)].

$$Cr(CO)_6 \rightleftharpoons Cr(CO)_5 + CO \qquad (56)$$

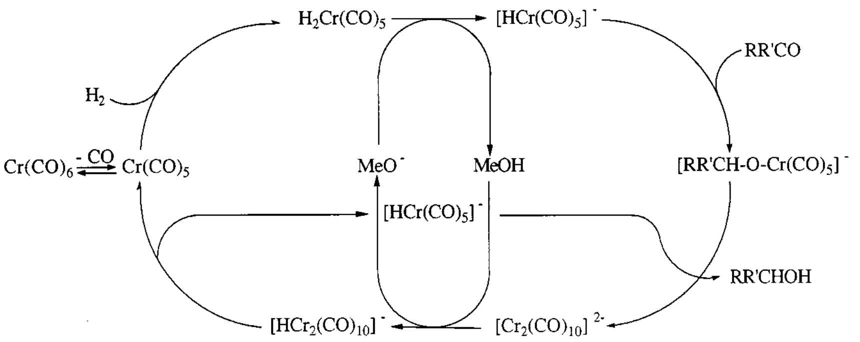
$$Cr(CO)_5 + H_2 \rightleftharpoons H_2Cr(CO)_5 \qquad (57)$$

$$H_2Cr(CO)_5 + MeO^- \rightleftharpoons [HCr(CO)_5]^- + MeOH \qquad (58)$$

The overall catalytic cycle is shown in Scheme 8.

The same monomeric anionic hydride is considered to be the active species when $[PPN]^+[Cr(CO)_5OAc]^-$ is used as a catalyst precursor.[81] Indeed, the acetatopentacarbonylchromate has been shown to be efficient for the hydrogenation of benzaldehyde and cyclohexanone under hydrogen pressure (47 bar, 125 °C) in THF (turnovers of 16−18 in 24 h).

With this system, generation of the active monomeric hydrido species has been proposed to occur according to Equation (59) and (60).



Scheme 8. Catalytic cycle for the hydrogenation of ketones with $Cr(CO)_6$/MeONa

$$[(CO)_5CrOAc]^- \rightleftharpoons [(CO)_4CrOAc]^- + CO \tag{59}$$

$$[(CO)_4CrOAc]^- \xrightarrow{H_2,\ CO} [HCr(CO)_5]^- + AcOH \tag{60}$$

Mechanistic models of H_2 activation by $[(CO)_4CrOAc]^-$ start with addition to generate an η^2-H_2 complex. Subsequent oxidative addition and reductive elimination would then generate $[HCr(CO)_5]^-$ and AcOH [Equation (60)]. As an alternative, the authors proposed an intramolecular ligand-assisted heterolytic cleavage, as represented in Figure 3.

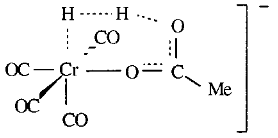
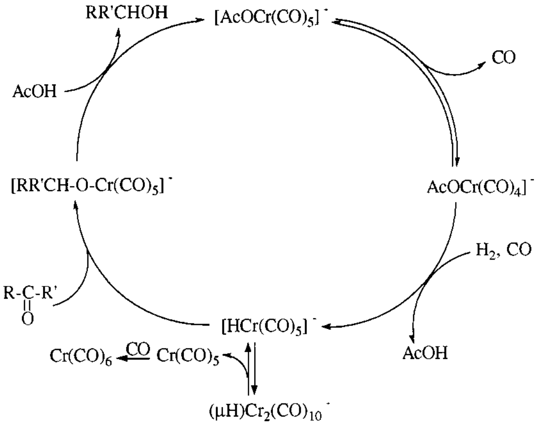


Figure 3. Intramolecular ligand-assisted heterolytic cleavage of H_2

The overall catalytic cycle is represented in Scheme 9. As a matter of fact, the hydrido binuclear complex (μ-H)$[Cr_2(CO)_{10}]^-$ ("6 o'clock position") is also an active catalyst precursor, albeit a less active one than the acetatocarbonylchromate.



