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Thermal decomposition of homo- and heterometallic (η^6-arene)tricarbonylchromium derivatives

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Abstract

The thermal decomposition of homo- and heterometallic (η^6-arene)tricarbonylchromium complexes in dry air has been investigated by thermogravimetric analysis. The final decomposition products are characterized by X-ray powder diffractometry which confirms the formation of Cr_2O_3, PdO and Co_2CrO_4.

Keywords: (η^6-arene)tricarbonylchromium; Propargyl amines; Heterometallic compound; TGA; XRD

1. Introduction

In the last three decades, (η^6-arene)tricarbonylchromium complexes have been shown to be a versatile class of organometallic compounds because of their interesting chemical and physical properties [1–3]. Usually these properties are evaluated by spectroscopic methods such as NMR, IR, UV–Vis and electrochemical techniques. The use of thermogravimetric analysis for the characterization of (η^6-arene)tricarbonylchromium complexes has been poorly explored [4–8], despite increasing use of this technique in the characterization of organometallic complexes [9–16]. Specially, in the case of carbonyl metal compounds, thermogravimetric analysis has been useful to evaluate the influence of additional ligands on the strength of M–CO bonds in terms of their σ-donor and π-acceptor capacity.

As a part of our studies on the synthesis, characterization and reactivity of propargyl amines with platinum metals [17,18], we report here the thermal behavior of a new class of homo- and heterometallic (η^6-arene)tricarbonylchromium compounds (Chart 1) and the characterization of the final decomposition products by X-ray powder diffractometry.

2. Experimental

The compounds $YCH(R)C{\equiv}CPh[Cr(CO)_3]$ (**1a**, R=H, Y=NMe_2; **1b**, R=Me, Y=NMe_2; **1c**, R=H, Y=$N(Me)CH_2Ph$), {Pd-*trans*-$C[(Ph)Cr(CO)_3]{=}C(Cl)CH_2NMe_2(\mu\text{-}Cl)\}_2$ (**2**), {Pd-*trans*-$C[(Ph)Cr(CO)_3]{=}C(Cl)CH_2NMe_2(Cl)(Py)$} (**3**) and $[Cr(Ph)(\mu^2\text{-}\eta^2\text{-}C{\equiv}CC(H)(Me)NMe_2)Co_2(CO)_6\}(CO)_3]$ (**4**) were prepared following synthetic procedures [19].

Thermogravimetric analysis was carried out under a dynamic flow of dry (<3 ppm H_2O) synthetic (N_2+O_2) air (25 $cm^3\ min^{-1}$) at a heating rate of 20°C min^{-1}

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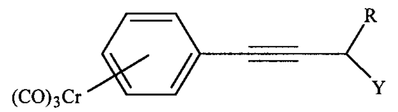
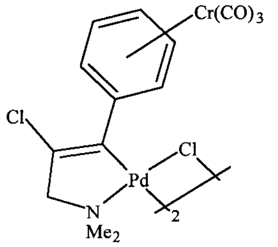


1a: R = H; Y = NMe $_2$
1b: R = Me; Y = NMe $_2$
1c: R = H; Y = N(Me)(CH $_2$Ph)



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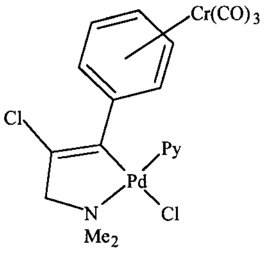

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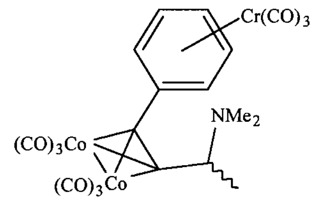

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using a TGS-2 Perkin-Elmer Thermoanalyzer. The X-ray diffractograms were obtained with a Kristalloflex 810 Siemens diffractometer with a step $2\theta=0.05°$ and using Cu K_{α} radiation (1.542 Å).

