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Avances en Química, 17(3), 83-89 (2022)
Artículo científico

(η^6-Arene)-tricarbonylchromium(0) complexes used in olefin hydroformylation reaction with syngas

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Recibido: 19/07/2022 **Revisado**: 26/12/2022 **Aceptado**: 30/12/2022
https://doi.org/10.53766/AVANQUIM/2022.17.03.01

Resumen

Complejos (η^6-Areno)-tricarbonilcromo(0) utilizados en la hidroformilación de olefinas con syngas. Los aldehídos son compuestos de gran interés científico a causa de sus aplicaciones químicas, especialmente considerando sus aplicaciones como materia prima en muchos procesos industriales y en la producción de productos secundarios tales como, disolventes, detergentes biodegradables, productos farmacéuticos, tensioactivos, lubricantes, otros. En este artículo describimos el uso de los cromo carbonilos comerciales: $[Cr(CO)_6]$ (**1**), $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ (**2a**), $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_3)]$ (**2b**), $[Cr(CO)_3(\eta^6\text{-}C_8H_8O_2)]$ (**2c**) y $[Cr(CO)_3(\eta^6\text{-}C_7H_8)]$ (**3**), como precursores catalíticos en reacciones de hidroformilación de 1-hexeno y ciclohexeno, utilizando gas de síntesis CO/H_2 y CO_2/H_2, en fase homogénea. En todos los casos se optimizaron las condiciones de reacción (temperatura, presión, relación CO/H_2, disolventes, relación sustrato/catalizador) y adicionalmente se estudió la actividad catalítica empleando exceso de ligandos y usando la prueba de mercurio para verificar la homogeneidad en el sistema catalítico. En las condiciones óptimas, se obtuvo un alto porcentaje de rendimiento y buena selectividad hacia aldehídos lineales a ramificados y, para el sistema CO_2/H_2, todos los catalizadores mostraron una conversión moderada hacia aldehídos y alcoholes lineales ramificados con y sin NaCl.

Palabras claves: hidroformilación; olefinas; cromo; organometálicos.

Abstract

Aldehydes are compounds with a great scientific interest in its chemical applications, especially to consider a raw material in many industrially and process for manufacturing secondary products, such as, solvents, biodegradable detergents, pharmaceuticals, surfactants, lubricants, other. In this paper we describe the use of commercial chromium carbonyl: $[Cr(CO)_6]$ (**1**), $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$(**2a**), $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_3)]$ (**2b**), $[Cr(CO)_3(\eta^6\text{-}C_8H_8O_2)]$ (**2c**) y $[Cr(CO)_3(\eta^6\text{-}C_7H_8)]$ (**3**), as catalytic precursors in hydroformylation reactions of 1-hexene and cyclohexene with syngas CO/H_2 and CO_2/H_2 in homogeneous phase. In all cases, the reactions conditions (temperature, pressure, CO/H_2 ratio, solvents, substrate/catalyst ratio) were optimized and additionally, the catalytic activity was studied employing excess ligands condition or mercury test to verify the homogeneity in the catalytic system. Under optimal conditions, a high percent yield and good selectivity for linear versus branched aldehydes, and for the CO_2/H_2 system, all the catalysts showed moderate conversion towards linear, branched aldehydes and alcohols with and without NaCl.

Keywords: Hydroformylation; Olefins; Chromium; Homogeneous catalysis; Organometallics.

Introduction

Olefins hydroformylation reaction catalyzed by a transition metal complex is an important industrial process to produce oxygenated compounds. The hydroformylation reactions of terminal olefins yields a mixture of *n*-aldehydes (linear), iso-aldehydes (branched), and alcohols. Nowadays, nearly 10 million metric tons of linear and branched aldehydes are produced yearly by the chemical industry giants, and in much smaller quantities, small companies manufacture fine chemicals and commodities with an output of several hundred thousand[1,2]. The feasibility of this reaction has been demonstrated in a broad range of conditions such as different organic solvents, aqueous-biphasic, ionic liquids[3], supercritical carbon

