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$(C_5H_5)_2Zr(CO)_2$ AND $(C_5H_5)_2Hf(CO)_2$, FIRST CARBONYL DERIVATIVES OF ZIRCONOCENE AND HAFNOCENE

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Summary

Syntheses of $(C_5H_5)_2Zr(CO)_2$ and $(C_5H_5)_2Hf(CO)_2$, as well as a more facile synthesis of $(C_5H_5)_2Ti(CO)_2$, are reported. Proposed structures are supported by mass spectra, NMR, and infrared data.

Catalytic hydrogenation of diphenylacetylene in the presence of the new carbonyls and $(C_5H_5)_2Ti(CO)_2$ is examined and indicates a reduced activity for the heavier metals.

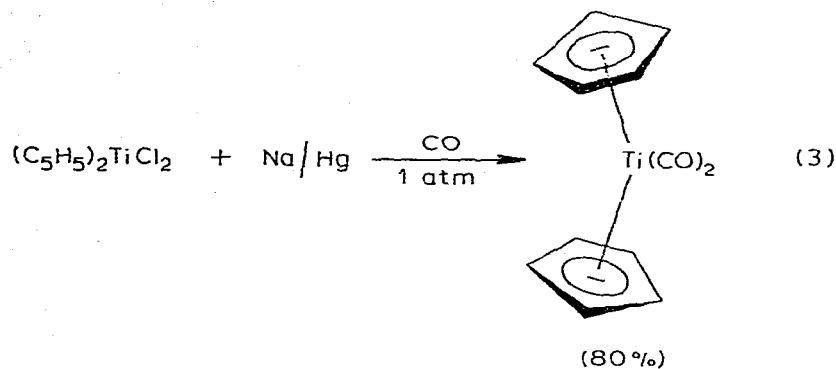
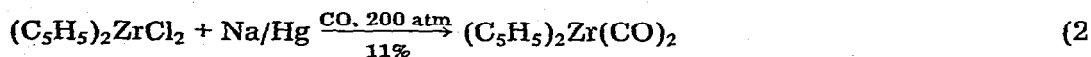
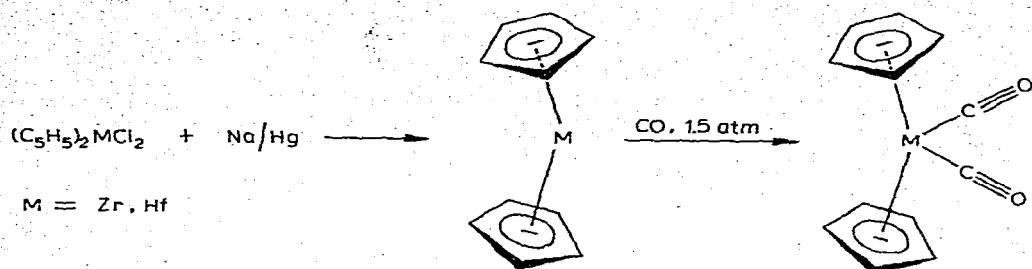
Introduction

Titanocene dicarbonyl has long been the only known carbonyl derivative of titanium [1] and, until the recent preparation of $(C_5H_5)_2Mo(CO)$ [2], $(C_5H_5)_2W(CO)$ [3], some vanadocene carbonyls [4], and $(C_5H_5)_2Ti(CO)(C_{14}H_{10})$ [5], the only known metallocene carbonyl. In view of the catalytic [5,6] and synthetic potential of such molecules [7], a synthesis of the related compounds $(C_5H_5)_2Zr(CO)_2$ and $(C_5H_5)_2Hf(CO)_2$ was pursued and is now reported.

Results and discussion

The preparation of $(C_5H_5)_2Zr(CO)_2$ and $(C_5H_5)_2Hf(CO)_2$ has been accomplished by reduction of the metallocene dichlorides in the presence of carbon monoxide and is believed to proceed via a zirconocene or hafnocene intermediate (eq. 1). Yields are increased only moderately by performing the reduction under high pressure carbon monoxide (eq. 2).

While $(C_5H_5)_2Ti(CO)_2$ has been synthesized previously, the methods have either given low yields [1] or involved synthesis of several intermediates to achieve a similar yield of $(C_5H_5)_2Ti(CO)_2$ [8,9]. Synthesis of $(C_5H_5)_2Ti(CO)_2$ by the route outlined in eq. 1 affords the best overall yields yet reported and is comparatively facile (eq. 3).



This is the first metallocene carbonyl reported for zirconium and the only known hafnium carbonyl. Previous attempts to prepare zirconium carbonyls resulted only in some compounds with Zr—O—C bonds [10]. Although preparation of $[(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CO})_2]_n$ [11] has been mentioned obliquely, the reported non-equivalent cyclopentadienyl groups make a true metallocene structure questionable. Zirconocene dicarbonyl and $(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CO})_2$, however, are genuine monomeric species with normal metallocene characteristics. They sublime readily without decomposition at $80^\circ\text{C}/10^{-4}$ torr, as brown-red and dark-red solids, respectively. The mass spectra of these solids are shown in Table 1 and strongly support the proposed structures.

