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ALLYL COMPLEXES OF DICYCLOPENTADIENYL-NIOBIUM(III) AND -TANTALUM(III)

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Summary

The synthesis and the properties of the complexes Cp_2TaCl_2, Cp_2M(allyl), Cp_2M(1-methylallyl) and Cp_2M(2-methylallyl) with M = Nb, Ta are described. The complex Cp_2TaCl_2 has one unpaired electron per tantalum atom, while the allyl complexes are diamagnetic. The IR and PMR spectra indicate that the allyl group is π-bonded to the metal. The mass spectra of the complexes are discussed; the thermal stability of the Cp_2Nb- and Cp_2Ta-(allyl) complexes was investigated by differential thermal analysis. The properties of the niobium and tantalum complexes are compared with those of the corresponding titanium complexes.

Introduction

Allylic complexes of dicyclopentadienyl-niobium(III) and -tantalum(III) have received little attention so far. In 1970 the synthesis and characterization of $Cp_2Nb(\pi\text{-}C_3H_5)$ was reported [1], and it was found to resemble closely the corresponding titanium complex [2]. The most striking difference between the titanium and niobium complex is the decrease (by 29 cm^{-1}) of the C=C stretching frequency of the π-allyl ligand in the niobium complex, indicating a stronger bonding between the allyl ligand and the metal in the latter compound. This was explained by assuming that in the case of $Cp_2Ti(\pi\text{-}C_3H_5)$ only one electron is available for back-bonding, while in $Cp_2Nb(\pi\text{-}C_3H_5)$ there are two [3].

Tebbe et al. [4, 5] described the use of Cp_2NbH_3 and Cp_2TaH_3 in hydrogenations. Their investigations show that the first compound is much more reactive than the latter. $Cp_2Nb(\pi\text{-}C_3H_5)$ and the 1-methylallyl complex, $Cp_2Nb(\pi\text{-}C_4H_7)$, were isolated from reaction mixtures of Cp_2NbH_3 with allene and butadiene, respectively. The complexes were characterized by their PMR spectra, but no further details were given [5].

To obtain a better understanding of the properties of these interesting compounds we prepared the complexes $Cp_2M(\pi\text{-allyl})$, $Cp_2M(\pi\text{-1-methylallyl})$ and $Cp_2M(\pi\text{-2-methylallyl})$ of niobium and tantalum and studied their properties by DTA, IR, PMR, and mass spectrometry. The properties of the compounds are compared with those of the analogous titanium complexes [2]. The complexes were prepared starting from dicyclopentadienylmetal dichlorides. Since dicyclopentadienyltantalum dichloride has not been reported previously, the preparation of this compound is also described.

Results and discussion

1. Synthesis

Cp_2TaCl_2 was prepared from $TaCl_5$ by two methods.

(i). By successive reaction of CpNa and HCl, by analogy with the preparation of Cp_2NbCl_2 [1]:

$$TaCl_5 + 5CpNa \rightarrow Cp_4Ta + 5NaCl + [Cp^\cdot]$$

$$Cp_4Ta + 2HCl \rightarrow Cp_2TaCl_2 + 2CpH$$

(ii). By successive reactions with isopropylmagnesium bromide and CpNa according to:

$$TaCl_5 + \text{i-PrMgBr} \rightarrow TaCl_4 + MgBrCl + [\text{i-Pr}^\cdot]$$

$$TaCl_4 + 2CpNa \rightarrow Cp_2TaCl_2 + 2NaCl$$

The latter method was found more convenient and gave better yields: 52 % *versus* 28 % for the first method. The compound was purified by vacuum sublimation.

Cp_2TaCl_2 is paramagnetic; the magnetic moment of 1.59 B.M. (temperature range 97-300 K) corresponds to one unpaired electron per unit of Cp_2TaCl_2 (μ_{eff} = 1.73 B.M. calculated for spin only). The IR, mass spectra and chemical reactions of this compound are analogous to those of Cp_2NbCl_2 [1].

The (methyl)allyldicyclopentadienyl complexes Cp_2MR (M = Nb or Ta; R = allyl, 1-methylallyl or 2-methylallyl) were prepared by the route analogous to that used for the corresponding titanium compounds [2], i.e. by reaction of 1 mole of dicyclopentadienylmetal dichloride with 2 moles of the methylallyl Grignard reagent in THF or ether:

$$Cp_2MCl_2 + 2RMgBr \rightarrow Cp_2MR + MgBrCl + [R^\cdot]$$

After extraction with n-pentane the diamagnetic compounds were purified by sublimation in vacuum. The corresponding paramagnetic titanium complexes were purified by recrystallization. All the compounds are very sensitive towards oxygen and water.

