

# Chromium(0) nitrosyl hydrides

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## Abstract

A general synthesis for the novel chromium hydrides *trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>] was developed, starting from [(η<sup>6</sup>-arene)Cr(CO)<sub>2</sub>(NO)][PF<sub>6</sub>]. Their spectroscopical properties and reactivity were studied and compared to those of the known *trans,trans*-[WH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>]. Very good correlations of all IR and NMR parameters were found between the chromium and tungsten congeners. The lighter homologues turned out to be less reactive than the heavier ones with respect to addition to C≡C and C=O bonds, which can be ascribed to the diminished hydridic polarization of the metal hydride bond in the chromium case.

## Introduction

Recently, we reported a detailed spectroscopic and structural study on tungsten hydrides of the type *trans,trans*-[WH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>], with R = Et, Me, Ph, OiPr, OMe, OPh [1]. Linear relationships could be found between Tolman's electronic parameter [2] and several IR and NMR parameters, which in turn could be directly related to the hydridic character and hence the reactivity of these compounds. In continuation of this work, we became interested in the syntheses of the, as yet unknown, chromium homologues. Their spectroscopic data and a comparison with those of the tungsten analogues might provide insight into the separation of metal and phosphine influences on these data.

## Experimental

### General

All preparations were carried out under an atmosphere of dry nitrogen by conventional Schlenk techniques. Solvents were dried and freshly distilled before use. IR spectra were recorded as a hexane solution on a Biorad FTS-45 instrument. Mass spectra were obtained from a Finnigan MAT-8230 mass spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were run on a Varian Gemini-200 spectrometer operating at 200 and 50.3 MHz, respectively, <sup>31</sup>P NMR spectra on a Gemini-300 at 121 MHz.

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### Preparations

#### *trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PEt<sub>3</sub>)<sub>2</sub>]

To a solution of [(η<sup>6</sup>-C<sub>6</sub>Me<sub>5</sub>H)Cr(CO)<sub>2</sub>(NO)][PF<sub>6</sub>] [3] (0.40 g, 0.93 mmol) in 20 ml of THF, 0.27 ml (1.85 mmol) of PEt<sub>3</sub> and 25 mg (1 mmol) LiBH<sub>4</sub> were added. After stirring for 10 min at room temperature the solvent was removed *in vacuo*. The residue was extracted with hexane and chromatographed through a silanized (Me<sub>3</sub>SiO saturated; Merck) silica column at -20 °C. Elution with hexane/THF (40:1 vol./vol.) afforded a yellow band, which after concentrating and chilling afforded yellow crystals (0.11 g, 32%). *Anal.* Calc. for C<sub>14</sub>H<sub>31</sub>CrNO<sub>3</sub>P<sub>2</sub>: C, 44.8; H, 8.3. Found: C, 44.3; H, 8.2%. MS: *m/z* 375 (*M*<sup>+</sup>), 347 (*M*<sup>+</sup> - CO), 319 (*M*<sup>+</sup> - 2CO), 288 (*M*<sup>+</sup> - H - 2CO - NO), 229 (*M*<sup>+</sup> - CO - PEt<sub>3</sub>), 201 (*M*<sup>+</sup> - 2CO - PEt<sub>3</sub>), 170 (*M*<sup>+</sup> - H - 2CO - NO - PEt<sub>3</sub>).

The use of [(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)Cr(CO)<sub>2</sub>(NO)][PF<sub>6</sub>], instead of [(η<sup>6</sup>-C<sub>6</sub>Me<sub>5</sub>H)Cr(CO)<sub>2</sub>(NO)][PF<sub>6</sub>] as a starting material in this and the following preparations resulted in a 5 to 10% improvement of the yield of the chromium hydride.