The ^1H NMR spectra in C_6D_6 show a sharp singlet due to cyclopentadienyl protons at τ 4.89 ppm for $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CO})_2$ and at τ 4.97 ppm for $(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CO})_2$, indicating equivalency of the cyclopentadienyl groups. Consistent with the proposed metallocene dicarbonyl structure, the infrared spectra of the new dicarbonyls show the normal absorptions expected of $\eta\text{-C}_5\text{H}_5$ metallocenes as well as two single, sharp carbonyl absorptions. Table 2 compares the frequencies of the zirconocene and hafnocene dicarbonyl infrared absorptions with those of titanocene dicarbonyl and shows the marked solvent dependence of these absorptions.

Since carbonyl stretching frequencies have been regarded as indicators of metal atom nucleophilicity [12], it appears that metal nucleophilicity of the above complexes increases as one proceeds down the group. Photochemical gen-

TABLE 1

MASS SPECTRA OF $(C_5H_5)_2Zr(CO)_2$ AND $(C_5H_5)_2Hf(CO)_2$

Mass number	Ion	Relative intensity	Mass number	Ion	Relative intensity
366	$(C_5H_5)_2Hf(CO)_2^+$	19	276	$(C_5H_5)_2Zr(CO)_2^+$	9
338	$(C_5H_5)_2Hf(CO)^+$	18	248	$(C_5H_5)_2Zr(CO)^+$	3
310	$(C_5H_5)_2Hf^+$	100	220	$(C_5H_5)_2Zr^+$	100
282	$(C_7H_7)Hf^+$	21	194	$(C_5H_5)_2Zr^+ - [C_2H_2]$	15
258	$(C_6H_6)Hf^+$	8	180	$(C_7H_6)Zr^+$	2
256	$(C_6H_4)Hf^+$	14	168	$(C_6H_6)Zr^+$	6
230	$(C_4H_2)Hf^+$	9	155	$(C_5H_5)Zr^+$	3
218	$(C_3H_2)Hf^+$	3	140	$(C_5H_5)Zr^+ - [CH_3]$	5
155	$(C_5H_5)_2Hf^{2+}$	21	129	$(C_3H_3)Zr^+$	5
141	$(C_7H_7)Hf^{2+}$	19	128	$(C_3H_2)Zr^+$	5
128	$(C_6H_4)Hf^{2+}$	6	127	$(C_3H)Zr^+$	5
			110	$(C_5H_5)_2Zr^{2+}$	10

TABLE 2

INFRARED CARBONYL ABSORPTIONS OF GROUP IVB DICARBONYLS

	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	Solvent
$(C_5H_5)_2Ti(CO)_2$	1975	1897	hexane
$(C_5H_5)_2Zr(CO)_2$	1978	1888	hexane
$(C_5H_5)_2Hf(CO)_2$	1923	1876	hexane
$(C_5H_5)_2Zr(CO)_2$	1964	1866	THF
$(C_5H_5)_2Hf(CO)_2$	1948	1848	THF

eration of Group IVB metallocenes [9] has recently been reported as well as their "interaction" with carbon monoxide. It seems likely that treatment of this proposed source of zirconocene or hafnocene should yield $(C_5H_5)_2Zr(CO)_2$ and $(C_5H_5)_2Hf(CO)_2$, respectively.

Since $(C_5H_5)_2Ti(CO)_2$ is known to be a hydrogenation catalyst [5,6], a comparison of the hydrogenation activity of this dicarbonyl with the new zirconocene and hafnocene carbonyls was undertaken and the results are presented in Table 3.

TABLE 3

HYDROGENATION OF DIPHENYLACETYLENE

Catalyst	% $C_6H_5C\equiv CC_6H_5$ recovered	% $C_6H_5CH=CHC_6H_5$ recovered	% $C_6H_5CH_2CH_2C_6H_5$ recovered
$(C_5H_5)_2Ti(CO)_2$	23	36	41
$(C_5H_5)_2Zr(CO)_2$	60	32	8
$(C_5H_5)_2Hf(CO)_2$	95	5	0

In all cases, hydrogenation of 400 mg of diphenylacetylene at 3 atm pressure was attempted using equimolar, catalytic amounts of the dicarbonyl. Titanocene dicarbonyl is the most efficient catalyst, followed by zirconocene dicarbonyl, with hafnocene dicarbonyl being nearly inactive under the conditions employed.

