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The reaction of potassium hydridopentacarbonylchromate with acrylates. X-ray structure of $[PPN]^+[CH_3CH(COOEt)Cr(CO)_5]^-$

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Abstract

$KHCr(CO)_5$ reacts with methyl acrylate in acetonitrile to give methyl propionate after acid hydrolysis. Monitoring the reaction by IR and NMR spectroscopy showed that the reaction mainly proceeds through the 1,2-addition product $K^+[CH_3CH(COOMe)Cr(CO)_5]^-$. However, in situ formation of methyl propionate (ca. 15%) before hydrolysis suggests that part of the reaction also occurs through the 1,4-adduct $K^+[CH_3CH{=}C(OMe)OCr(CO)_5]^-$. The PPN^+ salt of the 1,2-adduct obtained from ethyl acrylate was characterized by single crystal X-ray diffraction. © 2002 Published by Elsevier Science B.V.

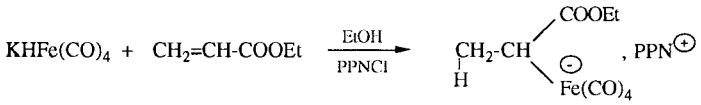
Keywords: Hydridocarbonylchromates; Acrylates; 1,2-Adduct; Alkyl–chromium bonds; X-ray structure

1. Introduction

In the last decade, we have studied the reaction of $K^+[HFe(CO)_4]^-$ with α,β-unsaturated carbonyl compounds such as acrylic acid derivatives [1,2]. This reaction promotes the selective reduction of the carbon–carbon double bond, as previously stated by Noyori et al. by using a slightly different reagent [3,4]. The mechanism of such reactions was examined in more detail in the case of ethyl acrylate and showed to involve the regioselective addition of $[HFe(CO)_4]^-$ on the activated carbon–carbon double bond, generating an alkyltetracarbonylferrate which could be isolated as bis(triphenylphosphine)iminium (PPN^+) salt (Eq. (1)) [2]. The structure of the latter was determined by X-ray crystallography [5].

On the basis of the observed regioselectivity, further investigations led us to design the first catalytic, regioselective hydrocarboxylation of acrylic acid into methylmalonic acid (Eq. (2)) [6,7].

Previously reported catalytic hydrocarboxylations of acrylic acid derivatives were known to proceed with the reverse regioselectivity, affording mainly succinic acid derivatives [8]. Interestingly, the $Fe(CO)_5$-based reaction can be performed under much milder conditions; however, its turnover frequency is low (TOF ~ 0.7 h^{-1}). This could be reflected by the reaction rate of the reduction of ethyl acrylate by $[HFe(CO)_4]^-$ [2].



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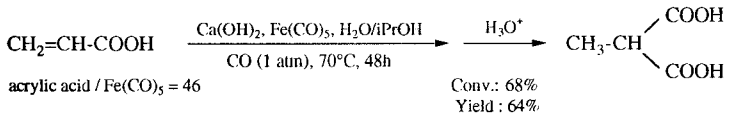

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Consequently, we recently decided to study the reactivity of the corresponding potassium hydridopentacarbonylchromate $K^+[HCr(CO)_5]^-$ [9]. Indeed, on the basis of studies by Darensbourg et al., this complex is considered to be a better hydride transfer agent than $[HFe(CO)_4]^-$ [10].

We first designed a very simple method for a reproducible, routine one-step preparation of $KHCr(CO)_5$ from $Cr(CO)_6$ [11]. As part of our study of the reactivity of this complex towards carbonyl compounds, we observed that $KHCr(CO)_5$ selectively reacts with the C=C bond of mesityl oxide to give 4-methylpentan-2-one in more 80% (GC yield) [12]. Furthermore, this reaction was much more rapid than that involving $KHFe(CO)_4$, an interesting observation in view of a possible use of $[HCr(CO)_5]^-$ for the functionalisation of α,β-unsaturated carbonyl compounds (vide supra). From that point of view, previous results from Darensbourg et al. were rather discouraging since these authors reported that the reaction of [PPN][$HCr(CO)_5$] with acrylonitrile needs 20 equivalents of acrylonitrile to consume the chromium hydride because of the formation of large amounts of oligomeric acrylonitrile side-products [13].