Scheme 9. Catalytic cycle for the hydrogenation of ketones with $[PPN]^+[Cr(CO)_5OAc]^-$

Based on the photocatalytic decomposition of formate ion using $Cr(CO)_6$ (vide supra), in situ generation of $[HCr(CO)_5]^-$ has been used for the catalytic hydrogenation of aldehydes [Equation (61)].[82]

$$RCHO + HCO_2^- + H_2O \xrightarrow[h\nu]{Cr(CO)_6\,/\,MeOH} RCH_2OH + HCO_3^- \tag{61}$$

Typical conditions, for instance in the case of heptanal: aldehyde/HCO_2Na/$Cr(CO)_6$ = 7.2:13:0.12 mmol in 40 mL of 95% aqueous MeOH at 60 °C (60 turnovers in 100 h).

As already stated, the photocatalytic decomposition of formate ion with $Cr(CO)_6$ generates $[HCr(CO)_5]^-$.[76] In the absence of an added substrate, this decomposition reaction produces dihydrogen [Equation (62) and (63)].

$$[HCr(CO)_5]^- + H_2O \longrightarrow H_2Cr(CO)_5 + OH^- \tag{62}$$

$$H_2Cr(CO)_5 \rightleftharpoons Cr(CO)_5 + H_2 \tag{63}$$

In the presence of an aldehyde, the reactive $[HCr(CO)_5]^-$ is diverted (partially or completely) from the above WGSR cycle into an aldehyde hydrogenation cycle. On the basis of kinetic and mechanistic studies, Equation (64)−(67) have been proposed.

$$[HCr(CO)_5]^- + RCHO \rightleftharpoons [HCr(CO)_4(RCHO)]^- + CO \tag{64}$$

$$[HCr(CO)_4(RCHO)]^- \longrightarrow [Cr(CO)_4(OCH_2R)]^- \tag{65}$$

$$[Cr(CO)_4(OCH_2R)]^- + H_2O \longrightarrow [HCr(CO)_4(OCH_2R)] + OH^- \tag{66}$$

$$[HCr(CO)_4(OCH_2R)] + CO \longrightarrow RCH_2OH + Cr(CO)_5 \tag{67}$$

Replacement of one CO ligand of $[HCr(CO)_5]^-$ by the aldehyde [Equation (64)] has been proposed to account for the fact that the aldehyde hydrogenation process is inhibited by carbon monoxide.

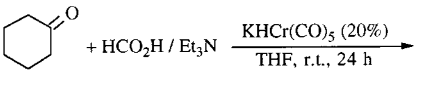
More recently, on the basis of the aforementioned stoichiometric reactivity of $KHCr(CO)_5$ with cyclohexanone (vide supra) and the hypothesis of an alkoxocarbonylchromate intermediate, a catalytic system has been designed for the transfer hydrogenation of ketones under very mild conditions.[49] In the presence of stoichiometric amounts of HCO_2H/Et_3N as a hydrogen-transfer agent, cyclohexanone was almost quantitatively (95%) reduced to cyclohexanol within 24 h using 20% $KHCr(CO)_5$ at room temp. in THF

Table 5. Transfer hydrogenation of ketones using 20% $KHCr(CO)_5$ in the presence of HCO_2H/Et_3N

Ketone	Conv. (%)[a]	Product (yield %)[b]
2-hexanone	38	2-hexanol (38)
acetophenone	25	1-phenylethanol (25)
3-methyl-2-butanone	45	3-methyl-2-butanol (45)
cyclohexanone	95	cyclohexanol (95)
4-*tert*-butylcyclohexanone	80	4-*tert*-butylcyclohexanols (80)[c]

[a] Ketone/$KHCr(CO)_5/HCO_2H/Et_3N$ = 1:0.2:1:1, 24 h at room temp. in THF. – [b] GC analysis with internal standards. – [c] *cis*/*trans* = 33:67.

[Equation (68)]. Using even lower amounts of $KHCr(CO)_5$ also proved possible [e.g. 10% $KHCr(CO)_5$: 83% yield after 24 h; 5% $KHCr(CO)_5$: 70% yield after 24 h], but complete conversion of cyclohexanone was only achieved after several days.