#### *trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PMe<sub>3</sub>)<sub>2</sub>]

As for the PEt<sub>3</sub> derivative. Yield 31%. *Anal.* Calc. for C<sub>8</sub>H<sub>19</sub>CrNO<sub>3</sub>P<sub>2</sub>: C, 33.0; H, 6.5. Found: C, 33.2; H, 6.5%. MS: *m/z* 291 (*M*<sup>+</sup>), 263 (*M*<sup>+</sup> - CO), 235 (*M*<sup>+</sup> - 2CO), 204 (*M*<sup>+</sup> - H - 2CO - NO), 159 (*M*<sup>+</sup> - 2CO - PMe<sub>3</sub>), 128 (*M*<sup>+</sup> - H - 2CO - NO - PMe<sub>3</sub>).

#### *trans,trans*-[CrH(CO)<sub>2</sub>(NO){P(OMe)<sub>3</sub>}<sub>2</sub>]

As for the PEt<sub>3</sub> derivative. Yield 36%. *Anal.* Calc. for C<sub>8</sub>H<sub>19</sub>CrNO<sub>9</sub>P<sub>2</sub>: C, 24.8; H, 4.9. Found: C, 24.9;

H, 4.9%. MS:  $m/z$  387 ( $M^+$ ), 331 ( $M^+ - 2\text{CO}$ ), 300 ( $M^+ - \text{H} - 2\text{CO} - \text{NO}$ ), 207 ( $M^+ - 2\text{CO} - \text{P}(\text{OMe})_3$ ), 176 ( $M^+ - \text{H} - 2\text{CO} - \text{NO} - \text{P}(\text{OMe})_3$ ).

*trans,trans*-[CrH(CO)<sub>2</sub>(NO){P(OPh)<sub>3</sub>}<sub>2</sub>]

As for the  $\text{PET}_3$  derivative. Yield *c.* 30%. This compound could not be obtained in a pure state, and was therefore only characterized by its <sup>1</sup>H NMR and IR spectra (see text).

*trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>]

To a solution of *trans,trans*-CrBr(CO)<sub>2</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub> [4] (0.50 g, 0.67 mmol) and 1.0 g (3.8 mmol) of PPh<sub>3</sub> in 25 ml THF were added 15 mg (0.80 mmol) LiBH<sub>4</sub>. After stirring for 5 min at room temperature the solvent was removed *in vacuo* and the residue washed twice with ethanol and pentane affording a yellow solid. Yield 0.26 g (58%). *Anal.* Calc. for C<sub>38</sub>H<sub>31</sub>CrNO<sub>5</sub>P<sub>2</sub>: C, 68.7; H, 4.7. Found: C, 67.4; H, 4.8%. MS:  $m/z$  663 ( $M^+$ ), 607 ( $M^+ - 2\text{CO}$ ), 345 ( $M^+ - 2\text{CO} - \text{PPh}_3$ ).

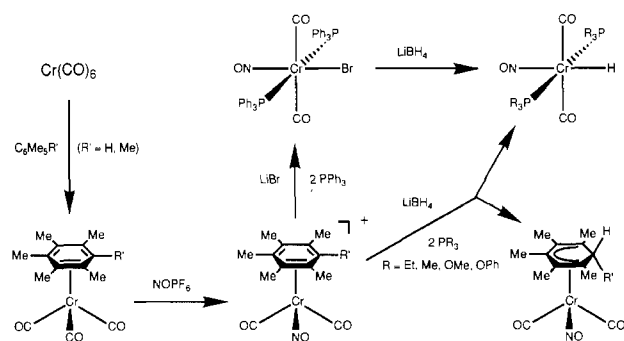
*trans,trans*-[Cr{C(CO<sub>2</sub>Me)=CH<sub>2</sub>}-  
(CO)<sub>2</sub>(NO)(PMe<sub>3</sub>)<sub>2</sub>]