dioxide (CO_2) pressure[4], and synthesis gas (syngas, CO/H_2) as reactant[5]. However, in 1971 Tucci Edmond patented this reaction employing some chromium complexes under extremes reactions conditions[6] and Dupont patented something similar for the first 30 elements of the periodic table that showed oxo-product activities[7], currently there are no references for arenes chromium complexes as a catalytic precursor in this type of reaction. Over the past 80 years, comprehensive research in this area has focused on homogeneous/heterogeneous organometallic complexes of Rh, Ru and Co catalyzed hydroformylation of olefins and syngas. Nonetheless, utilization of carbon monoxide (CO) suffers some disadvantages, such as the risk in handling, storage, transportation, and high toxicity. Therefore, activation of CO_2 using transition metal complexes has increased lately due to the interest as a renewable feedstock in the production of high value-added material, being an attractive alternative that may partially substitute fossil fuels in the petrochemical industry and also counteract the greenhouse effect[8]. For example, Tominaga and co-workers pioneered CO_2/H_2 system in hydroformylation reaction applying ruthenium cluster to achieve high conversion towards aldehydes in the presence of different type of salt[9]. This reaction proceeds through the reverse water gas shift reaction (RWGSR, $CO_2 + H_2 \rightarrow CO + H_2O$), which represent a friendly environmental alternative to be the carbon monoxide (CO) surrogate in carbonylation reactions[10]. There are many investigations in the literature concerning the evaluation of different metals and associated organic ligands in hydroformylation. In this decade, some surveys provided a concise summary about the applicability of alternative metals in hydroformylation[11,12]. This work explores the optimal reaction conditions for the hydroformylation of 1-hexene using arene chromium tricarbonyl (Figure 1(a-d)), chromium hexacarbonyl (figure 1(e)) as catalysts and CO/H_2, CO_2/H_2 as reactants. Activation of CO_2 in hydroformylation was studied with and without sodium chloride. To the best of our knowledge, this is the first example about hydroformylation of olefins in presence of CO/H_2 and CO_2/H_2 with arenes chromium complexes at low CO and CO_2 pressure.

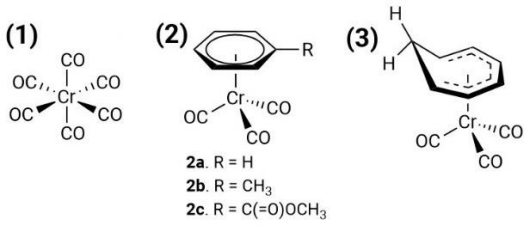


Fig. 1: Structure of $[Cr(CO)_6]$ (**1**); $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ (**2a**); $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_3)]$ (**2b**); $[Cr(CO)_3(\eta^6\text{-}C_8H_8O_2)]$ (**2c**) and $[Cr(CO)_3(\eta^6\text{-}C_7H_8)]$ (**3**).

Experimental Section

Materials

All manipulations and reactions were carried out under normal conditions. Solvents were used as supplied, and purity was verified by GC instrument. 1-hexene, cyclohexane, *cis*-, *trans*-2-hexene, cyclohexene, toluene, dimethylformamide (DMF), 1-methylimidazole (Aldrich Chemical), tetrahydrofurane (THF) (Fluka), *n*-heptane, heptanaldehyde, heptanol, (Riedel-Haen). Chromium complexes: $[Cr(CO)_6]$ **(1)**, $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ **(2a)**, $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_3)]$ **(2b)**, $[Cr(CO)_3(\eta^6\text{-}C_8H_8O_2)]$ **(2c)** and $[Cr(CO)_3(\eta^6\text{-}C_7H_8)]$ **(3)**, were supplied by Thermo Fisher Scientific (Alfa Aesar CA). The composition or integrity of complexes was corroborated using an infrared spectrum, Frontier Perkin Elmer in KBr disk. Dimethyltin dichloride, diphenyltin dichloride, di-*n*-propyltin dichloride, triphenyltin chloride and dibutyltin dichloride were supplied by Sigma Aldrich. Gases: Ar, CO, H_2, air and CO_2 were purchased from AGA-GAS.

