cipitate formed was filtered off, washed with methanol and ether, and dried to give 0.42 g (78%) Cp<sub>2</sub>VCl(NCS). Found: C, 47.69; H, 3.74; Cl, 12.76; N, 5.14; V, 18.45%. Calculated for  $C_{11}H_{10}$ ClNSV: C, 48.10; H, 3.67; Cl, 12.91; N, 5.10; V, 18.55%. Me<sub>3</sub>SiCl and excess Me<sub>3</sub>SiNCS were qualitatively determined by gas-liquid chromatography.

b) A mixture of 0.72 g Cp<sub>2</sub>VCl and 2.3 g Bu<sub>3</sub>SnNCS (1:2 ratio) in 30 ml toluene was heated in an evacuated ampul for 2 h at 120°C. The yellow-green precipitate formed was filtered off and washed with toluene in vacuum to give 0.70 g (71%) Cp<sub>2</sub>V(NCS)<sub>2</sub>. Found: N, 9.11; S, 21.49%. Calculated for  $C_{1,2}H_{1,0}N_2S_2V$ : N, 9.42; S, 21.57%. Vacuum distillation of the filtrate gave 1.52 g of a mixture of (Bu<sub>3</sub>Sn)<sub>2</sub> and Bu<sub>3</sub>SnCl, in which iodometric titration indicated 0.1 g (11%) (Bu<sub>3</sub>Sn)<sub>2</sub>. The yield of Bu<sub>3</sub>SnCl was 1.42 g (74%).

c) A mixture of 0.99 g Cp<sub>2</sub>VCl and 1.13 g Et<sub>3</sub>SnNCO (1:1 ratio) in 15 ml toluene was maintained in an evacuated ampul for 24 h at 20-25°C. The solution turned from blue to strong blue-violet [2]. Then 0.34 g HCl in dioxane (two-fold excess) was added to the solution obtained in vacuum. The ampul was opened in the air. A green precipitate of 0.50 g (42%) Cp<sub>2</sub>VCl(NCO) was isolated after 24 h. Found: C, 50.97; H, 4.20; Cl, 13.26; N, 5.39; V, 20.09%. Calculated for  $C_{11}H_{10}ClNOV$ : C, 51.09; H, 3.90; Cl, 13.71; N, 5.41; V, 19.70%.

## CONCLUSIONS

Vanadocene monochloride and vanadocene dichloride react with organotin and organosilicon pseudohalides,  $R_3MNCX$  ( $R_3M = Bu_3Sn$ ,  $Me_3Si$  and X = 0, S), to give the corresponding vanadium (IV) d<sup>1</sup>-complexes,  $Cp_2V(NCX)_2$  or  $Cp_2VC1(NCX)$ .

# LITERATURE CITED

1.	A. S. Gordetsov, V. N. Latyaeva, and A. N. Lineva, The Chemistry of Heteroorganic Com-
	pounds [in Russian], Gorki (1981), p. 31.
2.	A. S. Gordetsov, S. F. Zimina, V. V. Pereshein, and R. P. Zakharova, Zh. Obshch. Khim.,
	<u>56,</u> 722 (1986).
3.	G. Doyle and R. S. Tobias, Inorg. Chem., 7, 2479 (1968).
4.	G. A. Razuvaev, G. A. Abakumov, and V. K. Cherkasov, Usp. Khim., 54, 1235 (1985).

### HYDROGENATION OF n<sup>5</sup>-FLUORENYL LIGAND IN THE ACETYLATION

# OF n<sup>5</sup>-FLUORENYLTRICARBONYLMANGANESE

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Facile hydrogenation has been reported for the multiple bonds of the six-membered rings of transition metal  $n^5$ -indenyl complexes [1-3], which are similar to  $n^5$ -fluorenyl derivatives. However, attempts to hydrogenate the double bonds of the six-membered rings of the  $n^5$ -fluorenyl ligand in  $(n^5-C_{13}H_9)$   $(n^3-C_{13}H_9)$ ZrCl<sub>2</sub> proved unsuccessful [4].