2. Thermal stability and reactivity

The decomposition temperatures of the allyl complexes of Ti, Nb and Ta were determined by differential thermal analyses (DTA); heating rate 1,5°/min. The data are listed in Table 1. The results reveal little difference in thermal stability between the Cp_2Nb- and Cp_2Ta-(allyl) complexes. The complexes de-

TABLE 1

DTA DATA OF THE Cp_2MR COMPLEXES (°C)

M	R = allyl	R = 1-methylallyl	R = 2-methylallyl
Ti	84	80	90
Nb	118	110	126
Ta	109	101	116

compose at a somewhat higher temperature (by ca. 25°) than the corresponding Ti-compounds. In all cases, the decomposition temperature depends on the position of the substituent. The stability decreases if the methyl group is attached to the terminal carbon atom 1 of the allyl group and increases if a methyl group is attached to the central carbon atom 2. Although the compounds are all rather stable in the solid state, they differ markedly in their behaviour in solution. In the absence of air the titanium complexes are rather stable in common organic solvents, but the niobium and in particular the tantalum complexes tend to decompose. Probably, this indicates a greater polarity in the 4*d* and 5*d* than in the 3*d* allyl complexes.

3. *IR and PMR spectra*

The IR spectra of the complexes show a close resemblance. The frequencies for π-bonded cyclopentadienyl groups are found in the usual ranges. The C=C stretching frequencies of the allyl ligands (Table 2) are found around 1500 cm^{-1}, indicating that the allyl groups are π-bonded to the metal in all complexes. Martin [2] found this frequency at 1509 cm^{-1} for $Cp_2Ti(\pi\text{-allyl})$. For $Cp_2Nb(\pi\text{-allyl})$ Siegert [1] found the C=C stretching frequency at 1480 cm^{-1}. This low frequency indicates a considerable weakening of the C—C—C π bond of the ligand. This is ascribed to an effective back donation of electrons from the metal into the empty antibonding ligand orbital [3], indicating a stronger bonding between the allyl group and the metal atom. Generally, there is a stronger overlap of metal and allyl orbitals in compounds of 5*d* transition metals than in the corresponding allyl complexes of the 4*d* metals [6]. Therefore, the further decrease of the C=C stretching frequency in the Ta complex $Cp_2Ta(\pi\text{-allyl})$ to 1450 cm^{-1} is not unexpected.

The C=C stretching frequencies of the methylallyl ligands show a strong

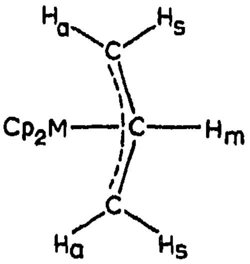
TABLE 2

IR DATA OF THE Cp_2MR COMPLEXES [ν(C=C) in cm^{-1}]

M	R = allyl	R = 1-methylallyl	R = 2-methylallyl
Ti[a]	1509	1533	1480
Nb	1480	1496	1460
Ta	1450	1461	1440

[a] Data from ref. 2.

TABLE 3

PMR DATA OF THE  COMPOUND[a, b]

Compound	H_{Cp}	H_m	H_s	H_a	CH_3	J(Hz)
Cp_2Ta(allyl)	4.54, 3.97 s (5)[c, d]	3.07 m (1)	3.07 q (2)	0.60 q (2)		J_{as} 5, J_{ma} 15 J_{ms} 9
Cp_2Nb(allyl)[e]	4.49, 4.01 s (5)	2.13 m (1)	2.91 q (2)	0.71 q (2)		J_{as} 5.0, J_{ma} 15.0 J_{ms} 9.5
Cp_2Ta(1-methylallyl)	4.50, 4.03 s (5)	1.26 m (1)	2.78 q (1)	0.48 m (2)	2.10 d (3)	$J_{s\text{—}CH_3}$ 5.5 J_{as} 5.5 J_{ma} 13, J_{ms} 9
Cp_2Nb(1-methylallyl)	4.50, 4.10 s (5)	1.00 m (1)	2.67 q (1)	0.49 m (2)	1.97 d (3)	$J_{s\text{—}CH_3}$ 5.5, J_{as} 4.5, J_{ma} 12, J_{ms} 9
Cp_2Ta(2-methylallyl)	4.52, 4.06 s (5)		3.08 d (2)	0.78 d (2)	2.00 s (3)	J_{as} 6.5
Cp_2Nb(2-methylallyl)	4.50, 4.13 s (5)		2.82 d (2)	0.83 d (2)	1.58 s (3)	J_{as} 5.5