Catalytic screening runs

The hydroformylation reactions were carried out in a high-pressure batch reactor Parr Instruments, 10 cm^3, 2500 psi maximum pressure, glass liner, internal magnetic stirrer, and temperature control. In a typical run, 1×10^{-3} g of the catalytic precursor was added into a glass liner with 2 mL of correspondent solvent and 600 equivalent of substrate (1-hexene), and 200 equivalent of substrate (1-hexene and cyclohexene) for CO_2/H_2 reactions, this solution was placed in the reactor and purged three times with Ar, after it was charged with CO/H_2 or CO_2/H_2. The reactor was heated to the desired temperature and, reaction time, at the end, the autoclave was cooled to room temperature.

Analysis of products

The reactants and products were analyzed in a Perkin-Elmer Autosystem GC 900, with FID detector and methyl silicone Quadrexcapilar column, (50 m × 0.20 mm, 0,52 μ film thickness), using H_2 as carrier gas.

Results and Discussions

Optimization of reaction parameters

Solvent effect: Table 1 showed a maximum overall conversion in **2b** in toluene and subsequently the overall conversion observed was **2a**>**2b**>**2c**>**3**; this behavior probably is due to possible interaction between toluene aromatic ring and the metallic center through a π bond, increasing the lability in the coordination sphere during the catalytic cycle[13]. On the other hand, THF favored the hydroformylation reaction probably to the ability to coordinate and stabilize the active species. Cyclohexane is a solvent with a poor possibility of stabilization of intermediate species in the catalytic reaction, showing a less overall conversion and selectivity. However, **1** and **2c** behaves differently; in this case probably the chromium complexes stabilize an intermediary species with THF and cyclohexane and much better in toluene, but the possibility is much lower with the other chromium complexes. Because toluene presents the best overall conversion, it was selected as solvent in subsequent experiments.

Table 1. Solvent optimization.

Complexes	Solvent	% Conv.	% Isom.	% Hyd.	% *n*-heptanal	% Branch.
1	THF	54.72	8.25	16.50	19.49	10.48
	Cyclohexane	53.72	14.75	29.50	6.24	3.23
	Toluene	34.70	10.38	20.76	2.94	0.62
2a	THF	54.72	8.25	16.50	19.49	10.48
	Cyclohexane	29.04	7.24	14.49	5.41	1.9
	Toluene	95.18	24.68	49.37	14.55	6.58
2b	THF	43.00	3.79	28.72	5.71	4.78
	Cyclohexane	10.11	9.03	–	1.08	–
	Toluene	94.89	8.93	–	52.66	35.06
2c	THF	60.02	7.76	13.35	24.53	14.38
	Cyclohexane	39.34	36.74	–	1.53	1.07
	Toluene	97.00	10.71	5.03	45.55	35.71
3	THF	2.03	–	–	1.49	0.54
	Cyclohexane	3.13	–	–	2.36	0.77
	Toluene	97.48	6.66	23.93	39.45	27.44

% Conv.: Total conversion, % Isom: isomerization, % Hyd.: hydrogenation, % Branch.: branched aldehydes. Substrate: 1-hexene; temperature: 180°C; substrate/catalyst ratio: 600:1; reaction time: 24 hours; pressure: 1000 psi; ratio [CO/H_2] (1:1).

Table 2. Temperature optimization.

Complexes	T(°C)	% Conv.	% Isom.	% Hyd.	% *n*-heptanal	% Branch.
1	120	5.4	0.91	1.82	2.67	–
	140	15.79	3.60	7.20	3.03	1.96
	160	74.56	8.25	16.30	39.33	10.48
	180	86.46	12.72	25.44	36.87	11.43
2a	120	54.20	12.07	24.14	13.44	4.55
	140	81.26	15.12	30.24	26.36	9.54
	160	91.36	24.77	49.54	11.74	5.31
	180	94.55	3.08	10.20	45.55	35.72
2b	120	48.65	11.32	22.64	11.30	3.66
	140	96.05	25.39	50.78	12.21	7.67
	160	94.94	2.93	5.86	49.82	36.33
	180	96.66	2.98	5.96	52.66	35.00
2c	140	24.78	11.56	12.16	1.06	–
	160	32.33	15.85	13.35	2.40	0.73
	180	99.08	3.11	16.45	45.00	34.52
3	145	14.66	2.87	8.31	2.67	0.81
	155	19.45	3.96	11.31	3.03	1.15
	175	98.56	8.34	25.35	39.33	25.54
	185	98.01	7.39	25.50	36.87	28.25