3. Results and discussion

Organometallic compounds decompose at high temperatures, usually generating as final products metallic oxides, pure metal particles and inorganic salts. The composition of the final products, however, depends on several variables such as the decomposition atmosphere (oxidizing, reducing or inert) and the organic ligands and metal center present. In the present work, the thermal decomposition of homo- and heterometallic chromium arene compounds is investigated. The purpose of this study is to reveal the influence of the propargyl amine moieties and metal fragments on the initial decomposition temperature as well as on the thermal decomposition mechanisms using thermogravimetric analysis and to characterize the final decomposition products using X-ray diffractometry. Table 1 lists the thermal analysis data for compounds **1a**–**1c** and **2**–**4**. The thermoanalytical curves for these compounds are shown in Figs. 1 and 2. Fig. 3 shows the X-ray diffraction patterns of final decomposition residues obtained from thermal decomposition of **1a**–**1c** and **2**–**4**, which have been identified by comparison with ASTM files [20].

The complex **1a** is stable up to 158°C beyond which an initial mass loss occurs corresponding to, by mass calculation, the loss of three CO groups and the uptake of 1/2 O_2. In the temperature range 198–466°C, the combustion of the $PhC{\equiv}CCH_2NMe_2$ ligand is observed followed by a consumption of 1/4 O_2. A constant mass was reached at 466°C and the residue

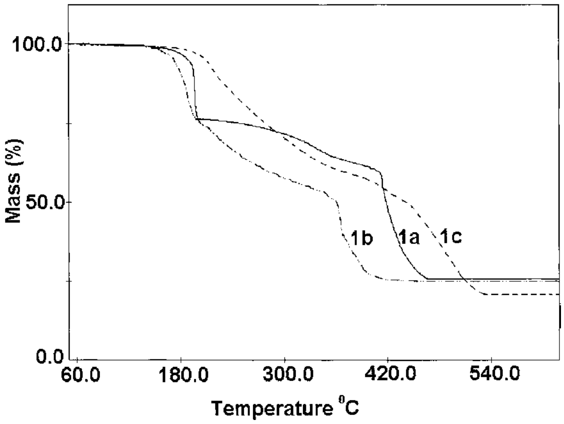

Fig. 1. TG curves of homometallic (η^6-arene)tricarbonylchromium complexes: $Me_2NCH_2C{\equiv}CPh[Cr(CO)_3]$ (———), $Me_2NCH(CH_3)C{\equiv}CPh[Cr(CO)_3]$ (– · –), $PhCH_2(Me)NCH_2C{\equiv}CPh[Cr(CO)_3]$ (- - -).

Table 1
Thermal analysis data for compounds **1a**–**1c**, and **2**–**4**

Compound	Step	T_i (°C)[a]	T_f (°C)[b]	Mechanism[c]	Δ*m* (%)[d]		Residue (%)	
					Theor	TG	Found	Calc.
1a	1	158	198	-3 CO, $+1/2$ O_2	23.05	23.61		
	2	198	466	organic ligand$+1/4$ O_2	51.18	50.70		
					(74.23)	(74.30)	25.70	25.77[e]
1b	1	139	195	-3 CO; $+1/2$ O_2	22.00	22.57		
	2	195	404	organic ligand$+1/4$ O_2	53.39	52.43		
					(75.39)	(75.00)	25.00	24.61[e]
1c	1	170	533	-3 CO, $+3/4O_2$, organic ligand	(79.51)	(79.32)	20.68	20.49[e]
2	1	60	172	-3 CO, $-Cl_2$, $+O_2$	26.16	27.77		
	2	172	525	$-$organic ligand$+1/4$ O_2	33.83	29.93		
					(58.05)	(57.70)	42.30	41.95[f]
3	1	124	147	-3 CO, $-Cl_2$, $+O_2$	22.32	21.94		
	2	147	520	$-$organic ligands$+1/4$ O_2	41.61	41.53		
					(63.93)	(63.47)	36.53	36.07[f]
4	1	85	240	-9 CO, $+2$ O_2	31.59	32.32		
	2	240	322	$-$organic ligand	29.10	28.80		
					(60.69)	(61.12)	38.88	39.31[g]

[a] T_i=initial temperature.

