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PREPARATION AND PROPERTIES OF HYDRIDOMANGANESE IODIDE AND BINARY MANGANESE COMPLEXES CONTAINING ORGANOALUMINUMS

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SUMMARY

A manganese hydride complex of a composition $MnHI(THF)_{1.5}$ (THF = tetrahydrofuran) has been prepared from manganese iodide and triethylaluminum in THF. Binary complexes of composition $MnAl_2(CH_3)_4I_4(THF)_4$ and $MnAl_2(C_2H_5)_4I_4(THF)_4$, prepared by the reactions of $MnI_{10}(THF)_n$ with triethylaluminum and trimethylaluminum, were found to be composed of manganese diiodide and alkylaluminum iodide units. These binary complexes gave, upon further reaction with trialkylaluminums, a binary hydrido–manganese complex, $Mn_2AlH_4I_6(THF)_8$. The complexes were characterized by elementary analyses, IR spectroscopy, magnetic susceptibility measurement and chemical reactions.

Alkyl– and hydrido–manganese compounds having carbonyl and cyclopentadienyl ligands are known[1], but the studies of such compounds without these ligands are very scarce. The preparations of somewhat impure dimethylmanganese and methylmanganese iodide from manganese iodide and methyllithium have been reported[2,3], but the characterization of these compounds does not appear quite unequivocal. No simple hydrido–manganese compounds without carbonyl or cyclopentadienyl ligands have been reported as far as we are aware*. We describe here the preparation of crystalline hydridomanganese(II) iodide and binary manganese complexes with organoaluminum compounds.

RESULTS AND DISCUSSION

Manganese diiodide tetrahydrofuranate $MnI_2(THF)_n$ and a manganese–iodine complex (I) with composition $MnI_{10}(THF)_n$ were employed as starting materials. Complex (I) was obtained as green crystals by the reaction of manganese diiodide with iodine in tetrahydrofuran (THF); it is stable only in the presence of this solvent and decomposes releasing iodine upon removal of THF by evaporation.

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* The reactions of "dialkylmanganese" species prepared *in situ* have been studied, see *e.g.* ref. 4.

$$MnI_2+I_2 \xrightarrow{THF} MnI_{10}(THF)_n$$

(I)

(1) *Preparation of hydridomanganese iodide (II)*

Hydridomanganese iodide (II) was prepared from manganese diiodide and triethylaluminum in THF.

$$MnI_2+AlEt_3 \xrightarrow{THF} MnHI(THF)_{1.5}$$

(II)

The solid hydrido complex (II) is stable only at low temperature in the absence of air. Above −20° (II) decomposes slowly evolving hydrogen. The addition of organoaluminum compounds such as triethylaluminum, diethylaluminum monoethoxide and diethylaluminum chloride stabilizes the complex and (II) can be recrystallized from THF in the presence of triethylaluminum which can be removed later by washing with n-hexane at −78°. In other solvents such as diethyl ether, acetone, alkyl halides, alcohols and dimethylformamide (II) readily decomposes with evolution of hydrogen. In hexane and toluene (II) is stable below −10°. Addition of other ligands such as triphenylphosphine, 2,2′-dipyridyl and pyridine causes replacement of coordinated THF and leads to decomposition of (II) with evolution of hydrogen. Reactions with olefins, such as acrylonitrile, methacrylonitrile, styrene, α-methylstyrene, ethylene and butadiene, all resulted in the decomposition and no polymers or hydrogenated products were formed.

Complex (II) was characterized by elemental analysis, magnetic susceptibility measurement and chemical reactions. On reaction with decanol, (II) evolved 97% of the theoretical yield of hydrogen for $MnHI(THF)_{1.5}$. Addition of deuterium oxide released hydrogen gas composed of 99% HD, 0.5% H_2 and a trace of D_2, the total amount corresponding to 70% of the theoretical value. The amount of hydrogen formed by thermolysis of (II) varied depending upon heating conditions such as the initial as well as the rate of increase of the bath temperature; the quantity of hydrogen evolved was about 50% of the theoretical value when (II) decomposed by raising the temperature at the rate of 5°/min in the range room temperature to 80°.