We have observed the hydrogenation of one double bond of the  $n^5$ -fluorenyl ligand in the acetylation of  $n^5$ -fluorenyltricarbonylmanganese (I) by the action of excess CH<sub>3</sub>COCl and AlCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>.  $n^5$ -(2-acetyl-3,4-dihydrofluorenyl)tricarbonylmanganese (III) was isolated in 6% yield in addition to the acetylated complex (II) [5] and the products of loss of the  $\pi$ ligand (IV) and (V). (See scheme on the next page.) Complex (III) is an orange crystalline compound with mp 137-139°C. The IR spectrum of (III) in CH<sub>2</sub>Cl<sub>2</sub> has bands for the terminal CO groups at 1956 and 2030 cm<sup>-1</sup> and for the COCH<sub>3</sub> group at 1672 cm<sup>-1</sup>, which is shifted toward lower frequencies by 15 cm<sup>-1</sup> in comparison with vC=O in complex (II) (1687 cm<sup>-1</sup>) due to conjugation with an aliphatic double bond. The mass spectrum of (III) shows peaks with m/z 348 (M<sup>+</sup>), 292 [M-2CO]<sup>+</sup>, 264 [M-3CO]<sup>+</sup>, and 262 [M-3CO-H<sub>2</sub>]. The ion with m/z 262 is absent in the mass spectrum of (II).

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The structure of (III) was confirmed by x-ray diffraction structural analysis, which showed that the independent part of the unit cell contains two molecules (A and B) with identical geometry (mean values are given). Cyclopentadienyl ring E of the dihydrofluorenyl ligand in (III) (Fig. 1) has n<sup>5</sup>-attachment to the manganese atom and is almost coplanar to aromatic ring F. The difference in the Mn-C(five-membered ring) bond lengths characteristic for n<sup>5</sup>fluorenyl [6, 7] and n<sup>5</sup>-indenyl complexes is observed. C<sup>9</sup> atom of the  $\pi$ -ligand is closest to the manganese atom: Mn-C<sup>9</sup>, 2.163; Mn-C<sup>10</sup>, 2.212; Mn-C<sup>11</sup>, 2.225; Mn-C<sup>12</sup>, 2.191; Mn-C<sup>13</sup>, 2.197 Å. 3,4-Dihydro ring D has half-chair conformation. The C<sup>2</sup>C<sup>1</sup>C<sup>10</sup>C<sup>11</sup> fragment is planar to the nearest ±0.04 Å, while C<sup>3</sup> and C<sup>4</sup> atoms extrude from this plane by 0.7 and -0.23 Å (toward and away from the Mn atom). The C<sup>1</sup>-C<sup>2</sup> bond length (1.353 Å) is characteristic for a C=C bond conjugated with C=0. The acetyl substituent is almost coplanar to the dihydrofluoroenyl system.

We should note the significant difference in the Mn-CO bond lengths:  $Mn-C^{16}$  (1.862)> Mn-C<sup>16</sup> (1.791) > Mn-C<sup>17</sup> (1.743 Å) in molecules A and B, apparently due to the effect of the  $n^{5}$ -ring [8].

We may assume that the reduction of a double bond of the  $n^{5}$ -fluorenyl ligand upon the acetylation of (I) proceeds through an ionic hydrogenation mechanism. In acid media, the partial protonation of the COCH, group of reaction product (II) probably proceeds initially. Conjugation of the CO group with the benzene ring double bonds leads to the induction of a