[b] T_f=final temperature.

[c] Mechanism proposed based on analysis of measured curves. The symbol (−) and (+) denote mass lost and mass gain, respectively.

[d] Δ*m*=mass variation; total percentual mass losses are showed in parentheses for each compound.

[e] Cr_2O_3.

[f] Cr_2O_3 and PdO.

[g] Co_2CrO_4.

was identified as Cr_2O_3 (ASTM card file 38-1479, Fig. 3(a)). The thermal decomposition of **1b** commences at 139°C with a mass loss attributable to the loss of three CO groups, as observed for **1a**, and the uptake of 1/2 O_2. The second step (195–404°C) is associated with the pyrolysis of the alkyne unit and uptake of 1/4 O_2. A constant mass was reached at 404°C and the final residue was identified as Cr_2O_3 (ASTM card file 38-1479, Fig. 3(a)). The thermoanalytical curve of **1c** shows that thermal degradation starts above 170°C. The decomposition step (170–533°C) suggests the loss of three CO groups, the uptake of 3/4 O_2 and pyrolysis of $PhC{\equiv}CCH_2N(Me)(CH_2Ph)$. A constant mass was reached at 533°C and the final decomposition product was identified as Cr_2O_3 (ASTM card file 38-1479, Fig. 3(a)).

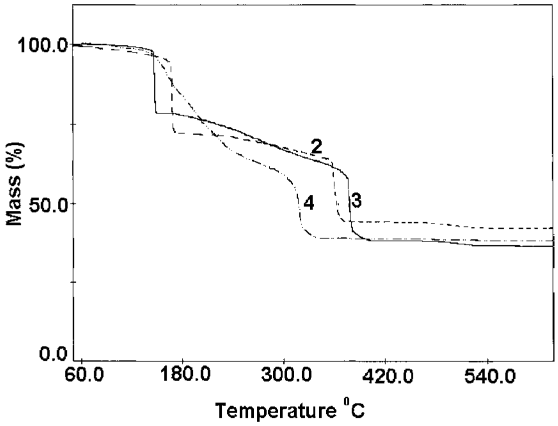

Fig. 2. TG curves of heterometallic (η^6-arene)tricarbonylchromium complexes: $\{Pd\text{-}trans\text{-}C[(Ph)Cr(CO)_3]{=}C(Cl)CH_2NMe_2(\mu\text{-}Cl)\}_2$ (- - -), $\{Pd\text{-}trans\text{-}C[(Ph)Cr(CO)_3]{=}C(Cl)CH_2NMe_2(Cl)(Py)\}$ (———), $[Cr(Ph)(\mu^2\text{-}\eta^2\text{-}C{\equiv}CC(H)\ (Me)NMe_2)Co_2(CO)_6\}(CO)_3]$ (– · –).

Summarizing the above results, the complexes **1a**–**1c** liberate CO groups at the beginning of the thermal decomposition process. However, the loss of these ligands occurs in two steps for **1a** and **1b**, and one step for **1c**, suggesting in this latter case that the thermal degradation process is faster than in **1a** and **1b**. Furthermore, it was observed that in the first step of thermal degradation of **1a** and **1b** there was a partial