We wish to report here our first results on the reactivity of $KHCr(CO)_5$ with alkyl acrylates.

2. Results and discussion

When $KHCr(CO)_5$ (**1**), is reacted with one equivalent of methyl acrylate in acetonitrile at room temperature, GC–MS analysis of the reaction medium after hydrolysis indicates complete consumption of methyl acrylate within 10 min and formation of methyl propionate in ca. 90% yield (Eq. (3)).

$$KHCr(CO)_5 + CH_2{=}CH{-}COOMe \xrightarrow[10\ min]{CH_3CN,\ RT\ H_3O^+} \underset{\sim 90\%}{CH_3CH_2COOMe} \quad (3)$$

The same reaction is observed in THF and in toluene although in the latter solvent the reaction rate is much lower, probably because of the very poor solubility of $KHCr(CO)_5$ in this solvent.

Monitoring the reaction in acetonitrile by IR analysis (carbonyl ligand region) indicated the appearance of the characteristic absorptions of $K^+[(\mu\text{-}H)Cr_2(CO)_{10}]^-$ (**2**), ($\nu = 2033$ (vw), 1942 (m) cm^{-1}) and of two new absorption bands at 1901 (s, broad) and 1849 (w) cm^{-1}). The major absorptions of some remaining amounts of the starting complex **1** ($\nu_{CO} = 1886$ (s) and 1855 (m) cm^{-1}) should be buried beneath the broad band at 1901 cm^{-1}. The new absorptions at 1901 and 1849 cm^{-1} correspond to a new carbonylchromium complex which may have a geometry similar to that of $[HCr(CO)_5]^-$.

These observations led us to examine the reactivity of the dinuclear hydride **2** for the reduction of methyl acrylate. Complex **2** does not significantly react (< 5%) with methyl acrylate for 5 h in acetonitrile at room temperature. It must be noted, however, that this complex has been reported to selectively reduce the carbon–carbon double bond of α,β-unsaturated carbonyl compounds when used in *refluxing* THF for 4 h [14]. Thus it appears that $[HCr(CO)_5]^-$ is the actual reducing species in the reaction of Eq. (3).

It was obviously interesting to get more insight into the mechanism by which the reaction occurs. Indeed, although the *pentacoordinate* $[HFe(CO)_4]^-$ regioselectively adds to acrylic esters to give the corresponding alkylferrate (Eq. (1)), the reaction of the *hexacoordinate* $[HCr(CO)_5]^-$ could proceed by another way. For instance, the reaction of ketones $R_2C{=}O$ with $[HFe(CO)_4]^-$ is believed to occur via nucleophilic attack of the iron atom on the carbonyl group of the ketone, generating $[(CO)_4Fe(H){-}CR_2O]^-$ species (Fe–C bond formation) [15]. In contrast, the reaction of $[HCr(CO)_5]^-$ with ketones is believed to occur via a hydride transfer, generating the corresponding chromium alkoxide $[R_2CH{-}O{-}Cr(CO)_5]^-$ (C–H and Cr–O bonds formation) [16]. In other words, the reaction of $KHCr(CO)_5$, with methyl acrylate could a priori proceed through any of three intermediates (Fig. 1).

The presence of the potassium enolate **5** is less likely, but cannot be ruled out since the unsaturated species '$Cr(CO)_5$' is known to be easily quenched by $[HCr(CO)_5]^-$ to give the dinuclear hydride $[(\mu\text{-}H)Cr_2(CO)_{10}]^-$, a reaction which is involved in the degradation of $[HCr(CO)_5]^-$ in the presence of traces of H^+ sources [9].