A solution of 0.30 g (1.0 mmol) of *trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PMe<sub>3</sub>)<sub>2</sub>] and 0.10 g (1.2 mmol) methylpropiolate in 20 ml hexane was stirred for 5 min at room temperature. Filtration over celite and subsequent chilling produced golden yellow crystals. Yield 0.36 g (93%). *Anal.* Calc. for C<sub>12</sub>H<sub>23</sub>CrNO<sub>5</sub>P<sub>2</sub>: C, 38.4; H, 6.1. Found: C, 37.9; H, 6.1%. MS:  $m/z$  375 ( $M^+$ ), 347 ( $M^+ - \text{CO}$ ), 319 ( $M^+ - 2\text{CO}$ ), 289 ( $M^+ - 2\text{CO} - \text{NO}$ ). IR (hexane): 1942 (vs, CO), 1668 (s, NO), 1692 (w, ester). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.20 (d, 8.4 Hz, 18H, P{CH<sub>3</sub>}<sub>3</sub>), 3.46 (s, 3H, OCH<sub>3</sub>), 5.41 (dt, <sup>2</sup>J(HH)=4.5 Hz, <sup>4</sup>J(HP)=4.3 Hz, 1H, vinylic H *cis*-Cr), 6.09 (dt, <sup>2</sup>J(HH)=4.5 Hz, <sup>4</sup>J(HP)=5.8 Hz, 1H, vinylic H *trans*-Cr). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 17.0 (d, 24 Hz, P{CH<sub>3</sub>}<sub>3</sub>), 49.9 (OCH<sub>3</sub>), 126.5 (t, <sup>3</sup>J(CP)=6.4 Hz, vinylic β-carbon), 171.4 (t, <sup>2</sup>J(CP)=23.5 Hz, vinylic α-carbon), 180.5 (CO<sub>2</sub>Me), 231.1 (t, <sup>2</sup>J(CP)=17.0 Hz, Cr-CO). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>): δ 11.6 (PMe<sub>3</sub>) ppm.

## Results

*Syntheses of trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>]  
(R = Et, Me, Ph, OMe and OPh)

The chromium hydrides were synthesized according to Scheme 1. Connelly and Kelly reported that the reaction of [(η<sup>6</sup>-arene)Cr(CO)<sub>2</sub>(NO)][PF<sub>6</sub>] with NaBH<sub>4</sub> affords the neutral cyclohexadienyl complex [(η<sup>5</sup>-cyclohexadienyl)Cr(CO)<sub>2</sub>(NO)] [3], as a result of a nucleophilic attack of H<sup>-</sup> on the arene ring. We found that if this reaction was carried out in the presence of two equivalents of phosphine, a concurrent attack



Scheme 1.

on the chromium centre is observed with formation of the chromium hydrides *trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>] (yield 30–40%), together with *c.* 20% of the cyclohexadienyl complex. If the sterically more demanding [(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)Cr(CO)<sub>2</sub>(NO)][PF<sub>6</sub>] was used as a starting material instead of [(η<sup>6</sup>-C<sub>6</sub>Me<sub>5</sub>H)Cr(CO)<sub>2</sub>(NO)][PF<sub>6</sub>], the attack of H<sup>-</sup> is directed somewhat more to the chromium centre, and a 5–10% better yield of the chromium hydride is obtained. Isolation and purification of the  $\text{PET}_3$ ,  $\text{PMe}_3$  and  $\text{P}(\text{OMe})_3$  derivatives was accomplished by column chromatography over silanized silica (the use of normal, rather acidic silica results in extensive decomposition) at  $-20^\circ\text{C}$  and recrystallization from hexane. Their composition was confirmed by elemental analyses and mass spectra and their constitution was in accord with NMR and IR data. The  $\text{P}(\text{OPh})_3$  derivative could not be obtained in a pure state and was therefore characterized only spectroscopically. The  $\text{PPh}_3$  derivative could also be synthesized by a simple H<sup>-</sup>/Br<sup>-</sup> metathesis starting from the known *trans,trans*-[CrBr(CO)<sub>2</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>] [4].

*Spectroscopic characteristics of trans,trans*-  
[CrH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>]

The IR and NMR data of *trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>], together with those of the tungsten congeners [1], are listed in Tables 1 and 2, respectively. The chromium and tungsten compounds are most likely isostructural, i.e. the three principal axes of the octahedron contain the two CO ligands, the two phosphorus ligands, and the NO and H ligands, respectively.