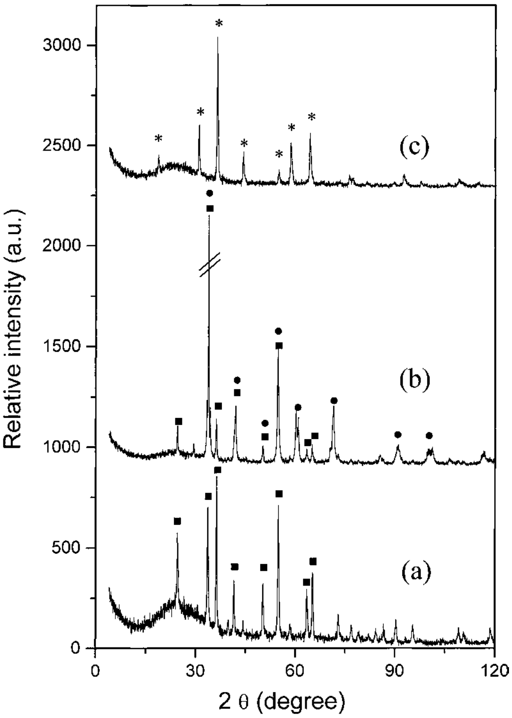

Fig. 3. X-ray diffractograms of the final decomposition products of the compounds: (a) **1a**-**1c**, (b) **2** and **3**, and (c) **4**. The crystalline phases identified in the samples are: (■) Cr_2O_3; (●) PdO; (∗) Co_2CrO_4.

consumption of O_2 suggesting the formation of Cr(II) species, probably CrO. The formation of CrO in these cases can be rationalized in terms of the presence of a reducing atmosphere during the thermal decomposition process generated from displacement of CO groups. Conversely, this behavior is not apparent during the thermal degradation of **1c** suggesting, in this case, that either this Cr(II) species is not formed or it is not detectable under the prevailing experimental conditions. Despite the production of Cr(II) species (for **1a** and **1b**), the XRD data indicate, in all cases, the formation of Cr_2O_3 as a final decomposition product (Fig. 3(a)). On the basis of the initial decomposition temperature, the following thermal stability order: **1c**>**1a**>**1b** is apparent.

The thermal decomposition of the dimeric species **2** starts at 60°C with a mass loss attributable to the loss of three CO groups, the loss of Cl_2 and the uptake of O_2. In the temperature range 172–525°C, a mass loss occurs which was attributed to the pyrolysis of the organic ligand and the uptake of 1/4 O_2. A constant mass was reached at 525°C and the final residue is identified as a mixture of Cr_2O_3 and PdO (ASTM card files 38-1479 and 06-0515, respectively; Fig. 3(b)). The thermal decomposition of monomeric species **3** starts at 124°C with a mass loss corresponding to, as observed for **2**, the loss of three CO groups, the loss of Cl_2 and the uptake of O_2. In the second step (147–520°C), a mass loss is associated with the pyrolysis of the organic ligands and the consumption of 1/4 O_2. A constant mass was reached at 520°C and the final residue was identified as a mixture of Cr_2O_3 and PdO (ASTM card files 38-1479 and 06-0515, respectively; Fig. 3(b)).

The thermogravimetric data for **2** and **3** (Table 1) show that both compounds decompose similarly generating as final products a mixture of Cr_2O_3 and PdO. These data indicate that the coordination of a pyridine ligand to a palladium atom, leads to a monomeric species, does not increase the number of decomposition steps and does not influence the composition of the final products. As expected, it was verified that the initial decomposition temperature of **2** is lower than that at **3**, indicating the higher thermal stability of **3**. The lower initial decomposition temperature of **2** can be understood considering the poor σ-donor character of a bridge chlorine atom as compared to a pyridine ligand.

The thermoanalytical curve of compound **4** shows that its thermal degradation starts above 85°C and the mass loss is associated with two steps. The first correspond to the loss of nine CO groups and the uptake of 2 O_2. The second step (240–322°C) is attributable to pyrolysis of the organic ligand. A constant mass was reached at 322°C and the final residue was identified as Co_2CrO_4 (ASTM card file 24-0326, Fig. 3(c)).

The lower initial decomposition temperature of **4** related to that found for **1b** (Table 1) indicates that the addition of the $Co_2(CO)_6$ fragment to C–C triple bond promotes a thermal destabilization. Assuming that the coordination of $Co_2(CO)_6$ unit to C–C triple bond is a reversible process [21], we can speculate that the first step of the thermal decomposition takes place with the displacement of a $Co_2(CO)_6$ fragment from C–C triple bond followed by loss of CO groups. The presence of cobalt atom generates as final decomposition product only one oxide Co_2CrO_4, which has been confirmed by X-ray diffraction (Fig. 3(c)).