(68)

When the catalytic reaction was performed at 0 °C, the rate was found to be lower. However, if after 24 h at 0 °C the mixture was allowed to warm to room temperature, the expected catalytic activity was restored. From reactions conducted at 60 °C, the yield of cyclohexanol remained below 50% (24 h) and did not increase further, suggesting competitive destruction of the catalytically active species.

The above system was tested for the catalytic reduction of some representative ketones for 24 h at room temperature (Table 5).

As expected in the light of literature data on the reduction of ketones with hydridometallates,[47,51,83] cyclohexanones are more rapidly reduced than methyl ketones. In the case of 4-*tert*-butylcyclohexanone, the preponderant formation of the *trans* alcohol is consistent with the hypothesis of an alkoxocarbonylchromate intermediate (vide supra).

5.4. Catalytic Hydrogenation of Imines

In combination with NaOMe in methanol, all Group 6B carbonylmetal compounds catalyze the hydrogenation of *N*-benzylideneaniline into *N*-benzylaniline under ca. 100 bar hydrogen pressure at 60−160 °C.[57] Although $Mo(CO)_6$ is the most active of the three hexacarbonylmetal compounds at low temperatures, the best conversions are achieved using $Cr(CO)_6$. Typical conditions are a temperature of 120 °C, 100 bar initial H_2 loading, and a catalyst/substrate ratio of 1:50 (Table 6).

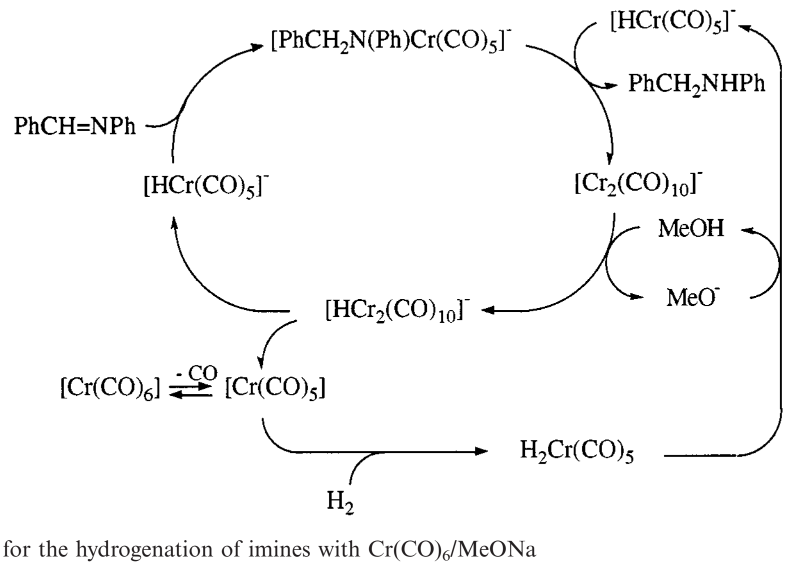
The reaction rate increases with increased H_2 pressure, while the process is inhibited by carbon monoxide. Accordingly, the active species has been suggested to be generated through the equilibrium described by Equation (69).

$$Cr(CO)_6 + H_2 + MeO^- \rightleftharpoons [HCr(CO)_5]^- + MeOH + CO \tag{69}$$

On the basis of a study of the stoichiometric reaction of $[Et_4N]^+[HCr(CO)_5]^-$ with imines (vide supra, Part 4), a catalytic cycle similar to that proposed for the hydrogenation of ketones has been suggested (Scheme 10).

6. Conclusion

The purpose of this review has been to point out the versatile properties of pentacarbonylhydridochromates