The Cr–H IR bands are of relatively strong intensity, as compared to most other M–H stretching frequencies [5]. This was also observed for the tungsten analogues, and indicates a rather strong hydridic polarization of the M–H bond. For some obscure reasons the NO bands of the  $\text{PMe}_3$  and  $\text{PET}_3$  derivatives could not be located. The three types of IR absorptions listed in Table 1 exhibit a good to excellent linear correlation with Tolman's electronic parameter ( $\nu(\text{CO})$ ): 1.000:

TABLE 1. IR data for *trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>]<sup>a</sup>

R	X <sup>b</sup>	$\nu(\text{CO})$	$\nu(\text{MH})$	$\nu(\text{NO})$
Et	6.30	1912 (1912)	1661 (1671)	<u>1633</u> (1592, 1622)
Me	8.55	1919 (1917)	1650 (1665)	<u>1631</u> (1590, 1627)
Ph <sup>c</sup>	13.25	1930 (1921)	1668 (1681)	1638 (1596, 1629)
OiPr <sup>d</sup>	19.05	<u>1946</u> (1942)	<u>1691</u> (1702)	1656 (1613, 1637)
OMe	24.10	1958 (1952)	1690 (1702)	1664 (1619, 1646)
OPh	30.20	1974 (1969)	1714 (1721)	1685 (1638)

<sup>a</sup>Hexane solution with vs, s, m intensities. Values between parentheses are those of *trans,trans*-[WH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>] taken from ref. 1; values in italics are  $\nu(\text{NO})$  of *trans,trans*-[WD(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>]. Underlined data are calculated from the formulas listed in Table 3. <sup>b</sup>Tolman parameter in cm<sup>-1</sup> taken from ref. 2b. <sup>c</sup>Data for *trans,trans*-[WH(CO)<sub>2</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>] from ref. 4, measured as a fluorolube mull. <sup>d</sup>*trans,trans*-[CrH(CO)<sub>2</sub>(NO){P(OiPr)<sub>3</sub>]<sub>2</sub>] was not synthesized.

TABLE 2. NMR data for *trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>]<sup>a</sup>

R	Cr- <sup>1</sup> H	Cr- <sup>13</sup> CO	Cr- <sup>31</sup> PR <sub>3</sub>	<sup>2</sup> J( <sup>31</sup> P- <sup>1</sup> H)	<sup>1</sup> J( <sup>31</sup> P- <sup>13</sup> C)
Et	-5.67 (-1.84)	242.2 (220.0)	53.8 (8.6)	36.6 (23.7)	15.7 (7.0)
Me	-5.46 (-1.27)	240.1 (218.7)	20.4 (-32.7)	41.0 (25.4)	16.0 (6.9)
Ph	-3.51 (0.64)	239.7 (218.2)	73.0 (28.7)	32.7 (22.4)	15.1 (6.4)
OiPr <sup>b</sup>	<u>-5.18</u> (-1.18)	<u>235.3</u> (214.1)	<u>154.6</u> (141.3)	<u>50.9</u> (31.5)	<u>23.9</u> (10.3)
OMe	-5.32 (-1.59)	232.0 (211.2)	161.5 (151.9)	53.7 (33.0)	23.7 (10.2)
OPh	-5.35 (-1.14)	<u>227.8</u> (207.5)	<u>153.0</u> (139.1)	56.5 (34.7)	<u>24.1</u> (10.4)

<sup>a</sup>Measured in C<sub>6</sub>D<sub>6</sub> at +22 °C. Data for *trans,trans*-[WH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>] are given in parentheses [1]. Underlined data are calculated from the formulas listed in Table 3. <sup>b</sup>*trans,trans*-[CrH(CO)<sub>2</sub>(NO){P(OiPr)<sub>3</sub>]<sub>2</sub>] was not synthesized.

