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CYCLOPENTADIENYLCYCLOHEPTATRIENYLMETAL COMPOUNDS OF ZIRCONIUM, NIOBIUM, MOLYBDENUM AND CHROMIUM

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Summary

The synthesis and properties of the compounds $(C_5H_5)M(C_7H_7)$ with M = Zr and Nb are described. The Zr compound is diamagnetic; its PMR spectrum shows two singlets with intensities in the ratio of 7/5; the niobium compound has one unpaired electron per molecule. The IR and mass spectra of the compounds are discussed. The mass spectra show a rearrangement of the parent ion to the dibenzenemetal ion. The properties of the compounds indicate that they have a sandwich structure. Improved syntheses of the compounds $(C_5H_5)M(C_7H_7)$ with M = Cr and Mo are also reported.

Introduction

Cyclopentadienylcycloheptatrienylmetal compounds, containing planar C_5H_5 and C_7H_7 rings, of a number of *3d* transition metals have been reported, namely $(C_5H_5)M(C_7H_7)$ with M = Ti [1], V [2], Cr [3]. So far only one sandwich compound of this type with a *4d* transition metal has been described [4], viz. $(C_5H_5)Mo(C_7H_7)$. We report below the syntheses and some of the properties of the new sandwich compounds $(C_5H_5)M(C_7H_7)$ with M = Zr and Nb, together with improved syntheses of the compounds $(C_5H_5)M(C_7H_7)$ with M = Cr and Mo. In the case of the Mo compound especially, our method gives much better yields (about 15%) than that previously used (1-2%) [4].

Experimental

All experiments were carried out under purified nitrogen. Solvents were purified by conventional methods and freed from oxygen by repeated degassing. The starting materials $CpZrCl_3$ [5], $MCl_3 \cdot 3THF$ (M = Cr [6], Mo [7]) were prepared by published procedures. The compounds Cp_2ZrCl_2 (Alfa Inorganics), $MoCl_5$ (BDH), $NbCl_5$ (Koch-Light), $CrCl_3 \cdot 6H_2O$ (Merck) and C_7H_8 (EGA) were used without purification.

TABLE 1

ANALYTICAL DATA FOR SOME CYCLOPENTADIENYLCYCLOHEPTATRIENYLMETAL COMPOUNDS

Compound	Found (calcd.) (%)			Yield (%)
	C	H	Metal	
$(C_5H_5)Zr(C_7H_7)$	58.63	5.18	36.90	30
	58.50	5.09	36.98	
	(58.25)	(4.89)	(36.86)	
$(C_5H_5)Nb(C_7H_7)$	58.33	4.88	37.10	5
	58.41	4.96	37.20	
	(57.85)	(4.86)	(37.29)	
$(C_5H_5)Mo(C_7H_7)$	57.34	4.91	37.75	15 (1.8 [a])
	57.36	4.97	37.90	
	(57.14)	(4.80)	(38.06)	
$(C_5H_5)Cr(C_7H_7)$	69.41	5.92	24.86	12 (3 [b])
	69.50	5.94	24.81	
	(69.22)	(5.80)	(24.97)	

[a] Ref. 4. [b] Ref. 3.

IR spectra were measured by means of a Hitachi EPI-G spectrophotometer; the samples were examined as mulls in Nujol (4000-400 cm^{-1}) or hexachlorobutadiene (4000-1200 cm^{-1}). NMR spectra were recorded on a Varian A60 high-resolution instrument; C_6D_6 was used as solvent (40°) with TMS as an internal standard. The mass spectra were run on an AEI MS9 instrument. ESR spectra were recorded on a Varian E3 X-band EPR spectrometer. Elementary analyses were carried out by the Analytical Department of this Laboratory. Analytical data and yields are collected in Table 1.