[a] C_6D_6 solution, 40°, TMS as an internal standard. [b] Values are given in δ (ppm.) [c] s = Singlet, d = doublet, q = quartet, m = multiplet. [d] Relative intensities in parenthesis. [e] Data from ref. 1.

dependence on the position of the methyl group. Substitution at carbon atom 1 causes a shift to higher frequencies whereas substitution at the central carbon atom causes a shift in the opposite direction. Evidently the most stable bond between the allyl ligand and the metal atom is found for the 2-methylallyl compounds, in agreement with the DTA data (Table 1). Similar observations have been made for $Cp_2Ti(\pi\text{-allyl})$ complexes [2].

The PMR spectra of the niobium and tantalum complexes show two absorptions (with equal intensities) due to the two non-equivalent π-bonded cyclopentadienyl rings, together with the pattern characteristic for the π-bonded allyl groups. The data are collected in Table 3.

4. *Mass spectra*

The fragmentation patterns of the complexes $Cp_2M(\pi\text{-allyl})$ (M = Ti, Nb, Ta) do not depend strongly on the nature of the metal and on the position of the methyl group. Therefore, only the spectra of the allyl complexes of Ti, Nb and Ta together with the methylallyl complexes of Ta are given in detail (see Tables 4-8). In all cases fragmentation starts with elimination of the allyl group.

TABLE 4

MASS SPECTRUM OF $Cp_2Ti(C_3H_5)^a$

m/e	Rel. int. (%)	Ion
219	12	$C_{10}H_{10}TiC_3H_5^+$
178	100	$C_{10}H_{10}Ti^{+\cdot}$
152	5	$C_8H_8Ti^+$
138	1	$C_7H_6Ti^+$
113	25	$C_5H_5Ti^+$
98	1	$C_4H_2Ti^+$
87	7	$C_3H_3Ti^+$
73	5	C_2HTi^+
66	10	$C_5H_6^+$

[a] Metastable peaks: 71.8, 145.0.

TABLE 5

MASS SPECTRUM OF $Cp_2Nb(C_3H_5)^a$

m/e	Rel. int. (%)	Ion	*m/e*	Rel. int. (%)	Ion
264	87	$C_{10}H_{10}NbC_3H_5^+$	183	3	$C_7H_6Nb^+$
262	30	$C_{10}H_{10}NbC_3H_3^+$	171	27	$C_6H_6Nb^+$
260	8	$C_{10}H_{10}NbC_3H^+$	170	8	$C_6H_5Nb^+$
224	70	$C_{10}H_{10}NbH^+$	169	18	$C_6H_4Nb^+$
223	100	$C_{10}H_{10}Nb^+$	158	8	$C_5H_5Nb^+$
221	7	$C_{10}H_8Nb^+$	111.5	2	$C_{10}H_{10}Nb^{2+}$
197	22	$C_8H_8Nb^+$	97.5	2	$C_8H_6Nb^{2+}$
195	12	$C_8H_6Nb^{+\cdot}$	85.5	1	$C_6H_6Nb^{2+}$

[a] Metastable peaks: 146.5, 148.4, 174, 190, 217, 218.

TABLE 6

MASS SPECTRUM OF $Cp_2Ta(C_3H_5)$[a]

m/e	Rel. int. (%)	Ion	*m/e*	Rel. int. (%)	Ion
352	61	$C_{10}H_{10}TaC_3H_5^+$	284	11	$C_8H_7Ta^+$
350	55	$C_{10}H_{10}TaC_3H_3^+$	283	16	$C_8H_6Ta^+$
348	11	$C_{10}H_{10}TaC_3H^+$	257	11	$C_6H_4Ta^+$
324	3	$C_{10}H_{10}TaCH^+$	176	3	$C_{13}H_{15}Ta^{2+}$
322	3	$C_{11}H_9Ta^+$	175	15	$C_{13}H_{13}Ta^{2+}$
313	13	$C_{10}H_{10}TaH_2^+$	174	24	$C_{13}H_{11}Ta^{2+}$
312	100	$C_{10}H_{10}TaH^+$	162	7	$C_{11}H_{11}Ta^{2+}$
311	33	$C_{10}H_{10}Ta^+$	161	10	$C_{11}H_9Ta^{2+}$
310	15	$C_{10}H_9Ta^+$	160	6	$C_{11}H_7Ta^{2+}$
309	12	$C_{10}H_8Ta^+$	148	9	$C_9H_7Ta^{2+}$
296	6	$C_9H_7Ta^+$	147	5	$C_9H_5Ta^{2+}$
285	13	$C_8H_8Ta^+$			

[a] Metastable peaks: 136, 276.6, 300, 346, 348.