$\nu(\text{CrH})$ : 0.953;  $\nu(\text{NO})$ : 0.990)\*, and hence also with the corresponding values of the tungsten analogues (see Table 3). Only the M-H and NO stretching frequencies of the PEt<sub>3</sub> derivative (both Cr and W) seem to fall somewhat out of the expected values based on the trends observed by Tolman. We explain this by a relatively large coupling of the *trans*-related M-H and NO stretching frequencies in this complex. This assumption seems to be justified by the fact that the  $\nu(\text{NO})$  values of the tungsten deuterides are much better in accord with Tolman's series (Table 1). The fact that the regression factor *a* is always greater than 1 for the IR data listed in Table 3 suggests that changes in the coordination sphere of chromium are 'felt' more intensively than for tungsten. This seems to be directly related to the smaller radius of chromium (1.85 Å), as compared to tungsten (2.02 Å). Finally, the excellent correlation between the IR data of the chromium and tungsten complexes allow us to calculate the missing values for the former, that is for those of the hypothetical *trans,trans*-[CrH(CO)<sub>2</sub>(NO){P(OiPr)<sub>3</sub>]<sub>2</sub>], as well as for the rather poorly resolved  $\nu(\text{NO})$  data of the chromium PMe<sub>3</sub> and PEt<sub>3</sub> derivatives (see Table 1).

All NMR parameters on the chromium hydrides that were measured (Table 2), show a good to very good

TABLE 3. Correlations between spectroscopic data of *trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>] and *trans,trans*-[WH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>]  
 $y(\text{Cr}) = a \cdot x(\text{W}) + b$ 

y, x	a	b	r <sup>a</sup>	n <sup>b</sup>
$\nu(\text{CO})$	1.051	-95	0.985	5
$\nu(\text{CrH})$	1.096	-174	0.993	5
$\nu(\text{NO})$	1.119	-149	1.000	3
$\delta(\text{Cr-}^1\text{H})$	0.877	-4.15	0.953	5
$\delta(\text{Cr-}^{13}\text{CO})$	1.128	-6.2	0.996	4
$\delta(\text{Cr-}^{31}\text{PR}_3)$	0.758	47.5	0.998	4
<sup>2</sup> J( <sup>31</sup> P- <sup>1</sup> H)	1.861	-7.7	0.991	5
<sup>2</sup> J( <sup>31</sup> P- <sup>13</sup> C)	2.334	-0.2	0.993	4

<sup>a</sup>Correlation coefficient. <sup>b</sup>No. of parameters.

correlation with those of the tungsten analogues (Table 3). Therefore, these correlations could also be used to calculate the missing values in Table 2.

The <sup>1</sup>H NMR shifts of the chromium hydrides are found at *c.* 4 ppm higher field, as compared to the corresponding values for the tungsten hydrides. This 'chromium effect' within the Group 6 metals has been observed in a number of other hydrides too, e.g. [MH(CO)<sub>5</sub>]<sup>-</sup> [6]. Interestingly, the somewhat exceptional chemical shift of the PPh<sub>3</sub> derivative is seen in both the chromium and tungsten complexes, and seems to be caused by ring current effects of the adjacent phenyl rings. The linear relationship between Cr and

\*Correlation coefficient (*r*).

W hydride shifts is only fairly good ( $r=0.953$ ). Again, we attribute this indirectly to a mere difference of atom radii, since this should result in variable distances between the phosphorus substituents and the hydride atom, which in turn causes irregular shielding effects among these complexes.