Synthesis of $(C_5H_5)Zr(C_7H_7)$. To a well-stirred suspension of $CpZrCl_3$ (4.84 g, 18.4 mmol) and C_7H_8 (6.2 g, 68 mmol) in 150 ml of ether, 70 ml of a 0.81 *M* solution of $i\text{-}C_3H_7MgBr$ in ether were slowly added at —20°. The mixture was allowed to warm slowly to room temperature. After refluxing for 15 min, the solvent was removed under reduced pressure. The residue was twice washed with n-pentane and sublimed at 120°/0.1 mm. The violet crystals obtained by sublimation were contaminated with some oil, which was removed by washing the crystals three times with a few ml of n-pentane. Re-sublimation at 120°/0.1 mm gave the pure product. The same compound was obtained similarly starting from Cp_2ZrCl_2.

Synthesis of $(C_5H_5)Nb(C_7H_7)$. To a well-stirred suspension of $NbCl_5$ (5.40 g, 20 mmol) and C_7H_8 (2.8 g, 30 mmol) in 100 ml of ether, one equivalent of CpNa and four equivalents of $i\text{-}C_3H_7MgBr$ were slowly added at —78°. The mixture was allowed to warm slowly to room temperature. After refluxing for 15 min, the solvent was removed under reduced pressure. The compound was purified as described above.

Synthesis of $(C_5H_5)Mo(C_7H_7)$. To a well-stirred suspension of $MoCl_3 \cdot 3THF$ (4.29 g, 10.2 mmol), C_7H_8 (2.8 g, 30 mmol) and freshly distilled C_5H_6 (0.7 g, 10.6 mmol) in 125 ml of THF, 30.0 ml of a 1.08 *M* solution of $i\text{-}C_3H_5MgBr$ in ether were slowly added at —20°. The mixture was allowed to warm slowly to room temperature. After stirring for 4 h the solvent was removed under reduced pressure. The residue was extracted twice with 150 ml of benzene. The extraction products were twice washed with 25 ml of n-pentane and sublimed at 120°/0.1 mm. Further purification was effected by recrystallization from ether.

Synthesis of (C_5H_5)Cr(C_7H_7). The synthesis was performed as described for the Mo compound. $CrCl_3 \cdot 3$ THF was used as starting material; n-hexane was used in the extraction and recrystallization.

Results and discussion

Elemental analyses and mass spectra of the Zr and Nb compounds indicate that the molecular formula is $(C_{12}H_{12})M$ (M = Zr, Nb). Both compounds are thermally very stable, but are much more sensitive to air and water than the corresponding Ti and V compounds. This is probably due to the increased polarity of the *4d* metal compounds compared with the *3d* metal complexes. The Zr compound is diamagnetic and its PMR spectrum shows two singlets at δ 5.23 and 5.31 ppm, with relative intensities of 7 to 5 *. The Nb compound is paramagnetic.