% Conv.: Total conversion, % Isom: isomerization, % Hyd.: hydrogenation, % Branch.: branched aldehydes. Substrate: 1-hexene; solvent: toluene, substrate/catalyst ratio: 600:1; reaction time: 24 hours; pressure: 1000 psi; ratio [CO/H_2] (1:1).

Table 3. Pressure optimization.

Complexes	Press. (psi)	% Conv.	% Isom.	% Hyd.	% *n*-heptanal	% Branch.
1	600	7.8	6.17	–	1.21	0.42
	800	24.50	20.14	–	3.28	1.08
	1000	86.46	12.72	25.44	36.87	11.43
	1200	63.39	38.15	–	13.81	11.43
2a*	600	23.25	4.46	15.86	2.93	–
	800	41.37	11.46	20.68	4.22	5.01
	1000	94.55	3.08	10.2	45.55	35.72
	1200	77.04	1.96	15.15	36.97	3.66
2b	600	16.30	0.44	15.86	–	–
	800	38.82	18.14	20.68	–	–
	1000	91.20	-	15.15	53.68	22.37
	1200	31.40	12.28	–	13.73	5.39
2c	600	23.25	4.46	15.86	2.93	–
	800	41.38	11.46	20.68	4.22	5.01
	1000	99.99	13.71	-	45.55	35.72
	1200	99.28	1.96	15.15	36.97	25.90
3	600	7.82	–	3.28	4.54	–
	800	54.74	5.27	23.04	18.23	8.20
	1000	97.48	6.66	23.93	39.45	27.44
	1200	88.32	–	3.31	57.70	27.31

% Conv.: Total conversion, % Isom: isomerization, % Hyd.: hydrogenation, % Branch.: branched aldehydes. Temperature: 180 °C, substrate: 1-hexene; solvent: toluene, substrate/catalyst ratio: 600:1; reaction time: 24 hours; ratio [CO/H_2] (1:1). (*) In **2a** was observed production of 19.3% of 1-heptanol at 1200 psi.

Table 4. Substrate/Catalyst ratio optimization.

Complexes	S/C Ratio	% Conv.	% Isom.	% Hyd.	% *n*-heptanal	% Branch
2a	400/1	25.41	5.6	15.43	3.18	1.20
	600/1	19.21	4.96	8.6	1.35	4.30
	800/1	94.55	3.08	10.2	45.55	35.72
	1000/1	65.73	–	2.86	36.97	25.90
2b	400/1	57.26	10.76	21.52	15.22	9.76
	600/1	98.80	2.93	5.86	53.68	36.33
	800/1	50.15	15.67	31.34	1.61	1.53
	1000/1	34.27	7.81	15.62	8.07	2.77
2c	400/1	40.20	7.28	10.91	16.27	4.83
	600/1	99.08	3.11	16.45	45.00	34.52
	800/1	81.52	4.37	12.17	42.95	22.03
	1000/1	28.48	7.37	17.18	0.75	3.18
3	400/1	56.71	–	8.19	35.55	12.97
	600/1	91.33	15.00	46.82	22.27	7.24
	800/1	97.48	6.66	23.93	39.45	27.44
	1000/1	9.06	1.42	6.70	0.94	–

% Conv.: Total conversion, % Isom: isomerization, % Hyd.: hydrogenation, % Branch.: branched aldehydes. Temperature: 180 °C, substrate:1-hexene; solvent: toluene; reaction time: 24 hours; pressure: 1000 psi; ratio [CO/H_2] (1:1).