The amount of THF in the complex varied somewhat depending upon the drying conditions. The average THF content in (II), obtained by drying the complex at −30° for 1 day at 10^{-2} to 10^{-3} mm, was 1.5 mol/Mn but this value decreased to 1.2 by drying at −10° for 5 days.

The infrared spectrum of (II) shows strong and broad bands at 1770 and 800 cm^{-1} in addition to bands due to coordinated THF at 1028 and 865 cm^{-1}. The band at 1770 cm^{-1}, which disappears on allowing the sample to stand at room temperature, may be due to the Mn–H stretching vibration. The complex had a magnetic susceptibility of 17.7×10^{-6} emu · g^{-1} at 30° corresponding to a magnetic moment of 3.47 B.M. This value is somewhat smaller than the magnetic moment with 3 unpaired electrons.

As a route to hydridomanganese iodide the formation of an ethylmanganese complex which releases ethylene was considered quite plausible. However, no ethylene was detected in the gas phase during the reaction and only ethane and C_4 hydrocarbons were found. A possible explanation for this fact is that dimerization of ethylene had occurred but no evidence was obtained to support such a catalytic dimerization by the isolated complex (II).

(2) *Formation of binary complexes containing manganese and aluminum components*

In contrast to other transition alkylmetals which are destabilized[5], the manganese hydride (II) can be stabilized by addition of organoaluminum compounds. The organoaluminum compounds do not simply act as scavengers for O_2 and H_2O, and in their absence (II) decomposed in vacuo at much lower temperatures evolving hydrogen with a solution color change. The precise reason of the stabilizing effect of the organoaluminum compounds is not clear. Investigation of the effect of organoaluminum compounds on the stabillity of the manganese hydride led to the isolation of some new relatively stable complexes containing both manganese and aluminum components.

(2*a*) *Formation of* $MnAl_2(CH_3)_4I_4(THF)_4$ *(III)*. The reaction of $MnI_{10}(THF)_n$ (I) with trimethylaluminum in THF yielded a light green crystalline complex (III) of composition $MnAl_2(CH_3)_4I_4(THF)_4$. In the course of the reaction methane together with a trace of ethane were evolved. The composition of (III) was determined on the basis of elementary analysis, infrared spectrum and chemical reactions. Complex (III) is thermally stable and can be recrystallized from hot THF containing trimethylaluminum. Heating the solid complex by raising the bath temperature at the rate of 5°/min led to the melting of (III) at 70° and the complex changed from light green through yellow to pink. Upon further heating to 180° iodine was liberated. The amount of methane formed was minor. Reaction of (III) with decanol liberated 81% of methane calculated for (III). Dissolution of (III) in THF in the absence of trimethylaluminum gave a yellow solution from which an orange complex of composition of $MnI_2(THF)_n$ ($n \sim 3$) was isolated. Neither methane nor ethane was evolved during the reaction.

These results suggest the presence of the following equilibrium in the THF solution:

$$\underset{\text{(III)}}{MnAl_2(CH_3)_4I_4(THF)_4} \overset{\text{THF}}{\rightleftharpoons} MnI_2(THF)_n + 2(CH_3)_2AlI(THF) \qquad (1)$$

The addition of trimethylaluminum to the THF solution containing (III) hinders the dissociation of (III) as suggested in Eqn. 1. The addition of Lewis bases such as pyridine and dipyridyl to (III) gives manganese complexes without a methyl group as proved by the absence of gas evolution upon treatment of the isolated base-coordinated manganese complex with alcohol. The methyl groups in (III) are thought to be attached to the soluble aluminum-containing product, since no gas evolution was observed upon reaction of (III) with the bases. Whether manganese in (III) is directly bonded to aluminum or bridged through a methyl group or halogen atoms is not clear at present. However, a structure with bridging methyls seems unlikely since no methyl group transfer from aluminum to manganese is observed during the decomposition of (III) with THF and other Lewis bases, as indicated by the absence of methane or ethane which would be evolved by decomposition of a methylmanganese complex.