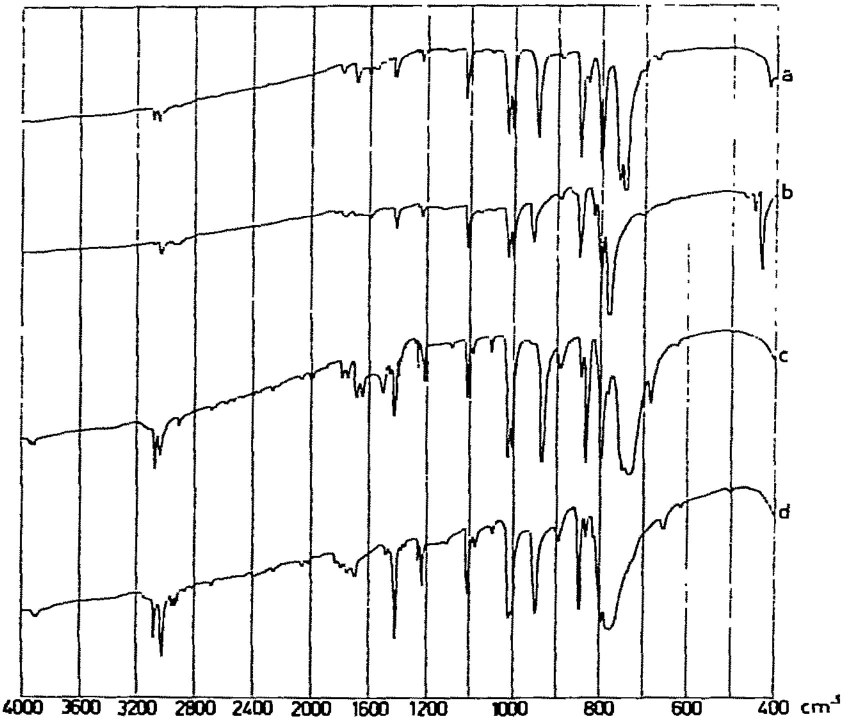

Fig. 1. IR spectra of $(C_5H_5)Ti(C_7H_7)$ (a), $(C_5H_5)V(C_7H_7)$ (b), $(C_5H_5)Zr(C_7H_7)$ (c), $(C_5H_5)Nb(C_7H_7)$ (d).

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* See ref. 8 for a detailed ^1H and ^{13}C NMR study of this type of compound.

In the temperature range 5-120 K a moment of 2.0 *B.M.* was measured (corrected for induced diamagnetism), roughly corresponding with one unpaired electron per molecule (calculated for spin only: $\mu_{eff} = 1.73$ *B.M.*). Its ESR spectrum in toluene solution (0°) shows the expected ten lines (nuclear spin ^{93}Nb 9/2). Even on cooling to −140° no proton hyperfine splitting was observed. The isotropic ^{93}Nb coupling constant and the isotropic *g* value are 33.8 *G* and 1.988 respectively.

The IR spectra of the Zr and Nb compounds closely resemble the spectra of the corresponding Ti and V compounds (see Fig. 1). The absorptions characteristic for π-bonded C_5H_5 and C_7H_7 ligands are found in the usual range [1, 2]. This provides strong evidence for a sandwich structure of the Zr and Nb compounds.

TABLE 2

MASS SPECTRUM OF $(C_5H_5)Zr(C_7H_7)$

m/e	Rel. int.	Ion	*m/e*	Rel. int.	Ion
246	69	$C_{12}H_{12}Zr^+$	110	7	$C_{10}H_{10}Zr^{2+}$
220	11	$C_{10}H_{10}Zr^+$	109	13	$C_{10}H_8Zr^{2+}$
218	3	$C_{10}H_8Zr^+$	108	4	$C_{10}H_6Zr^{2+}$
205	2	$C_9H_7Zr^+$	104	9	$C_8H_8^+$
194	9	$C_8H_8Zr^+$	97	7	$C_8H_8Zr^{2+}$
193	7	$C_8H_7Zr^+$	96	10	$C_8H_6Zr^{2+}$
192	6	$C_8H_6Zr^+$	94	10	$C_7H_{10}^+$
181	2	$C_7H_7Zr^+$			
180	2	$C_7H_6Zr^+$	93	7	$C_7H_9^+$
179	2	$C_7H_5Zr^+$	92	19	$C_7H_8^+$
172	4	$C_6H_{10}Zr^+$	91	100	$C_7H_7^+$
170	11	$C_6H_8Zr^+$	89	5	$C_7H_5^+$
168	47	$C_6H_6Zr^+$	84	9	$C_6H_6Zr^{2+}$
166	22	$C_6H_4Zr^+$	83	6	$C_6H_4Zr^{2+}$
156	4	$C_5H_6Zr^+$	79	19	$C_6H_7^+$
155	5	$C_5H_5Zr^+$	78	12	$C_6H_6^+$
154	4	$C_5H_4Zr^+$	77	13	$C_6H_5^+$
153	4	$C_5H_3Zr^+$	70	3	$C_4H_2Zr^{2+}$
144	4	$C_4H_6Zr^+$	67	7	$C_5H_7^+$
142	7	$C_4H_4Zr^+$	66	85	$C_5H_6^+$
141	7	$C_4H_3Zr^+$	65	44	$C_5H_5^+$
140	10	$C_4H_2Zr^+$	63	11	$C_5H_3^+$
129	6	$C_3H_3Zr^+$	53	3	$C_4H_5^+$
128	7	$C_3H_2Zr^+$	52	3	$C_4H_4^+$
127	7	C_3HZr^+	51	9	$C_4H_3^+$
123	12	$C_{12}H_{12}Zr^{2+}$	50	4	$C_4H_2^+$
122	7	$C_{12}H_{10}Zr^{2+}$	41	4	$C_3H_5^+$
121	4	$C_{12}H_8Zr^{2+}$	40	19	$C_3H_4^+$
116	4	$C_2H_2Zr^+$	39	32	$C_3H_3^+$
115	4	C_2HZr^+	38	7	$C_3H_2^+$