	Molecule A			Molecule B		
Atom	x	Y .	Z	X	Y	. <b>Z</b>
Mn	42946(5)	69757(3)	13972(2)	105565(5)	53003(3)	36498(2)
01	4870(3)	8542(1)	884(1)	10077 (3)	3694(1)	4114(1)
O2	1286(3)	7401(2)	1940(1)	13559(3)	4874(2)	3101(1)
$O_3$	2335(3)	6389(2)	273(1)	12441(3)	5889(2)	4791(1)
·O4	5560(3)	8623(2)	3844(1)	9588(3)	3618(2)	1262(1)
C1	5005(4)	6930(2)	2874(1)	9873(4)	5361(2)	2179(1)
$C^2$	5482(4)	7651(2)	3078(2)	9430(4)	4633(2)	1977 (2)
$C_3$	6355(5)	8193(2)	2687(2)	8546(5)	4086(2)	2360(2)
C <sup>4</sup>	7389(4)	7803(2)	2255(1)	7490(4)	4470(2)	2789(2)
·C <sup>»</sup>	7949(4)	6795(2)	962(2)	6880(4)	5471(2)	40/6(1)
"C"	7880(5)	6263(2)	481(2)	6884(4)	6021(2)	4547 (2)
C'	6945(5)	5570(2)	473(2)	7810(4)	6719(2)	4562(2)
C°	5975(4)	5379(2)	931(2)	8833(4)	6903(2)	4117(2)
107 C10	4992(4)	5951(2)	1939(1)	9871(4)	6329(2)	3110(1) 2750(4)
	5477(4)	0045(2) 7095(0)	2291(1)	9386(4)	5040(2)	2739(1)
.012		1085(2)	1974(1)	8256(3)	5199(2)	3070(1)
C13	5044(4)	0040(2) 5044(2)	1450(1)	/902(4)	0002(2) 6225(2)	3634(4)
C14	5911(4)	<b>5941 (2)</b> 7077 (9)	1420(1)	8929(4)	0000(2)	464 (2)
C15	2005 (5)	7522(2)	$\frac{5071(2)}{2029(2)}$	9940(4)	4290(2)	1401(2)
CIE		7000(2)	4030(2) 4074(4)	10940(3)	4100(0)	3051(1)
Č17	2/56(4)	72/8(2)	1718(1)	10300(4)	5038(2)	3330(2)
۰C18	3091(4)	6615(2)	707(2)	14000 (4)	5652(2)	4349(2)
HI	439(4)	658(2)	311(1)	1054(4)	570(2)	197(2)
H3.1	695(4)	856(2)	293(1)	786(4)	363(2)	209 (2)
H3.2	523(6)	852(3)	237(2)	953(7)	370(4)	267 (3)
H4.1	775(4)	814(2)	197 (2)	710(4)	408(2)	309 (2)
H4-2	840(5)	764(2)	254(2)	646(5)	460(2)	253(2)
H2	860(4)	724(2)	98(2)	626(5)	498(2)	408(2)
He	858(4)	635 (2)	18(2)	610(4)	592(2)	487(2)
'H'	694(4)	521(2)	15(2)	774(4)	710(2)	488 (2)
Ha	534(4)	490(2)	93(2)	933 (5)	737 (3)	412(2)
H <sup>9</sup>	430(3)	555(2)	204(1)	1056(4)	677(2)	301(2)
H15.1	417(7)	702(4)	404 (3)	983(7)	559(4)	125 (3)
H15.2	418(6)	768(3)	445(2)	1056(6)	473(3)	66(2)
H13.3	272(6)	760(3)	385(2)	1187 (6)	471 (3)	108(2)

TABLE 1. Atomic Coordinates (×10<sup>4</sup>, ×10<sup>5</sup> for Mn, ×10<sup>3</sup> for H)



Fig. 1. Structure of molecule A in crystalline  $n^{5}$ -(2-acetyl-3,4-dihydrofluorenyl)tricarbonylmanganese projected on the plane of the  $n^{5}$ -ring. The hydrogen atoms are not shown.

positive charge on the carbon atom of the ring with substituent addition of a hydride ion from the medium. The ionic hydrogenation of  $\alpha$ , $\beta$ -unsaturated ketones such as benzalaceto-phenone and dibenzalacetone in the case of insufficient hydride ion donor (1:1 substrate: hydride ion donor ratio) proceeds selectively at the C=C bond with the formation of the corresponding saturated ketones in high yield [9].

### EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer. The mass spectra were taken on an MS-30 mass spectrometer.

The x-ray diffraction structural analysis was carried out on a Syntex P2<sub>1</sub> automatic four-circle diffractometer using MoKa radiation and a graphite monochromator at -120°C. The calculations were carried out on an Eclipse S/200 computer using the INEXTL programs [10]. The unit cell parameters of the monoclinic crystals at -120°C are as follows: a = 8.147(4), b = 16.966(6), c = 21.878(8) Å,  $\beta$  = 96.62(3)°, V = 3004(2) Å<sup>3</sup>, z = 8, C<sub>10</sub>H<sub>13</sub>MnO<sub>4</sub>, d<sub>calc</sub> = 1.53 g/cm<sup>3</sup>, space group P2<sub>1</sub>/c,  $\mu$ (MoK<sub>a</sub>) = 9.4 cm<sup>-1</sup>. The intensities of 4301 independent reflections with I ≥ 20 were measured by  $\theta/2\theta$  scanning ( $2\theta \le 55^{\circ}$ ). The structure was solved by the heavy atom method and refined in the block diagonal method of least squares in the anisotropic approximation for the nonhydrogen atoms and isotropic approximation for the hydrogen atoms to R = 0.040 and R<sub>W</sub> = 0.047 (weighting scheme W<sup>-1</sup> =  $\sigma_F^2$  + 0.0001  $F_{exp}^2$ ). The atomic coordinates are given in Table 1. The temperature factors may be obtained from the authors.

<u>Preparation of  $n^3$ -(2-Acety1-3,4-dihydrofluorenyl)tricarbonylmanganese (III).</u> A solution of 1.5 ml (19.01 mmoles) CH<sub>3</sub>COC1 and 0.66 g (4.94 mmoles) AlC1<sub>3</sub> in 50 ml CH<sub>2</sub>Cl<sub>2</sub> was added dropwise with stirring to a solution of 0.75 g (2.47 mmoles) (I) [11] in 75 ml CH<sub>2</sub>Cl<sub>2</sub> at 20°C. After 1 h, the mixture was poured into water. The organic layer was separated, washed with water, dried, and evaporated. The residue was subjected to chromatography on a florisil column. The broad yellow zone was eluted with CH<sub>2</sub>Cl<sub>2</sub> and repeated chromatography on a florosil column gave 0.34 g (40%) (II), 0.02 g (6%) (III), 0.05 g (7%) (IV), and 0.12 g (27%) (V). Products (II), (IV), and (V) were identified according to their IR, PMR, and mass spectra [5].

# CONCLUSIONS

The acetylation of  $\eta^5$ -fluorenyltricarbonylmanganese is accompanied by the hydrogenation of the  $\eta^5$ -fluorenyl ligand and formation of  $\eta^5$ -(2-acetyl-3,4-dihydrofluorenyl)tricarbonylman-ganese, whose structure was established by x-ray diffraction structural analysis.

### LITERATURE CITED

- 1. E. O. Fischer, Z. Naturforsch., 9, 381 (1954).
- 2. R. B. King and M. B. Bisnette, Angew. Chem., Int. Ed. Engl., 2, 400 (1963).
- 3. F. R. P. Wild, L. Zsolnai, G. Huttner, and H. H. Brintzinger, J. Organomet. Chem., 232, 233 (1982).
- 4. E. Samuel, Bull. Soc. Chim. France, No. 11. 3548 (1966).
- 5. I. A. Lobanova, V. I. Zdanovich, P. V. Petrovskii, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1384 (1987).
- 6. C. Kowald and J. A. Wunderlich, Acta Crystallogr., <u>32</u>, 820 (1976).

- 7. J. L. Atwood, R. Shakir, J. L. Malito, et al., J. Organomet. Chem., <u>165</u>, 65 (1979).
- 8. J. W. Chinn, Jr. and M. B. Hall, J. Am. Chem. Soc., 105, 4930 (1983).
- 9. N. M. Loim, Chemical Sciences Candidate's Dissertation, Moscow (1970).
- 10. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, Kristallografiya, 28, 1029 (1983).
- 11. N. E. Kolobova, I. A. Lobanova, and V. I. Zdanovich, Izv. Akad. Nauk SSSR, Ser. Khim., 1651 (1980).