The infrared spectrum of (III) showed new bands at 2930, 1195, 1040, 990, 958, and 839 cm^{-1} which are not observed in the spectrum of $MnI_2(THF)_n$. The band at 2930 cm^{-1} is assigned to the C–H stretching vibration of the methyl group bonded to aluminum. Two strong bands at 990 and 839 cm^{-1} may be due to the C–O–C stretching vibrations of the coordinated THF.

Complex (III) had a magnetic susceptibility of 13.4×10^{-6} emu·g^{-1} at 15° corresponding to a magnetic moment of 5.30 B.M. which is somewhat lower for the value expected for spin-free five unpaired electrons.

(2*b*) *Formation of* $MnAl_2(C_2H_5)_4I_4(THF)_4$ *(IV)*. A similar reaction of MnI_{10}-$(THF)_n$ with triethylaluminum gave a light green crystalline complex (IV) of composition of $MnAl_2(C_2H_5)_4I_4(THF)_4$. This complex behaves similarly to its methyl homolog (III). Alcoholysis with decanol gave 74% of ethane calculated for (IV). Dissolution of (IV) in THF yielded $MnI_2(THF)_n$. Addition of dipyridyl led to the decomposition of (IV) giving a dipyridyl coordinated manganese complex. Complex (IV) did not initiate the polymerization of acrylonitrile or of styrene; a pale yellow acrylonitrile-coordinated complex was obtained.

(2*c*) *Formation of* $Mn_2AlH_4I_6(THF)_6$ *(V)*. Further reactions of complexes (III) and (IV) with an excess of triethylaluminum yielded a manganese hydride complex (V) containing aluminum. Complex (V) is much more stable than the simple manganese hydride (II) since it can be recrystallized from hot THF in the absence of aluminum compounds. Hydrolysis of (V) with D_2O (D_2O content 99.9%) gave hydrogen containing 99.0% of HD and 1.0% of H_2, the total amount of gas evolved being 94% of the value calculated for (V). Thermolysis of (V) up to 150°C released H_2 which amounted 33% of the calculated value. The infrared spectrum of (V) is very similar to that of $MnHI(THF)_{1.5}$ (II) and shows C–O–C stretching vibrations of the coordinated THF at 1028 and 865 cm^{-1} and a broad strong absorption at 1775 cm^{-1} which disappears allowing the KBr disc of the sample to stand in contact with air. The similarity between the spectra of (V) and (II) strongly suggests that the hydrogens are at least in part attached to manganese and that the manganese hydride complex is stabilized by the aluminum component. The suitable Lewis basicity of THF may help to stabilize the binary complexes. The addition of strong bases such as pyridine causes decomposition of (V), on other hand (V) also decomposes in solvents other than THF, *e.g.* in diethylether, evolving hydrogen. Acrylonitrile decomposed the complex whereas butadiene and isoprene did not react with (V). Isobutyl vinyl ether and styrene were polymerized by (V) probably by a cationic mechanism. By analogy to complexes (III) and (IV), complex (V) may be regarded as an adduct of $2MnHI + AlH_2I$.

Details of complexes prepared in the present work are summarized in Table 1 together with their properties. The binary complexes containing the transition metal and the aluminum component reported herein represent part of a series of binary complexes containing titanium or vanadium combined with aluminum compounds and THF or diethyl ether[6].