Scheme 10. Catalytic cycle for the hydrogenation of imines with $Cr(CO)_6$/MeONa

$M^+[HCr(CO)_5]^-$. These complexes are easy to prepare from $Cr(CO)_6$, and may find interesting applications as selective reducing agents in organic synthesis. As stoichiometric reagents, they have been shown to react either by H^- (or D^-) transfer or by a SET process, depending on the substrate. In comparison with similar carbonylhydridometallates, $[HCr(CO)_5]^-$ is a better H^--transfer agent than $[HFe(CO)_4]^-$ and a better electron-transfer agent than $[HW(CO)_6]^-$. As homogeneous catalysts, $M^+[HCr(CO)_5]^-$ species can be generated under various conditions and react mainly as H^--transfer agents towards electrophiles. The mechanisms of these reactions have been delineated and regeneration of the active species is generally well understood. It is to be expected that the knowledge of the different reaction pathways established for $M^+[HCr(CO)_5]^-$ species will allow extension of their application to other catalytic reactions. For instance, it is somewhat surprising that no attempted carbonylation reaction has hitherto been reported. Efforts in this area are currently underway in this laboratory.

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[1] L. Mond, C. Langer, F. Quincke, *J. Chem. Soc.* **1890**, 749–753.
[2] M. Berthelot, *C. R. Acad. Sci.* **1891**, *112*, 1343–1349.
[3] L. Mond, F. Quincke, *J. Chem. Soc.* **1891**, *59*, 604–607.
[4] J. P. Collmann, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, California, **1987**.
[5] C. D. Frohning, in *New Syntheses with Carbon Monoxide* (Ed.: J. Falbe), Springer-Verlag, New York, **1980**, p. 340–371.
[6] B. Cornils, in *New Syntheses with Carbon Monoxide* (Ed.: J. Falbe), Springer-Verlag, New York, **1980**, p. 1–225.
[7] A. Mullen, in *New Syntheses with Carbon Monoxide* (Ed.: J. Falbe), Springer-Verlag, New York, **1980**, p. 243–308.
[8] F. Calderazzo, R. Ercoli, G. Natta, *Organic Synthesis via Metal Carbonyls* (Eds.: I. Wender, P. Pino), Wiley Interscience, New York, **1968**, vol. 1, p. 1–272.
[9] J. P. Collman, *Acc. Chem. Res.* **1975**, *8*, 342–347.
[10] H. M. Colquhoun, D. J. Thompson, M. V. Twigg, *Carbonylation*, Plenum Press, New York, **1991**.
[11] J. J. Brunet, *Chem. Rev.* **1990**, *90*, 1041–1059 and references therein.
[12] J. J. Brunet, R. Chauvin, O. Diallo, F. Kindela, P. Leglaye, D. Neibecker, *Coord. Chem. Rev.* **1998**, *178–180*, 331–351.
[13] M. Y. Darensbourg, C. E. Ash, *Adv. Organomet. Chem.* **1987**, *27*, 1–50.
[14] A. Job, A. Cassal, *Bull. Soc. Chim. Fr.* **1927**, *41*, 1041–1046.
[15] G. P. Boldrini, A. Umani-Ronchi, *Synthesis* **1976**, 596–598.
[16] W. A. Herrmann, K. Öfele, C. Zybill, *Synthetic Methods of Organometallic and Inorganic Chemistry* (Ed.: W. A. Herrmann), Georg Thieme Verlag, New York, **1997**, p. 8–10.
[17] M. D. Grillone, *Inorg. Synth.* **1985**, *23*, 27–32.
[18] H. Behrens, R. Weber, *Z. Anorg. Allg. Chem.* **1957**, *291*, 122–130.
[19] H. Behrens, W. Klek, *Z. Anorg. Allg. Chem.* **1957**, *292*, 151–161.
[20] L. B. Handy, P. M. Treichel, L. F. Dahl, R. G. Hayter, *J. Am. Chem. Soc.* **1966**, *88*, 366–367.
[21] M. Y. Darensbourg, J. C. Deaton, *Inorg. Chem.* **1981**, *20*, 1644–1646.
[22] M. Y. Darensbourg, S. Slater, *J. Am. Chem. Soc.* **1981**, *103*, 5914–5915.