The reaction of **1** with methyl acrylate was studied by NMR (CD_3CN as solvent). After 5 min reaction, the ^{1}H-NMR (400.13 MHz) spectrum of the soluble fraction exhibits three different methoxy singlets assigned to (i) unreacted methyl acrylate ($\delta_{MeO} = 3.73$ ppm) (ca. 15%), (ii) methyl propionate ($\delta_{MeO} = 3.63$ ppm) (ca.

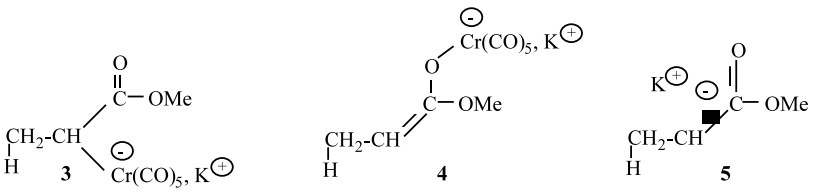

Fig. 1. Possible reaction intermediates.

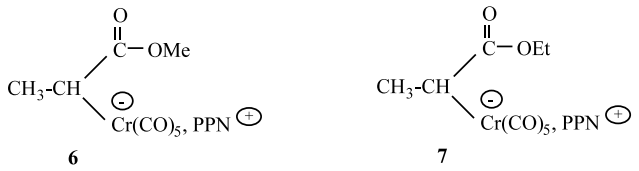

Fig. 2. PPN^+ salts of the 1,2-adducts of $[HCr(CO)_5]^-$ with methyl and ethyl acrylates.

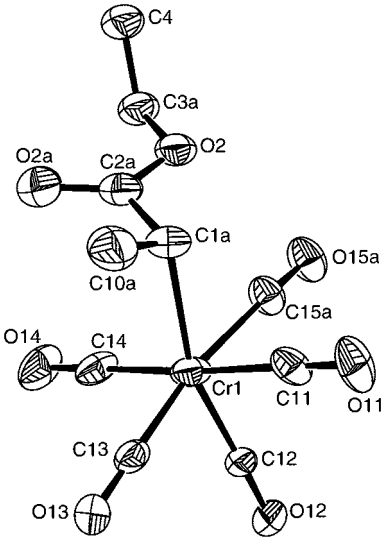

Fig. 3. Molecular structure of **7** with atom labelling. Ellipsoids represent 50% probability.

15%) and (iii) another compound which exhibits a methoxy signal at 3.48 ppm (ca. 70%). Others signals in the 0–3 ppm region were difficult to assign in the spectrum of the crude reaction mixture. Examination of the hydride region indicates the presence of some amounts of unreacted **1** ($\delta = -6.99$ ppm) and of the dinuclear hydride **2** ($\delta = -19.50$ ppm).

After evaporation of the solvent (and low boiling compounds) under reduced pressure, a new ^{1}H-NMR (400.13 MHz) spectrum was registered in CD_3CN, which indicated the presence of a nearly pure compound exhibiting the following signals: (i) a singlet at 3.48 ppm, (ii) a quadruplet at 1.72 ppm ($J = 6.6$ Hz) and (iii) a doublet at 1.42 ppm ($J = 6.6$ Hz). The ^{13}C-NMR (100.6 MHz) spectrum exhibits signals at 14.10 ppm (d, $J = 135$ Hz), 21.70 ppm (q, $J = 124$ Hz), 48.65 ppm (q, $J = 144$ Hz), 185.40 ppm (s) and 223.22 ppm (s, *cis* CO), 227.65 (s, *trans* CO) together with some minor signals in the carbonyl ligands region, assigned to **1** and **2**. The above spectral data are in full agreement with the formula of the 1,2-adduct, **3**. Solutions of **3** in CD_3CN are stable for days at room temperature under argon.