Temperature effect: According to Table 2, the efficiency of this system de-pends on the temperature employed. As the temperature increases, the catalytic activity of all chromium complexes increases exponentially. Between 140 ºC and 160 ºC, hydrogenation and hydroformylation reactions are favored. At 180 ºC the overall conversion is reached, and the system is chemoselective toward branched and linear aldehydes. At temperature higher than 180 °C, the catalyst decomposes into metallic particles[14]. Consequently, the optimal temperature selected was 180 ºC. The best catalyst under this condition was **2b**, which shows lower hydrogenation and isomerization, and a high conversion and selectivity towards oxo products, especially in a toluene medium where the stabilization of intermediary species may be possible through π-π stack interactions.

Pressure effect: Pressure effects are showed in Table 3. From 600 to 800 psi, there are low conversions towards aldehydes products, where only isomerization and hydrogenation products are observed. Previously, has reported this behavior with rhodium and ruthenium carbonyls[15]. 1000 psi was chosen as optimal pressure for this study for **2a**, **2b**, **2c** and **3**, favoring aldehyde hydroformylation products with 75% of conversion, except for **1**, which shows 48.30% of conversion towards aldehydes products and also favoring hydrogenation and isomerization reactions. Nevertheless, it is important to highlight for **2a** the reduction of the initially produced aldehydes to the corresponding 1-heptanol at 1200 psi, in this case a possible thermodynamic product.

Substrate/catalyst ratio: The Table 4 showed an optimal substrate/catalyst ratio for **2b** and **2c** of 600/1 with high conversion of the >90% in linear and branched aldehyde and very low isomerization and hydrogenation products. Whereas that the **2a** and **3** presented a major conversion (>80%) to linear and branched aldehyde with 800/1, and similarly the hydrogenation and isomerization is very low. This result is especially important because the hydrogenation is a competition reaction in hydroformylation[16,17]. Here, the advantage of one reaction with respect to other is the result of the activation energies in initial steps of the reactions, which determines of rate of the reactions. It is possible that both reactions follow a common path at the beginning and then forks, that is, there is a lateral outlet for one of the reactions. Presumably, the hydrogenation reaction has less steps in the catalytic cycle, although this does not necessarily implicate that it will be faster[18]. The activation energies of the preliminary steps of the routes of hydrogenation and hydroformylation are similar and the reaction rates too, taking into consideration the stability of M─H bonds and π-M─alkene or M─(CO)─R (acyl group) complexes, which makes it difficult to predict the regioselectivity in this case.

Syngas ratio effect ($CO:H_2$): Table 5 showed that the optimal $CO:H_2$ ratio corresponds to 1:1 $CO:H_2$ with total conversion and selectivity to aldehyde products very high. However, an increment in the CO ratio decreases the activity favoring production of isomerization, hydrogenation and hydroformylation in equal parts, and increase of H_2 ratio reduces activity, and isomerization is the predominant reaction. The **2b** complex showed a different behavior when the CO ratio rise, the activity diminished and isomerization and hydrogenation are favored, while H_2 ratio increase, the activity decreases notably. On the other hand, **2c** showed a poor performance with increments in CO ratio but a major H_2 ratio implies a low activity and selectivity towards aldehydes products. This result is very important since, increase concentration of CO would stabilize a different catalytic species and for this reason the activity and selectivity can be diminished. Additionally, increase H_2 ratio, contributes to formation of hydrides chromium intermediary highly stabilized, which normally are inactive under these reaction conditions.

Table 5. Syngas ratio effect ($CO:H_2$).

Complexes	CO/H_2 Ratio	% Conv.	% Isom.	% Hyd.	% *n*-heptanal	% Branch.
1	1/1	86.46	12.72	25.44	36.87	11.43
	3/1	36.70	12.92	11.16	12.62	–
	2/1	12.99	–	10.88	2.11	–
2a	1/1	94.55	3.08	10.20	45.55	35.72
	1/2	24.20	–	19.75	4.45	–
	1/3	59.10	29.9	6.24	15.39	7.57
	3/1	83.60	16.22	32.45	16.23	18.70
	2/1	69.13	18.93	37.86	3.30	9.04
2b	1/1	98.80	2.93	5.86	36.33	53.68
	1/2	14.21	10.12	–	1.41	2.68
	1/3	–	–	–	–	–
	3/1	4.21	1.32	–	0.87	2.02
	2/1	2.11	–	–	–	2.11
2c	1/1	99.18	3.11	16.45	34.52	45.00
	1/2	42.48	11.74	–	11.67	19.07
	1/3	–	–	–	–	–
3	1/1	97.49	66.66	23.93	27.44	39.45