Experimental

Mass spectra were obtained in a Varian MAT 111 mass spectrometer with direct inlet system. In a typical determination, the accelerating voltage was 820 V, the ionizing voltage was 80 eV, the source pressure was 5×10^{-6} torr, and the source temperature was 50°C. All spectra presented are monoisotopic for ^{90}Zr , ^{180}Hf , ^{12}C , and ^1H . Infrared spectra were determined using a Perkin-Elmer 457 infrared spectrometer. NMR spectra were determined on a Varian model T-60. All reported chemical shifts are relative to TMS and were determined in C_6D_6 . A 500 ml Parr autoclave was used for the high pressure experiments.

Hafnocene dichloride and $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$ were obtained from Alfa/Ventron, while diphenylacetylene was purchased from Aldrich Chemical Company. All solvents were distilled from LiAlH_4 prior to use and all operations were carried out under a purified nitrogen atmosphere unless otherwise noted. Microanalytical analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

1. Preparation of $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CO})_2$

$(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$ (200 mg, 0.80 mmol) was dissolved in 50 ml of dry, oxygen-free toluene. Na/Hg alloy (1.5 ml, 2.0 mmol Na/ml) was added to the solution. The mixture then was stirred at room temperature under 1 atm of carbon monoxide. After 12 h, the stirring was terminated and a red-brown or gold solution had formed. Filtration yielded a golden solution which left a dark solid when the solvent was removed in vacuo. Sublimation at 10^{-4} torr at 80°C yielded 21 mg (0.07 mmol) of purple-red, air-sensitive, $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CO})_2$ (yield ca. 9%). Anal.: Found: C, 51.7; H, 3.7; Zr, 32.7; O, 11.9 (by difference). $\text{C}_{12}\text{H}_{10}\text{O}_2\text{Zr}$ calcd.: C, 51.9; H, 3.6; Zr, 32.9; O, 11.6%.

2. Preparation of $(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CO})_2$

$(\text{C}_5\text{H}_5)_2\text{HfCl}_2$ (200 mg, 0.53 mmol) was treated exactly as described for $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CO})_2$. Upon filtration, a red solution was obtained. Evaporation of the solvent in vacuo and sublimation of the residue onto a water-cooled probe yielded 60 mg (0.16 mmol) of dark-red, air-sensitive $(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CO})_2$ (yield ca. 30%). Anal.: Found: C, 39.3; H, 2.7; Hf, 48.8; O, 9.2 (by difference). $\text{C}_{12}\text{H}_{10}\text{HfO}_2$ calcd.: C, 39.6; H, 2.7; Hf, 48.9; O, 8.8%.

3. Preparation of $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$

$(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ (500 mg, 2.00 mmol) was dissolved in 50 ml of toluene and 5 ml of Na/Hg alloy (2.0 mmol Na/ml) was added to the solution. The mixture was stirred under an atmosphere of carbon monoxide for 8 h at room temperature to yield a bright-red solution. Filtration, removal of the solvent in vacuo, followed by sublimation of the residue at 60°C/ 10^{-4} torr gave 380 mg (1.62 mmol) of bright-red $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ (yield ca. 81%) as identified by its ^1H NMR and mass spectrum.

4. Autoclave preparation of $(C_5H_5)_2Zr(CO)_2$

$(C_5H_5)_2ZrCl_2$ (200 mg, 0.80 mmol) was treated exactly as in preparation 1 except that the reaction was carried out in an autoclave under 200 atm of carbon monoxide. 25 mg (0.09 mmol) of $(C_5H_5)_2Zr(CO)_2$ (yield ca. 11%) were obtained by sublimation.

5. Hydrogenation of diphenylacetylene with $(C_5H_5)_2Zr(CO)_2$

Zirconene dicarbonyl (44 mg, 0.15 mmol) and diphenylacetylene (400 mg, 2.25 mmol) was dissolved in 30 ml of toluene and syringed into a Kontes reaction vessel which was subsequently pressurized to 3 atm with H_2 . Heating the mixture overnight at $110^\circ C$ resulted in an orange solution and a small amount of white, zirconium-containing precipitate. The solution was removed by syringe and the solvent evaporated in vacuo. The organic solids were then isolated by sublimation at $75^\circ C/10^{-3}$ torr and analyzed by volatilizing them at $215^\circ C$ into the mass spectrometer. The white, zirconium-containing precipitate was not further characterizable.

6. Hydrogenation of diphenylacetylene with $(C_5H_5)_2Hf(CO)_2$

Hafnocene dicarbonyl (57 mg, 0.15 mmol) was treated exactly as in 5. Upon hydrogenation, a light yellow solution and a small amount of white precipitate were obtained. The solution was treated as in 5, and the resulting organic solids similarly analyzed.

7. Hydrogenation of diphenylacetylene with $(C_5H_5)_2Ti(CO)_2$

Titanocene dicarbonyl (57 mg, 0.15 mmol) was treated exactly as described in 5. After hydrogenation, a blue-green solution was obtained. Solvent was removed in vacuo and substantial amounts of $Cp_2Ti(CO)_2$ remained. This carbonyl was allowed to decompose in air so that the hydrocarbons could be isolated by sublimation. Analysis was carried out as in 5.

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