TABLE 7

MASS SPECTRUM OF Cp_2Ta(1-methylallyl)[a]

m/e	Rel. int. (%)	Ion	*m/e*	Rel. int. (%)	Ion
366	22	$C_{10}H_{10}TaC_4H_7^+$	257	4	$C_6H_4Ta^+$
362	2	$C_{10}H_{10}TaC_4H_3^+$	183	1	$C_{10}H_{10}TaC_4H_7^{2+}$
336	2	$C_{10}H_{10}TaC_2H^+$	182	3	$C_{10}H_{10}TaC_4H_5^{2+}$
313	10	$C_{10}H_{10}TaH_2^+$	181	7	$C_{10}H_{10}TaC_4H_3^{2+}$
312	100	$C_{10}H_{10}TaH^+$	180.5	4	$C_{10}H_{10}TaC_4H_2^{2+}$
311	13	$C_{10}H_{10}Ta^+$	174	1	$C_{10}H_{10}TaC_3H^{2+}$
310	9	$C_{10}H_9Ta^+$	168	3	$C_{10}H_{10}TaC_2H^{2+}$
309	5	$C_{10}H_8Ta^+$	155.5	2	$C_{10}H_{10}Ta^{2+}$
308	3	$C_{10}H_7Ta^+$	154	3	$C_{10}H_7Ta^{2+}$
285	6	$C_8H_8Ta^+$	141.5	2	$C_8H_6Ta^{2+}$
284	6	$C_8H_7Ta^+$			
283	6	$C_8H_6Ta^+$			

[a] Metastable peaks: 89.1, 134, 149, 266.

TABLE 8

MASS SPECTRUM OF Cp_2Ta(2-methylallyl)[a]

m/e	Rel. int. (%)	Ion	*m/e*	Rel. int. (%)	Ion
366	100	$C_{10}H_{10}TaC_4H_7^+$	285	24	$C_8H_8Ta^+$
362	12	$C_{10}H_{10}TaC_4H_3^+$	283	23	$C_8H_6Ta^+$
336	10	$C_{10}H_{10}TaC_2H^+$	257	14	$C_6H_4Ta^+$
326	69	$C_{10}H_{10}TaCH_3^+$	181	28	$C_{10}H_{10}TaC_4H_3^{2+}$
324	13	$C_{10}H_{10}TaCH^+$	180.5	18	$C_{10}H_{10}TaC_4H_2^{2+}$
312	100	$C_{10}H_{10}TaH^+$	168	15	$C_{10}H_{10}TaC_2H^{2+}$
311	61	$C_{10}H_{10}Ta^+$	155.5	10	$C_{10}H_{10}Ta^{2+}$
309	23	$C_{10}H_8Ta^+$	154	11	$C_{10}H_7Ta^{2+}$
297	6	$C_9H_8Ta^+$	148	8	$C_9H_7Ta^{2+}$
296	11	$C_9H_7Ta^+$	141.5	11	$C_8H_6Ta^{2+}$

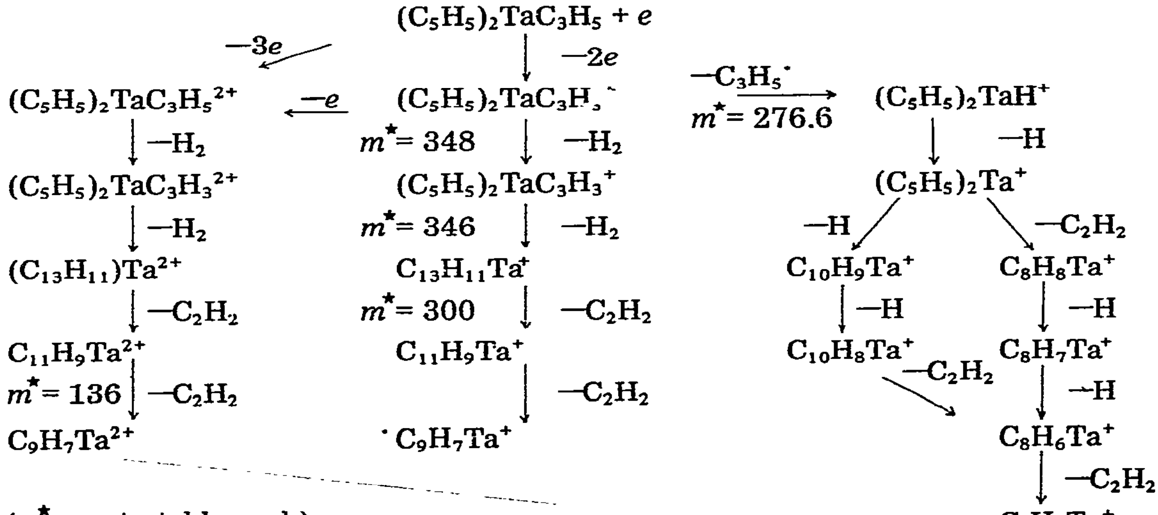
[a] Metastable peaks: 134, 149, 266, 290.6, 297, 322.