STUDY OF THE REACTIONS OF HALOGEN AND MERCURY HALOGEN DERIVATIVES OF METAL CARBONYLS WITH SAMARIUM AND YTTERBIUM

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In a continuation of investigations into the metal carbonyl derivatives of the bivalent and tervalent lanthanides [1, 2] we have studied the reactions of the halides  $L(CO)_mMX$ and mercury halides  $L(CO)_mHgX$  of metal carbonyls (M being an atom of a transition metal) with the zero-valent lanthanides Ln in relation to their oxidative addition through the M-X and M-HgX bonds.

The basis used for this are the reactions of Ln with R-I (R being, alkyl, aryl, carbonyl [3, 4], which lead to Grignard-like reagents RLnI, as well as the reactions of Ln with RHgI which give the heterobimetallic intermediates R-Hg-LnI [5].

It has been shown that in the reactions of  $L(CO)_m M-X$  with activated Sm and Yb, depending on the reaction conditions, the nature of the lanthanide and the transition metal, and the ratio of the reactants, either metal carbonyl derivatives of bivalent Sm or Yb (I)-(XVII) are formed or mixtures of the mono- and bis-metal carbonyl derivatives of the tervalent lanthanides

 $L(CO)_{m}M-X+nLn^{0} \longrightarrow \begin{array}{c} \xrightarrow{-20-30^{\circ}, THF} L(CO)_{m}MLnX \\ (I)-(XVII) \\ \xrightarrow{20-30^{\circ}, THF} L(CO)_{m}MLnX_{2}+[L(CO)_{m}M]_{2}LnX \end{array}$ 

 $\begin{array}{l} L(CO)_m MLnX: L(CO)_m M = M(CO)_5, \quad M = Mn, \quad Ln = Sm, \quad X = Cl(I), \quad Br(II), \quad I(III); \\ Ln = Yb, \quad X = Cl(IV), \quad Br(V), \quad I(VI), \quad M = Re, \quad Ln = Yb, \quad X = Cl(VII), \quad Br(VIII), \quad I(IX); \\ L(CO)_m M = Co(CO)_4, \quad Ln = Yb, \quad X = I(X); \quad L(OC)_m M = Mo(CO)_3 Cp, \quad M = Mo, \quad Ln = Sm, \\ X = Cl(XI), \quad Br(XII), \quad I(XIII); \quad Ln = Yb, \quad X = Cl(XIV), \quad Br(XV), \quad I(XVI); \quad M = W, \\ Ln = Yb, \quad X = I(XVII). \end{array}$ 

The pentacarbonyl halides of Mn are more reactive than the Re analogs, in accordance with the values of their reduction potentials [6].

The optimum conditions for the synthesis of the Mn complexes (I)-(IV) are: reaction temperature 0°C and 2-3-fold excess of lanthanide. For the Re derivatives (VII)-(IX) it is analogous but using a 2-3-fold (X = CI) or 3-4-fold (X = Br) excess of lanthanide. In the case of  $(CO)_5$ ReI, irrespective of the reaction conditions, mixtures of rhenium pentacarbonyl derivatives of bivalent and tervalent Sm and Yb are formed.

A convenient method for obtaining the complexes (CO)<sub>5</sub>ReLnI (Ln = Yb (IX) or Sm (XVIII) is the reaction of (CO)<sub>5</sub>ReHgI with the activated lanthanides in THF at -10 to -20°C. (CO)<sub>5</sub>ReHgI +  $nLn^{0} \rightarrow$  (CO)<sub>5</sub>ReLnI + Hg (IX), (XVIII)

According to the IR spectra the reactions of  $(CO)_{5}$  MnHal (Hal Cl, Br) with Ln, irrespective of the conditions, give mixtures of Ln<sup>3+</sup> complexes of the type  $(CO)_{5}$ MnLnX<sub>2</sub> and  $[(CO)_{5}Mn]_{2}$ LnX.

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