% Conv.: Total conversion, % Isom: isomerization, % Hyd.: hydrogenation, % Branch.: branched aldehydes. H_2 and CO Ratio, reactions conditions: Temperature: 180 °C, substrate:1-hexene; solvent: toluene; substrate/catalyst ratio: 600:1; reaction time: 24 hours; pressure: 1000 psi.

Mercury drop test

The mercury drop test[19] was carried out to confirm a hydroformylation in homogeneous phase and not through metal particles product of the chromium carbonyl decomposition. The results are presented in Table 6 and prove that the reaction does not change appreciably in the presence of the mercury drop compared with the reaction in absence of mercury drop. In conclusion, the catalytic reaction is running under homogeneous conditions, as was noted above in other catalytic system with arene chromium carbonyl complexes[20].

Table 6. Mercury drop test.

Complexes	Without mercury	With mercury
	Oxo products	
1	77.69	72.64
2a	90.72	88.14
2b	90.01	88.60
2c	79.52	74.58
3	66.89	62.64

Temperature: 180 °C, substrate/catalyst ratio: 600:1; reaction time: 24 hours; solvent: toluene; pressure 1000 psi CO/H_2 1:1. Substrate: 1-hexene.

Turnover numbers (TON) and turnover frequencies (TOF) in catalytic hydroformylation with chromium catalysts

Table 7 compiled the TON and TOF obtained for the homogeneous phase chromium catalysts. Since these results, it might be concluded that the chromium complexes **1**, **2a**, **2b**, **2c**, **3** can convert a high number of moles of 1-hexene substrate per mole of catalyst. However, to low TOF values, the hydroformylation reaction is slow, possibly because of the formation of multiple chromium/substrate species[21] a process capable of moving the chemical equilibrium to dissociated substrate, suggesting a significant diminution in reaction rate. Additionally, it is plausible that local concentrations of substrate will be affected by diffusion aspects[22]. In general terms, the catalytic behavior of arene tricarbonyl chromium(0) com plexes in olefin hydroformylation is a viable alternative to traditionally transition metal catalysts used (Rh, Ir, Ru, Pd,Pt)[23] but perhaps especially because the cost/benefit ratio, in terms of catalytic activity and selectivity is acceptable.

Table 7. Turnover numbers (TON) and turnover frequencies (TOF).

Complexes	Substrate/solvent	Time (h)	TON	TOF (h^{-1})
1			600.1	24.9
2a			593.7	24.7
2b	1-hexene/toluene	24	593.7	24.7
2c			594.5	24.8
3			584.9	24.4

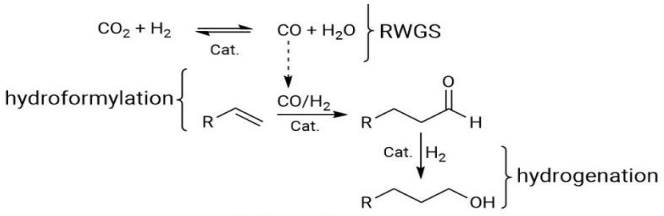
Triphenylphosphines and organotin test

This study was done to find out if the tin(II) and tin(IV) halides as additive to the system had a synergic effect over the activity of the catalyst. In facts, some studies exist about the positive influence in the hydroformylation when $SnCl_2$ is used *in situ*[24]. The studies were carried out under the optimal conditions, such as toluene solvent, a temperature of 180 °C, 1000 psi pressure with $CO:H_2$ 1:1, substrate/catalyst ratio of 600:1, and the stochiometric molar relation was 10 mol%. The following tin-halides were studied: dimethyltin dichloride, diphenyltin dichloride, di-*n*-propyltin dichloride, triphenyltin chloride and dibutyltin dichloride. The results suggest the opposite, an inhibitor effect in the catalytic activity in all cases.