The corresponding bis(triphenylphosphine)iminium (PPN^+) salt, **6**, was easily obtained by metathesis with PPNCl, followed by classical work-up. Its NMR spectra are identical to those of the potassium salt (vide supra). The IR spectrum of **6** exhibits absorption bands at 1903 (s, sharp) and 1849 (m) cm^{-1}. Satisfactory elemental analyses were obtained for the formula $C_{45}H_{37}NO_7CrP_2$, indicating that the adduct contains only one chromium atom, as expected.

Unfortunately, it has not been possible to obtain satisfactory single crystals for **6**. However, performing the reaction of **1** with *ethyl* acrylate, followed by metathesis with PPNCl as above, allowed isolation of convenient single crystals of the adduct **7** (Fig. 2), which were submitted to X-ray diffraction analysis, confirming the proposed structure (see below).

Nevertheless, the ^{1}H-NMR observation of methyl propionate in the reaction medium before hydrolysis (vide supra) raises some questions. Indeed, control experiments indicated that **1** (tenfold excess) does not react with the isolated adduct **3** for 5 h at room temperature in acetonitrile. Furthermore, **3** was found to be poorly reactive towards water in the same solvent. Thus, the in situ formation of methyl propionate is unlikely to arise from **3**. In contrast, alkoxochromium complexes $[ROCr(CO)_5]^-$ are known to react easily with $[HCr(CO)_5]^-$ to give the stable dinuclear hydride anion and ROH [17]. These chromium alkoxides are also especially sensitive to weak acids such as traces of water [17]. It is thus proposed that, in the reaction of **1** with methyl acrylate in acetonitrile, in situ generated methyl propionate (ca. 15%) arises from **4** by either of the above reactions.

On the basis of this hypothesis, it is proposed that the reaction of **1** with methyl acrylate proceeds by initial hydride transfer on the terminal sp^2 carbon of the carbon–carbon double bond, generating an enolate intermediate which further reacts with the unsaturated '$Cr(CO)_5$' species by either the carbon or the oxygen site, as for the C/O alkylation of ambident enolate and phenoxide ions [18]. (Note, however, that concerted processes cannot be ruled out.) According to this proposal, the reaction should occur without dissociation of a carbonyl ligand from $[HCr(CO)_5]^-$. This was confirmed by further experiments which showed that the reaction proceeds exactly at the same rate (identical IR and NMR spectra after 10 min reaction) when conducted under carbon monoxide (1 atm, bubbling).

3. X-ray crystallographic study of 7

A molecular view of the anion with atom labelling scheme is shown in Fig. 3. Crystal data and structure refinement are provided in Table 1. It is interesting to note that this anion is fluxional in the solid state since one CO group and the alkyl fragment are statistically distributed on two sites around the metal atom. Only one of the conformation is shown in Fig. 3. To the best

of our knowledge, there is only one structural report on a similar alkylchromium derivative, the ylide [$(CO)_5$-CrCH(Me)(NC_5H_4Me)] [19]. A comparison of related bond lengths and angles are presented in Table 2. The geometry is roughly identical. However, although the occurrence of a disordered distribution induces large discrepancies and errors, the Cr–C(alkyl) bond is significantly shorter in **7**. The rather long Cr–C(alkyl) bond determined for [$(CO)_5$CrCH(Me)(NC_5H_4Me)] is certainly related to the presence of the large pyridinium substituent.