In the Ti-complexes, this elimination occurs in one step; in the Nb and particularly in the Ta complexes, however this reaction takes place stepwise. This is again in agreement with a stronger metal—allyl bond in the *4d* and *5d* complexes. As an example, the fragmentation pattern of $Cp_2TaC_3H_5$ is given in Scheme 1.

This stepwise elimination results in the formation of hydrides. In particular for the Ta complexes hydride ions are of a great abundance. In the compounds Cp_2Ta(allyl) and Cp_2Ta(1-methylallyl), the Cp_2TaH^+ ion is more abundant than the parent ion. Obviously, The Cp_2TaH^+ ion is a relatively stable one.

During the degradation of both the Cp_2Ta(allyl) and the Cp_2Nb(allyl) compounds doubly charged ions appear. These ions are of greatest abundance in the Ta complexes, which indicates that the higher oxidation state of Ta is more stable than that of Nb.

SCHEME 1



(m^* = metastable peak)

Conclusions

The results described show the close relationship between the allyldicyclopentadienyl compounds of Ti, Nb and Ta. Especially noteworthy is, the similar influence of the methyl group on the properties of the compounds. In 1957 Lanpher [7] found that introduction of a methyl group on the central carbon atom (2) of allylsodium decreases the C=C stretching frequency by 15 cm^{-1}. Introduction of a methyl group on the terminal carbon atoms (1) in the *syn* position caused a shift of 25 cm^{-1} to higher frequency, whereas a methyl group in an *anti* position gave a smaller shift (10 cm^{-1}) to lower frequencies. In Cp_2Ti(1-methylallyl) the methyl substituent increases the C=C stretching frequency by 24 cm^{-1} (see Table 2). From this and steric arguments Martin [2] concluded that the methyl group in Cp_2Ti(1-methylallyl) occupies the *syn* position. This was confirmed by a crystal-structure determination of the Cp_2Ti(1, 2-dimethylallyl) complex [8]. The Nb and Ta complexes show similar shifts of the C=C stretching frequencies as the Ti compounds (Table 2); so we conclude that in the Nb and Ta compounds the methyl group on the terminal carbon atom is again in the *syn* position.

Within these series of complexes gradual changes in properties occur depending primarily on the nature of the central atom in the order Ti, Nb, Ta. While the metal—allyl bond is strengthened in the order Ti, Nb, Ta, and the Nb and Ta compounds are more robust in the solid state, the stability of the Nb and particularly of the Ta compounds in solutions is lower than that of the Ti compounds. This is probably caused by an increase of polarity of the metal ligand bonds.

The considerable increase in abundance of hydride ions in the mass spectra in the order $Ti < Nb < Ta$ parallels the fact that dicyclopentadienyl hydrides of Nb and Ta have been isolated as stable compounds whereas hydrides of Cp_2Ti have not. Tebbe et al. [4, 5] have found the activity of Nb cyclopentadienyl complexes in hydrogenation reactions to be larger than that of the corresponding Ta complexes. We may speculate that the highest activity will be found for dicyclopentadienyl compounds of titanium. The considerable activity of such compounds in hydrogenation reactions has been reported [9] but to our knowledge no investigations are reported in which Ti, Nb and Ta compounds have been tested under comparable conditions.