4. Conclusions

The thermoanalytical curves of **1a–1c** show that the presence of different propargyl amine moieties do not cause changes in the number of decomposition steps and in the composition of the final products. However, these propargyl amine moieties influence in the initial temperature of decomposition. It was seen that the presence of a second transition metal (Pd, Co) coordinated to (η^6-C_6H_5)tricarbonylchromium unit promotes the thermal destabilization of the heterobimetallic compounds. By contrast, the formation of a mixture of two oxides in the thermal decomposition of compounds **2** and **3** (Cr, Pd), the heterometallic complex **4** (Cr, Co) promotes the exclusive formation of an unique oxide, Co_2CrO_4.

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References

[1] L.S. Hegedus, Transition Metals in the Synthesis of Complex Organic Molecules, Chapter 10, University Science Books, Mill Valley, CA, 1994.

[2] M.F. Semmelhack, in: B.M. Trost (Ed.), Comprehensive Organic Synthesis, vol. 4, Pergamon Press, Oxford, UK, 1991, p. 517.

[3] S.G. Davies, Organotransition Metal Chemistry, Applications to Organic Syntheses, Pergamon Press, Oxford, UK, 1982, p. 166, p. 1013.

[4] J.A. Connor, H.A. Skinner, Y. Virmani, J. Chem. Soc., Faraday Trans. I 69 (1973) 1218.

[5] F.A. Adedeji, D.L.S. Brown, J.A. Connor, M.L. Leung, I.M. Paz-Andrade, H.A. Skinner, J. Organomet. Chem. 97 (1975) 221.

[6] D.L.S. Brown, J.A. Connor, C.P. Demain, M.L. Leung, J.A. Martinho-Simoes, H.A. Skinner, M.T. Zafarani, J. Organomet. Chem. 142 (1977) 321.

[7] J.A. Connor, J.A. Martinho-Simoes, H.A. Skinner, M.T. Zafarani-Moattar, J. Organomet. Chem. 179 (1979) 331.

[8] G. Al-Takhin, J.A. Connor, H.A. Skinner, M.T. Zafarani-Moattar, J. Organomet. Chem. 179 (1984) 188.

[9] O.L. Casagrande Jr., F.C. Stedile, I.J.R. Baumvol, L. Amaral, A.E. Gerbase, F.O.V. Da Cunha, Polyhedron 16 (1997) 171.

[10] O.L. Casagrande Jr., A.E. Mauro, Polyhedron 16 (1997) 2193.

[11] O.L. Casagrande Jr., A.E. Mauro, Quimica Nova 19 (1996) 357.

[12] T.S. Andy Hor, L.T. Phang, Thermochim. Acta 178 (1991) 287.

[13] P.O. Lumme, H. Knuuttila, Polyhedron 14 (1995) 1553.

[14] P. Román, J.I. Beitia, A. Luque, C. Guzmán-Miralles, Polyhedron 13 (1994) 2819.

[15] H. Langfelderová, V. Jorík, J. Cervená, J. Therm. Anal. 39 (1993) 489.

[16] E. Jóna, I. Horváth, M. Kubranová, V. Jorik, J. Therm. Anal. 39 (1993) 187.

[17] J. Dupont, O.L. Casagrande Jr., A.C. Aiub, J. Beck, M. Hörner, A. Bortoluzzi, Polyhedron 13 (1994) 2583.

[18] J. Dupont, O.L. Casagrande Jr., A.C. Aiub, N.R. Basso, C.M. Mössmer, M. Hörner, A. Bortoluzzi, J. Coord. Chem. 40 (1996) 35.

[19] E.L.S. Gomes, V. Caliman, J. Dupont, O.L. Casagrande, Jr., M. Hörner, V. Young, Jr., Organometallics (1999), submitted.

[20] Powder Diffraction File of the Joint Committee on Powder Diffraction Standards, published by the International Center of Diffraction Data, Swarthmore, PA 19081 (1982).

[21] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, vol. 20, University Science Books, Mill Valley, CA, 1987, p. 861.