Table 1
Crystal data and structure refinement for **7**

Empirical formula	$[C_{10}H_9CrO_7](C_{36}H_{30}NP_2)$
Formula weight	825.67
Temperature (K)	160(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.746(5)
b (Å)	12.679(5)
c (Å)	15.661(5)
α (°)	75.546(5)
β (°)	83.668(5)
γ (°)	83.221(5)
V (Å^3)	2044.5(14)
Z	2
Crystal size (mm)	$0.46 \times 0.28 \times 0.18$
Theta range for data collection (°)	2.25–24.71
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-18 \le l \le 18$
Reflections collected	17 828
Independent reflections	6565 [$R_{int} = 0.0497$]
Completeness to theta = 24.22°	94.2%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6565/182/584
Goodness-of-fit on F^2	1.019
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0546$, $wR_2 = 0.1419$
R indices (all data)	$R_1 = 0.0924$, $wR_2 = 0.1656$
Largest difference peak and hole (e Å^{-3})	0.749 and −0.938

Table 2
Comparison of the Cr–C(alkyl) geometries in complex **7** and in the related [$(CO)_5$CrCH(Me)(NC_5H_4Me)] complex [19]

	[$(CO)_5$CrCH(Me)-(NC_5H_4Me)]	**7**
Cr(1)–C(1)	2.250 (6) Å	2.168(13); 2.188(12) Å
C(1)–C(10)	1.521(8) Å	1.527(15); 1.524(13) Å
C(1)–X(2)	1.489(7) Å [X = N]	1.441(13); 1.437(11)Å [X = CO_2Et]
Cr(1)–C(1)–C(10)	115.5(4)°	112.1(8); 111.8(6)°
Cr(1)–C(1)–X(2)	111.1(3)° [X = N]	107.6(8); 107.0(6)° [X = CO_2Et]
C(10)–C(1)–X(2)	110.7(5)° [X = N]	110.9(11); 111.2(9)° [X = CO_2Et]

4. Experimental

4.1. General

All reactions were performed under Ar using standard Schlenk tube techniques. CH_3CN (SDS) was distilled over P_2O_5 and stored under molecular sieves. CD_3CN (SDS) was used as received. All solvents were deaerated by bubbling Ar before use. NMR spectra were registered on a Bruker AC 200 or AMX 400 apparatus. IR spectra were registered on a Perkin–Elmer 1725X FTIR spectrometer with CaF_2 windows (0.5 mm). GC analyses were performed on a Hewlett–Packard HP 5890 apparatus equipped with a 30 m capillary HP 5 column and GC–MS analyses on a Hewlett–Packard HP 6890 apparatus (EC Wax, 30 m capillary column) equipped with a HP 5973 M ion detector. Elemental analyses (C, H, N) were performed on a Perkin–Elmer 2400 apparatus.

$KHCr(CO)_5$ [11] and $KHCr_2(CO)_{10}$ [20] were prepared according to published procedures.

4.2. Reaction of *1* with methyl acrylate

A solution of methyl acrylate (0.2 mmol) and toluene (internal standard, ca 0.1 mmol) in MeCN (1.5 ml) is added to a suspension of $KHCr(CO)_5$ in MeCN (0.5 ml). After 10 min stirring at room temperature, an aliquot (0.1 ml) is withdrawn, and dropped into 0.2 ml of Et_2O. The resulting solution is acidified with ca. 1 μl of trifluoroacetic acid and analysed by GC, indicating complete conversion of methyl acrylate and formation of methyl propionate in ca. 90% yield.

4.3. Synthesis of the adduct *7*

A solution of $KHCr(CO)_5$ (1 mmol) in THF (2 ml) is added to ethyl acrylate (1 mmol) in THF (6 ml). After 1 h stirring, a solution of PPNCl (0.8 mmol) in CH_2Cl_2 (5 ml) is added. After 1 h, the solvents are evaporated under reduced pressure and the resulting solid dissolved in 5 ml CH_2Cl_2. This solution is filtered over celite 545, and evaporated under vacuum at ca. −60 °C. After washing with Et_2O (2 ml), **7** is obtained as an orange solid (yield: 87%, purity (NMR): 100%). Satisfactory single crystals were obtained by very slow addition of diisopropyl ether (3 ml) to a solution of the above solid in CH_2Cl_2 (1 ml).