Metastable peaks m^* 114.7 46.5

TABLE 3

MASS SPECTRUM OF $(C_5H_5)Nb(C_7H_7)$

m/e	Rel. int.	Ion	*m/e*	Rel. int.	Ion
249	100	$C_{12}H_{12}Nb^+$	144	2	$C_4H_3Nb^+$
248	7	$C_{12}H_{11}Nb^+$	143	5	$C_4H_2Nb^+$
247	20	$C_{12}H_{10}Nb^+$	142	2	C_4HNb^+
245	2	$C_{12}H_8Nb^+$	132	2	$C_3H_3Nb^+$
223	6	$C_{10}H_{10}Nb^+$	131	2	$C_3H_2Nb^+$
222	1	$C_{10}H_9Nb^+$	130	1	C_3HNb^+
221	8	$C_{10}H_8Nb^+$	124.5	16	$C_{12}H_{12}Nb^{2+}$
220	2	$C_{10}H_7Nb^+$	123.5	4	$C_{12}H_{10}Nb^{2+}$
219	2	$C_{10}H_6Nb^+$	122.5	1	$C_{12}H_8Nb^{2+}$
208	1	$C_9H_7Nb^+$	119	1	$C_2H_2Nb^+$
197	5	$C_8H_8Nb^+$	118	2	C_2HNb^+
196	3	$C_8H_7Nb^+$	111.5	1	$C_{10}H_{10}Nb^{2+}$
195	6	$C_8H_6Nb^+$	110.5	9	$C_{10}H_8Nb^{2+}$
194	2	$C_8H_5Nb^+$	109.5	2	$C_{10}H_6Nb^{2+}$
183	1	$C_7H_6Nb^+$	98.5	2	$C_8H_8Nb^{2+}$
171	15	$C_6H_6Nb^+$	97.5	6	$C_8H_6Nb^{2+}$
170	3	$C_6H_5Nb^+$	91	1	$C_7H_7^+$
169	12	$C_6H_4Nb^+$	85.5	4	$C_6H_6Nb^{2+}$
168	2	$C_6H_3Nb^+$	84.5	2	$C_6H_4Nb^{2+}$
158	1	$C_5H_5Nb^+$	78	1	$C_6H_6^+$
157	1	$C_5H_4Nb^+$	66	1	$C_5H_6^+$
156	1	$C_5H_3Nb^+$	65	1	$C_5H_5^+$
145	2	$C_4H_4Nb^+$			