The  $^{13}\text{C}$  NMR shifts of the CO ligands in the chromium hydrides are found at *c.* 21 ppm lower field than those of tungsten, which is also seen in many other Group 6 metal carbonyls (cf.  $\text{W}(\text{CO})_6$ :  $\delta$  191.4 ppm and  $\text{Cr}(\text{CO})_6$ :  $\delta$  211.2 ppm) [7]. This trend is a general one on going to the lighter element within a certain group of the periodic table [8] and has been attributed to a lower anisotropy effect of the attached, lighter metal. However, this chemical shift difference is only approximately constant, since in the ideal case the regression factor of *a* in Table 3 should be equal to 1, which it is not ( $a=1.128$ ). This means that for lower  $^{13}\text{C}$  NMR shifts (higher shielding) the difference converges and this seems to reflect the higher M–C distance on going down the Tolman's series (and decreasing M–P distance, due to a better  $\pi$ -acceptor capability of the  $\text{PR}_3$  group)\* and hence the smaller influence of the metal anisotropy on the  $^{13}\text{C}$  NMR shift of the CO ligand.

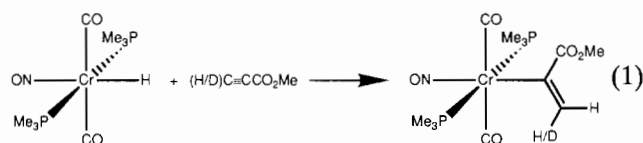
The  $^{31}\text{P}$  NMR shifts of the phosphorus ligands are much more downfield for the chromium hydrides, than for the tungsten analogues. This is also a general phenomenon among the Group 6 series [10] and again can be attributed to a systematically lower neighbouring anisotropy effect of the lighter element. Although the phosphorus ligands used and their  $^{31}\text{P}$  NMR shifts vary widely, there is an excellent correlation between the chemical shifts in the Cr and W derivatives ( $r=0.998$ ). In addition there is a very good correlation between the  $^{31}\text{P}$  NMR shifts of the free phosphorus ligands and those in the chromium ( $r=0.990$ ) and tungsten complexes ( $r=0.997$ ), a correlation that has been observed in a number of other complexes, too [11], but for which no satisfactory explanation has yet been given.

The two *cis*-related two-bond couplings to  $^{31}\text{P}$  in the chromium complexes are about twice as large as in the tungsten ones. This again is in concert with the smaller atom radius of chromium. The multiplication factor of 2.334 for  $^2J(^{31}\text{P}-^{13}\text{C})$  on going from the tungsten to the chromium derivative, is similar to the value which can be calculated for  $\text{M}(\text{CO})_5(\text{PR}_3)$ : 1.95 [7, 12].

#### Reactivity of *trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>]

The chemistry of *trans,trans*-[WH(CO)<sub>2</sub>(NO)(PR<sub>3</sub>)<sub>2</sub>] is dominated by the hydridic character of the W–H bond, which is exemplified by its affinity towards (Lewis)

acids [13] and its facile addition reaction with  $\text{C}\equiv\text{C}$  [14] and  $\text{C}=\text{O}$  bonds [15]. It is generally known that the hydrides of the lighter elements within a triad of the periodic table are less hydridic than the heavier ones [16]. It is thus expected that the chromium hydrides are less reactive than the tungsten congeners. This is confirmed by the observation that in contrast to its tungsten analogue, *trans,trans*-[CrH(CO)<sub>2</sub>(NO)(PMe<sub>3</sub>)<sub>2</sub>] does not react with either benzaldehyde, salicylaldehyde, or the methyl ester of 2-butyric acid. It does however react with the methyl ester of propionic acid by insertion of the  $\text{C}\equiv\text{C}$  bond and formation of a vinyl–chromium species (eqn. (1)).



The vinyl–chromium compound was fully characterized and its spectroscopic parameters are very similar to those of its tungsten analogue [14]. When the deuterated  $\text{DC}\equiv\text{CCO}_2\text{Me}$  was used as a substrate the  $^1\text{H}$  NMR spectrum of the insertion product showed the absence of the signal at 5.41 ppm (see 'Experimental'), which was attributed to the *cis*-Cr vinylic H atom. This confirms that, as for the tungsten analogue, a selective *trans*-insertion had occurred.

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\*A correlation was found between Cr–C bond length and  $^{13}\text{C}$  NMR shift of CO in complexes of the type  $\text{Cr}(\text{CO})_x\text{L}_{6-x}$  [9].

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