Catalytic explorations using CO_2/H_2 of chromium carbonyls catalysts in hydroformylation reactions

The study of catalytic activity using CO_2/H_2 via reverse water-gas shift (RWGS)[25] activation as a source of CO (scheme 1), was carried out by means of NaCl addition as promoter to prevent excessive hydrogenation of the 1-hexene to hexane[26]. According to the Table 8, the **2a** complex in presence of CO_2/H_2, showed a poor hydroformylation activity in the solvents system. On other hand, using toluene and without NaCl was favored hydrogenation reaction, but using DMF and with NaCl, production of *n*-heptanol was observed as a reduction product of the aldehyde[27]. The **1** and **2c** chromium complexes presented moderate conversion towards *n*-heptanol, 42.19% and 15.15%, respectively. The best catalytic performance was observed in **3** under the presence of NaCl and with toluene as solvent, with 61.45% of total conversion towards aldehydes, followed of **1** with 1-methylimidazole (M-Im) and without NaCl with a 41.09%.

The results obtained with solvents as toluene, 1-methylimidazole and especially with tetrahydrofuran can be attributed to the coordinative capacity to the metallic center through forma-



Scheme 1

Table 8. Solvent influence of CO_2/H_2 via reverse water-gas shift (RWGS)in catalytic transformation of 1-hexene.

Complexes	Solvent	NaCl	% Conv	% Hyd.	% Ald.	% Alc.
1	M-Im	-	41.09	–	41.09	–
	toluene	+	1.85	–	–	1.85
	DMF	+	42.19	–	–	42.19
	THF	+	2.73	–	2.73	–
	n-heptano	+	2.65	–	2.65	–
2a	M-Im	-	8.42	–	8.42	–
	DMF	+	23.31	–	–	23.31
	M-Im	+	4.67	–	4.67	–
	toluene	-	71.75	71.75	–	–
2b	M-Im	-	5.38	–	5.38	–
	THF	+	2.73	–	2.73	–
	toluene	-	5.77	5.77	–	–
	M-Im	+	1.66	–	1.66	–
2c	M-Im	-	4.65	–	4.65	–
	DMF	+	15.15	–	–	15.15
3	toluene	-	28.87	–	28.87	–
	toluene	+	61.45	–	61.45	–
	THF	-	2.25	–	2.25	–
	THF	+	7.06	–	7.06	–
	n-heptane	-	1.3	–	1.3	–
	n-heptane	+	18.94	–	18.94	–
	M-Im	-	4.21	–	4.21	–

Temperature: 175 °C; substrate:1-hexene; salt: NaCl in equimolar quantities; substrate/catalyst ratio: 200:1; pressure: 1000 psi; ratio (CO_2/H_2) (1:1); reaction time: 24 hours. (M-Im: 1-methylimidazole; THF: tetrahydrofuran; DMF: *N*,*N*-dimethylformamide)

Table 9. Solvent influence using CO_2/H_2 via reverse water-gas shift (RWGS) in the catalytic transformation of 1-cyclohexene.

Complexes	Solvent	NaCl	% Conv	% Ald.	% Alc.
1	*n*-heptane	-	12.66	8.42	4.24
	M-Im	-	17.98	17.98	–
	DMF	-	5.92	5.92	–
	THF	+	2.47	0.93	1.54
	toluene	+	3.50	–	3.50
2a	*n*-heptane	-	3.99	2.67	1.32
	n-heptane	+	60.58	45.91	14.67
	M-Im	+	6.03	2.05	3.98
	DMF	-	6.74	–	6.74
	THF	-	3.86	3.86	–
2b	*n*-heptane	-	2.90	2.90	–
	n-heptane	+	6.71	1.86	4.85
	M-Im	-	2.07	2.07	–
	M-Im	+	7.25	7.25	–
	DMF	-	3.71	3.71	–
	THF	-	1.08	1.08	–
2c	M-Im	+	19.06	19.06	–
	DMF	+	2.79	2.79	–
	THF	-	28.67	19.20	9.47
	THF	+	0.65	0.65	–
3	*n*-heptane	+	21.78	–	–
	DMF	-	3.55	3.55	–
	DMF	+	2.43	–	–
	THF	-	1.79	1.79	–
	toluene	+	19.51	15.24	–