[23] M. Y. Darensbourg, S. Slater, *Inorg. Synth.* **1983**, *22*, 181–184.
[24] D. J. Darensbourg, A. Rokicki, M. Y. Darensbourg, *J. Am. Chem. Soc.* **1981**, *103*, 3223–3224.
[25] D. H. Gibson, F. U. Ahmed, K. R. Phillips, *Organometallics* **1982**, *1*, 679–681.
[26] M. D. Grillone, L. Palsmisano, *Transition Met. Chem.* **1989**, *14*, 81–89.
[27] J. J. Brunet, R. Chauvin, B. Donnadieu, P. Leglaye, D. Neibecker, *J. Organomet. Chem.* **1998**, *571*, 7–13.
[28] D. J. Darensbourg, J. A. Froelich, *J. Am. Chem. Soc.* **1978**, *100*, 338–340.
[29] D. J. Darensbourg, A. Rokicki, *Organometallics* **1982**, *1*, 1685–1693.
[30] M. Y. Darensbourg, R. Bau, M. W. Marks, R. R. Burch Jr., J. C. Deaton, S. Slater, *J. Am. Chem. Soc.* **1982**, *104*, 6961–6969.
[31] M. B. Smith, R. Bau, *J. Am. Chem. Soc.* **1973**, *95*, 2388–2389.
[32] R. C. Hines, K. F. Preston, J. J. Springs, A. Williams, *Organometallics* **1990**, *9*, 2298–2304.
[33] S. C. Kao, M. Y. Darensbourg, W. Schenk, *Organometallics* **1984**, *3*, 871–876.
[34] R. G. Hayter, *J. Am. Chem. Soc.* **1966**, *89*, 4376–4382.
[35] M. D. Grillone, B. B. Kedzia, *J. Organomet. Chem.* **1977**, *140*, 161–168.
[36] M. Y. Darensbourg, C. E. Ash, L. W. Arndt, C. P. Jansen, K. A. Youngdahl, Y. K. Park, *J. Organomet. Chem.* **1990**, *383*, 191–199.
[37] Y. Ruiz-Morales, G. Schreckenbach, T. Ziegler, *Organometallics* **1996**, *15*, 3920–3923.
[38] R. M. Laine, R. G. Rinker, P. C. Ford, *J. Am. Chem. Soc.* **1977**, *99*, 252–253.
[39] G. Doyle, *J. Organomet. Chem.* **1975**, *84*, 323–328.
[40] D. J. Darensbourg, A. Rokicki, *J. Am. Chem. Soc.* **1982**, *104*, 349–350.
[41] C. Bo, A. Dedieu, *Inorg. Chem.* **1989**, *28*, 304–309.
[42] S. C. Kao, P. L. Gaus, K. Youngdahl, M. Y. Darensbourg, *Organometallics* **1984**, *3*, 1601–1603.
[43] T. E. Cole, R. Pettit, *Tetrahedron Lett.* **1977**, 781–784.
[44] R. J. Kinney, W. D. Jones, R. G. Bergman, *J. Am. Chem. Soc.* **1978**, *100*, 7902–7915.
[45] S. C. Kao, M. Y. Darensbourg, *Organometallics* **1984**, *3*, 646–647.
[46] P. L. Gaus, S. C. Kao, M. Y. Darensbourg, L. W. Arndt, *J. Am. Chem. Soc.* **1984**, *106*, 4752–4755.
[47] P. L. Gaus, S. C. Kao, K. Youngdahl, M. Y. Darensbourg, *J. Am. Chem. Soc.* **1985**, *107*, 2428–2434.
[48] R. A. Grey, G. P. Pez, A. Wallo, *J. Am. Chem. Soc.* **1981**, *103*, 7536–7542.
[49] J. J. Brunet, R. Chauvin, P. Leglaye, *Eur. J. Inorg. Chem.* **1999**, 713–716.
[50] P. L. Gaus, L. M. Jones, L. A. Zamiska, *Polyhedron* **1989**, *8*, 653–657.
[51] L. Marko, Z. Nagy-Magos, *J. Organomet. Chem.* **1985**, 285, 193–203.
[52] S. C. Kao, C. N. Spillett, C. Ash, R. Lusk, Y. K. Park, M. Y. Darensbourg, *Organometallics* **1985**, *4*, 83–91.
[53] R. E. Dessy, R. L. Pohl, R. B. King, *J. Am. Chem. Soc.* **1966**, *88*, 5121–5124.
[54] C. E. Ash, P. W. Hurd, M. Y. Darensbourg, M. Newcomb, *J. Am. Chem. Soc.* **1987**, *109*, 3313–3317.
[55] M. Y. Darensbourg, B. Floris, K. A. Youngdahl, *Tetrahedron Lett.* **1989**, *30*, 1781–1784.
[56] B. Andrieu, J. J. Brunet, O. Diallo, J. Lienafa, unpublished results.
[57] J. Palagyi, Z. Nagy-Magos, L. Marko, *Transition Met. Chem.* **1985**, *10*, 336–338.
[58] W.-F. Liaw, C.-J. Liu, C.-H. Lai, *J. Chinese Chem. Soc*. **1992**, 39, 409–413.
[59] M. Y. Darensbourg, C. E. Ash, L. W. Arndt, C. P. Janzen, K. A. Youngdahl, *J. Organomet. Chem.* **1990**, *383*, 191–199.