Metastable peaks m^* 199.7 197.7 174.0 172.1 148.4 146.5 123.0 121.0 117.4

The mass spectra of the Zr and Nb compounds (see Tables 2 and 3) also indicate that the structures of the 3*d* and 4*d* metal compounds are similar. The most remarkable feature in these spectra is the degradation path of the parent ions, $(C_{12}H_{12})M^+$, by elimination of benzene to give the ions $(C_6H_6)M^+$. As reported previously by Müller and Mertschenk [9], substituted $(C_5H_5)V(C_7H_7)$ compounds rearrange in the mass spectrometer. From the parent ion $[(C_5H_5)V(C_7H_7)]^+$, migration of a CH fragment from the seven- to the five-membered ring occurs, to give the ion $(C_6H_6)_2V^+$. Similar observations have been made for substituted $(C_5H_5)Ti(C_7H_7)$ compounds [10], and in the Zr and Nb compounds such rearrangement of the parent ions $[(C_5H_5)M(C_7H_7)]^+$ to $(C_6H_6)_2M^+$ seems to occur. It is noteworthy that the relative intensities of the ions $(C_6H_6)M^+$ decrease in the sequence Zr > Nb $\gg$ Mo. The same trend is observed in the 3*d* metal compounds [1, 11].

The mass spectra of the Zr and Nb compounds are more complicated than those of the corresponding 3*d* metal compounds. This generally observed feature [4, 12] is probably caused by a somewhat better overlap of the 4*d* metal and ligand orbitals, resulting in a stronger metal to carbon bond. Thus a stepwise elimination of the ligands becomes more favourable for the 4*d* metal com-

SCHEME 1

PARTIAL FRAGMENTATION SCHEME FOR $(C_5H_5)Zr(C_7H_7)$

$$\underset{(m = 246)}{C_{12}H_{12}Zr^+} \xrightarrow[m^* = 114.7]{-C_6H_6\ (m = 78)} \underset{(m = 168)}{C_6H_6Zr^+}$$

$$\underset{(m = 91)}{C_7H_7^+} \xrightarrow[m^* = 46.5]{-C_2H_2\ (m = 26)} \underset{(m = 65)}{C_5H_5^+}$$

SCHEME 2

PARTIAL FRAGMENTATION SCHEME FOR $(C_5H_5)Nb(C_7H_7)$

$$\begin{tikzcd}
\underset{(m = 249)}{C_{12}H_{12}Nb^+} \arrow[r, "-C_2H_2(m = 26)", "m^* = 199.7"'] \arrow[rrr, bend left, "\substack{-C_6H_6\ (m = 78) \\ m^* = 117.4}"] & \underset{(m = 223)}{C_{10}H_{10}Nb^+} \arrow[r, "-C_2H_2(m = 26)", "m^* = 174.0"'] & \underset{(m = 197)}{C_8H_8Nb^+} \arrow[r, "-C_2H_2(m = 26)", "m^* = 148.4"'] & \underset{(m = 171)}{C_6H_6Nb^+} \\
\underset{(m = 247)}{C_{12}H_{10}Nb^+} \arrow[r, "-C_2H_2(m = 26)", "m^* = 197.7"'] & \underset{(m = 221)}{C_{10}H_8Nb^+} \arrow[r, "-C_2H_2(m = 26)", "m^* = 172.1"'] & \underset{(m = 195)}{C_8H_6Nb^+} \arrow[r, "-C_2H_2(m = 26)", "m^* = 146.5"'] & \underset{(m = 169)}{C_6H_4Nb^+} \\
\underset{(m = 171)}{C_6H_6Nb^+} \arrow[r, "-C_2H_2(m = 26)", "m^* = 123.0"'] & \underset{(m = 145)}{C_4H_4Nb^+} & \underset{(m = 169)}{C_6H_4Nb^+} \arrow[r, "-C_2H_2(m = 26)", "m^* = 121.0"'] & \underset{(m = 143)}{C_4H_2Nb^+}
\end{tikzcd}$$

pounds; notable is the fragmentation of the Nb compound by successive elimination of acetylene. Partial fragmentation schemes for the Zr and Nb compounds are given in Schemes 1 and 2.

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