Experimental

All experiments were carried out under purified nitrogen. Solvents were purified by conventional methods and freed from oxygen before use by repeated degassing and saturating with nitrogen. Cp_2NbCl_2 [1], $Cp_2Nb(C_3H_5)$ [1] and the Cp_2Ti(allyl) complexes [2] were prepared by published procedures. Allyl-, crotyl- and isopropyl-magnesium bromide were prepared in ether; 2-methylmagnesium chloride was prepared in THF. Elementary analyses were carried out in the microanalytical department of this University under the supervision of Mr. W.M. Hazenberg. IR spectra were measured by means of a Hitachi-EPI-G spectrophotometer; the samples were embedded in KBr discs excluding oxygen as described previously [2] or suspended in Nujol between KBr discs. Mass spectra were run on an AEI MS 9 mass spectrometer; the samples were introduced directly into the ion source using a metal probe. PMR spectra were recorded on a Varian A 60 high-resolution instrument. Thermograms were recorded using a low-temperature DTA apparatus [10].

Dicyclopentadienyltantalum dichloride

To a stirred suspension of 33 mmol of $TaCl_5$ in 200 ml of ether, 55 ml of a 0.60 *M* solution of i-PrMgBr in ether were added dropwise. After the colour of the suspension had changed from white to green, 66 mmol CpNa were added. The reaction mixture was refluxed for one hour. The solvent was removed at reduced pressure and the residue was evaporated to dryness. The pure compound was obtained by sublimation at 300°/0.1 mmHg; yield 17.3 mmol (52%) of brown crystals of Cp_2TaCl_2. (Found: C, 31.31; H, 2.78; Ta, 47.70. $C_{10}H_{10}Cl_2Ta$ calcd.: C, 31.44; H, 2.64; Ta, 47.37 %.)

(2-Methylallyl)dicyclopentadienyltantalum and other complexes

To a stirred and cooled (0°) suspension of Cp_2TaCl_2 (3.18 g, 8.4 mmol) in 200 ml of ether, 50 ml of a 0.37 *M* solution of 2-methylallylmagnesium chloride in THF was slowly added. The green reaction mixture was stirred for one hour. After this, the solvent was removed under reduced pressure. The residue was extracted with 150 ml of pentane. After removing the pentane at reduced pressure, the green residue was sublimed at 130°/0.1 mmHg; yield 0.6 g (1.6 mmol, 19 %) of green crystals of $Cp_2Ta(C_4H_7)$. The other complexes Cp_2M(allyl) (M = Ta, Nb) were prepared in essentially the same way. Analytical data and yields are given in Table 9.

TABLE 9

ANALYTICAL DATA OF THE Cp_2M(allyl) COMPLEXES

Compound	Yield	Analysis found (calcd.) (%)		
	(%)	C	H	M
$(C_5H_5)_2$Ta(allyl)	8	44.33 (44.33)	4.55 (4.29)	51.35 (51.38)
$(C_5H_5)_2$Ta(2-methylallyl)	19	45.79 (45.91)	4.73 (4.68)	49.64 (49.41)
$(C_5H_5)_2$Ta(1-methylallyl)	13	45.40 (45.91)	4.81 (4.68)	50.07 (49.41)
$(C_5H_5)_2$Nb(2-methylallyl)	35	60.40 (60.44)	6.30 (6.16)	33.51 (33.40)
$(C_5H_5)_2$Nb(1-methylallyl)	22	60.16 (60.44)	6.43 (6.16)	33.15 (33.40)

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References

1 F.W. Siegert and H.J. de Liefde Meijer, J. Organometal. Chem., 23 (1970) 177.
2 H.A. Martin and F. Jellinek, J. Organometal. Chem., 8 (1967) 115.
3 H.J. de Liefde Meijer and F. Jellinek, Inorg. Chim. Acta, 4 (1970) 651.
4 E.K. Barefield, G.W. Parshall and F.N. Tebbe, J. Amer. Chem. Soc., 92 (1970) 5234.
5 F.N. Tebbe and G.W. Parshall, J. Amer. Chem. Soc., 93 (1971) 3793.
6 W.R. McClellan, H.H. Hoehn, H.N. Cripps, E.L. Muetterties and B.W. Howk, J. Amer. Chem. Soc., 83 (1961) 1601.
7 E.J. Lanpher, J. Amer. Chem. Soc., 79 (1957) 5578.
8 R.B. Helmholdt, F. Jellinek, H.A. Martin and A. Vos, Rec. Trav. Chim. Pays-Bas, 86 (1967) 1263.
9 H.A. Martin, M. v. Gorkum and R.O. de Jongh, J. Organometal. Chem., 36 (1972) 93.
10 J.C. Wildervanck, Thesis, Groningen, 1970.