4.4. Crystal structure determination of *7*

Data were collected on a Stoe IPDS diffractometer. The final unit cell parameters were obtained by the

least-squares refinement of 8000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections.

The structure was solved by direct methods (SIR92) [21] and refined by least-squares procedures on F^2. All H atoms attached to carbon were introduced in calculation in idealised positions [d(CH) = 0.96 Å] and treated as riding models. One of the carbonyl group C(15)–O(15) and the alkyl CH(Me)(COOEt) fragment exchange each other on two coordination sites around the chromium leading to a disorder arrangement with an occupancy ratio of 70/30. This disordered distribution was treated using the available tools in SHELXL-97 [22]. Least-squares refinements were carried out by minimising the function $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$, having values listed in Table 1.

Calculations were carried out with the SHELXL-97 program using the integrated system WINGX(1.63) [23]. Molecular view was realised with the help of ORTEP [24].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 163293. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] For a review on $[HFe(CO)_4]^-$, see: J.J. Brunet, Chem. Rev. 90 (1990) 1041.
[2] J.J. Brunet, E. Passelaigue, J. Organomet. Chem. 375 (1989) 203.
[3] R. Noyori, I. Uemada, T. Ishigami, J. Org. Chem. 37 (1972) 1542 The exact nature of the reagent was later determined by Collman et al. [4].
[4] J.P. Collman, R.G. Finke, P.L. Matlock, R. Wahren, R.G. Komoto, J.I. Brauman, J. Am. Chem. Soc. 100 (1978) 1119.
[5] J.J. Brunet, F. Dahan, E. Passelaigue, Acta Crystallogr. Sect. C 48 (1992) 1103.
[6] J.J. Brunet, E. Passelaigue, Organometallics 9 (1990) 1711.
[7] J.J. Brunet, E. Passelaigue, FR Demande 89 13055 (Rhône-Poulenc), 1989.
[8] (a) A. Matsuda, Bull. Chem. Soc. Jpn. 42 (1969) 571; (b) J.G. Reuvers, W. Richter, R. Krummer, Ger. Offen. DE. 3,332,018 1985. Chem. Abstr. 103 (1985) 177968.
[9] J.J. Brunet, Eur. J. Inorg. Chem. (2000) 1377.
[10] S.C. Kao, C.N. Spillet, C. Ash, R. Lusk, Y.K. Park, M.Y. Darensbourg, Organometallics 4 (1985) 83.
[11] J.J. Brunet, R. Chauvin, B. Donnadieu, P. Leglaye, D. Neibecker, J. Organomet. Chem. 571 (1998) 7.
[12] J.J. Brunet, R. Chauvin, P. Leglaye, Eur. J. Inorg. Chem. (1999) 713.
[13] M.Y. Darensbourg, B. Floris, K.A. Youndahl, Tetrahedron Lett. 30 (1989) 1781.
[14] G.P. Boldrini, A. Umani-Ronchi, Synthesis (1976) 596.
[15] L. Marko, M.A. Radhi, I. Otvös, J. Organomet. Chem. 218 (1981) 369.
[16] L. Marko, Z. Nagy-Magos, J. Organomet. Chem. 285 (1985) 193.
[17] P.L. Gauss, S.C. Kao, K. Youngdahl, M.Y. Darensbourg, J. Am. Chem. Soc. 107 (1985) 2428.
[18] O.A. Reutov, A.L. Kurts, Russ. Chem. Rev. 46 (1977) 1040.
[19] F. Cohen, R. Goumont, H. Rudler, J.C. Daran, R.A. Toscano, J. Organomet. Chem. 431 (1992) C6.
[20] M.D. Grillone, L. Palmisano, Transition Met. Chem. 14 (1989) 81.
[21] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.
[22] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
[23] L.J. Farrugia, WINGX, J. Appl. Crystallogr. 32 (1999) 837.
[24] L.J. Farrugia, ORTEP3, J. Appl. Crystallogr. 30 (1997) 565.