[60] J. P. Collman, S. R. Winter, *J. Am. Chem. Soc.* **1973**, *95*, 4089−4090.
[61] C. P. Casey, S. M. Neumann, *J. Am. Chem. Soc.* **1976**, *98*, 5395−5396.
[62] M. Green, A. G. Orpen, I. D. Salter, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1984**, 2497−2503.
[63] K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42−P43.
[64] C. L. Thomas, *Catalytic Processes and Proven Catalysts*, Academic Press, New York, **1970**.
[65] K. Weissermel, H.-J. Arpe, *Industrial Organic Chemistry*, VCH, New York, **1993**.
[66] P. C. Ford, *Acc. Chem. Res.* **1981**, *14*, 31−37.
[67] A. D. King Jr., R. B. King, D. B. Yang, *J. Am. Chem. Soc.* **1981**, *103*, 2699−2704.
[68] R. B. King, *J. Organomet. Chem.* **1999**, *586*, 2−17, and refs. cited therein.
[69] R. G. Pearson, H. Mauermann, *J. Am. Chem. Soc.* **1982**, *104*, 500−504.
[70] R. B. King, C. C. Frazier, R. M. Hanes, A. D. King, Jr., *J. Am. Chem. Soc.* **1978**, *100*, 2925−2927.
[71] A. D. King, R. B. King, D. B. Yang, *J. Chem. Soc., Chem. Commun.* **1980**, 529−530.
[72] A. D. King Jr., R. B. King, E. L. Sailers, *J. Am. Chem. Soc.* **1981**, *103*, 1867−1868.
[73] W. A. R. Slegeir, R. S. Sapienza, R. Rayford, L. Lam, *Organometallics* **1982**, *1*, 1728−1730.
[74] D. J. Darensbourg, M. Y. Darensbourg, R. R. Burch, J. A. Froelich, M. J. Incorvia, *Adv. Chem. Ser.* **1979**, *173*, 106−120.
[75] H. Nagorski, M. J. Mirbach, M. F. Mirbach, *J. Organomet. Chem.* **1985**, *297*, 171−176.
[76] D. E. Linn, R. B. King, A. D. King, Jr., *J. Mol. Catal.* **1993**, *80*, 151−163.
[77] D. J. Darensbourg, C. Ovalles, *J. Am. Chem. Soc.* **1984**, *106*, 3750−3754.
[78] H. W. Choi, R. M. Gavin, E. L. Muetterties, *J. Chem. Soc., Chem. Commun.* **1979**, 1085.
[79] G. O. Evans, C. J. Newell, *Inorg. Chim. Acta* **1978**, *31*, L387−L389.
[80] D. J. Darensbourg, C. Ovalles, *J. Am. Chem. Soc.* **1987**, *109*, 330−3336.
[81] P. A. Tooley, C. Ovalles, S. C. Kao, D. J. Darensbourg, M. Y. Darensbourg, *J. Am. Chem. Soc.* **1986**, *108*, 5465−5470.
[82] D. E. Linn, Jr., R. B. King, A. D. King, Jr., *J. Mol. Catal.* **1993**, *80*, 165−179.
[83] K. Jothimony, S. Vanchesan, J. Kuriacose, *J. Mol. Catal.* **1985**, *32*, 11−16.

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