Temperature: 175 °C; substrate:cyclohexene; salt: NaCl in equimolar quantities; substrate/catalyst ratio: 200:1; pressure: 1000 psi; ratio (CO_2/H_2) (1:1); reaction time: 24 hours. (M-Im: 1-methylimidazole; THF: tetrahydrofuran; DMF: *N*,*N*-dimethylformamide).

tion of intermediate species[28] type $M(0)(THF)_x(CO)_y$ that are available to interact with the substrate and participate in varied forms within the catalytic cycle. The poor result observed with *n*-heptane solvent can be explained due to the low polarity of this solvent that cannot stabilize intermediate species in the catalytic cycle. In the case of 1-methylimidazole, the results are better in the absence of NaCl, obtaining likely branched aldehydes[29].

The Table 9 showed the results of the solvent influence of CO_2/H_2 via RWGS in catalytic transformation of cyclohexene. In the case of **2a** the hydroformylation was maxima with a non-polar solvent as *n*-heptane in presence of NaCl; whereas in toluene and absence of NaCl the hydrogenation reaction is promoted, but in NaCl presence the carbonylation products is favored, a behavior previously reported[25,30]. The best catalytic performance was observed in **2a**, followed for **2c** using toluene and without NaCl, with 28.67% conversion towards aldehydes and alcohol products, and 1-methylimidazole in NaCl presence with 19.06% of aldehydes, then **3** in *n*-heptane and toluene, with NaCl yielded 21.78% towards alcohol and 19.07% of oxo products respectively. The chromium carbonyl **1**with 1-methylimidazole without NaCl produce 17.98% of aldehyde, but with *n*-heptane solvent and without NaCl, a 12.66% conversion was observed in aldehydes and alcohol products. The catalyst with poor performance was **2b**, showed low activity with 1-methylimidazole and NaCl presence, yielded 7.25% towards aldehydes, and 6.71% with *n*-heptane solvent in NaCl presence, towards aldehydes and alcohols.

Conclusions

Under optimum reaction parameters ($CO:H_2$ 1000 psi, T = 180 ºC, time = 24 h and substrate/catalyst ratio: 600/1) the oxygenated products of hydroformylation of 1-hexene were observed using as catalyst the commercial chromium carbonyl: $[Cr(CO)_6]$ **(1)**, $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ **(2a)**, $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_3)]$ **(2b)**, $[Cr(CO)_3(\eta^6\text{-}C_8H_8O_2)]$ **(2c)** and $[Cr(CO)_3(\eta^6\text{-}C_7H_8)]$ **(3)**. The best result was observed when using toluene as solvent, and the mercury drop test showed undoubtedly that in the working all chromium catalyst operate in regular conditions of homogeneous catalysis. Respect to its catalytic efficiency was observed: **2b**>**2c**>**2a**>**1**>**3**. Furthermore, the addition of triphenylphosphines or organotin compounds did not show a positive or synergetic effect in the catalysis, on the contrary, an inhibitor effect in the catalytic activity was observed. This catalyst showed an interesting activity in CO_2 activation via reverse water-gas shift (RWGS) in catalytic transformation of the substrates 1-hexene and cyclohexene, with solvents as toluene, 1-methylimidazole and tetrahydrofuran and with NaCl addition using as promoter to prevent excessive hydrogenation. In these experimental conditions was observed the catalytic efficiency with the following sequence: **2a**> **3**> **1**> **2c**>> **2b**. The results are very interesting to the possible applications, especially because the arene chromium carbonyl constituting an economical alternative to the traditional metal complexes catalyst of rhodium, ruthenium, palladium, iridium, among others. Additionally, the possibilities in green chemistry will be remarkable, with a substrate/catalyst ratio: 600/1 in accessible condition to CO_2 chemical activation via reverse water-gas shift (RWGS).

Acknowledgement

Thanks to CDCHT–ULA for financial support through the project C-492-99-08-AA.

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