EXPERIMENTAL

All procedures were carried out under a purified nitrogen. Solvents, dehydrated by usual methods, were distilled and stored under nitrogen before use. Manganese powder (200 mesh, purity over 99.5%) was used as purchased. Other reagents such as trimethylaluminum, triethylaluminum, diethylaluminum monochloride, 2,2'-dipyridyl, triphenylphosphine, decanol, deuterium oxide and iodine were used without purification.

TABLE 1

PROPERTIES OF SINGLE AND BINARY MANGANESE COMPLEXES

Complex	*Composition*	*Properties*
I	$MnI_{10}(THF)_n$	Green microcrystals; releases iodine on the loss of THF
II	$MnHI(THF)_{1.5}$	Light green plates, dec. below −10°
III	$MnAl_2(CH_3)_4I_4(THF)_4$	Light green plates, m.p. 70° (dec.)
IV	$MnAl_2(C_2H_5)_4I_4(THF)_4$	Light green plates, m.p. 40° (dec.)
V	$Mn_2AlH_4I_6(THF)_8$	Light green needles, dec. 70–80°

Analytical methods. The manganese content was determined by a Volhard method after treatment of the sample with sulfuric acid, hydrogen peroxide and the removal of iodine. The iodine content was determined by a Mohr method after treatment of the sample with sodium hydroxide solution and removal of precipitated manganese dioxide by filtration. The aluminum content was determined, after the removal of manganese dioxide, by a gravimetric method. Tetrahydrofuran contained in the sample was determined by gas chromatography after displacement with pyridine using toluene as the internal reference. The quantities of alkanes evolved in chemical reactions of the complexes were measured by volumetric methods and identified by gas chromatography and mass spectrometry.

Infrared spectra were recorded on a Hitachi Grating Spectrophotometer EPI-G using KBr discs prepared under nitrogen.

Preparation of MnI_2

Anhydrous manganese iodide was prepared by a reported method[7] subject to modification. Manganese powder (15 g) was added to a THF solution (250 ml) containing iodine (80 g) and the reaction mixture was stirred for 12 h at 50°. After cooling, a creamy precipitate which formed was filtered off, then washed with THF to remove the unreacted iodine. The precipitate was dissolved in 250 ml of hot THF, filtered hot to remove unreacted iodine, cooled to −20° and kept overnight to yield orange plates. After recrystallization from THF the compound was dried in vacuum at −10° yielding THF-coordinated manganese diiodide, $MnI_2(THF)_n$, which upon further evacuation at 50° for 2–3 days lost THF and gave amorphous pink manganese diiodide; yield, 70% (Found: Mn, 18.5: I, 82.0. MnI_2 calcd.: Mn, 17.8: I, 82.2%).

Preparation of $MnI_{10}(THF)_n$ *(I)*

Iodine (20 g) was added to THF (150 ml) containing MnI_2 (10 g) and the solution was stirred for 2 h at room temperature. The green fine crystals with a metallic lustre which formed, were separated by filtration and washed three times with 100 ml of THF to remove unreacted MnI_2 and iodine. The complex was dried in vacuum at −20° to the extent that the crystals were slightly wet with THF. Further removal of THF causes the dissociation of iodine with color changes to red and then to brown. The atomic ratio of Mn/I in the wet sample was 1/10.3.

$MnHI(THF)_{1.5}$ *(II)*

When several grams of MnI_2 in 200 ml of THF cooled at −78° was added

20–30 ml of triethylaluminum (Al/Mn = 10–15) a brown solution was obtained which was stirred at −10 to −20° for 3 to 7 days during which time the solution turned from brown to dark brown, and green crystals with a dark brown precipitate deposited. Hexane (50–100 ml) was added to the solution, which was kept further for 1–2 days at −20° to obtain further crops of the light green crystals. These were separated from the solution by filtration (which allows the removal of most of the dark precipitate) and recrystallized from 100 ml of THF containing 3–5 ml of triethylaluminum. The recrystallization process was repeated 3–4 times keeping the temperature below −5° until the THF solution became clear light yellow. The light green fluorescent plates thus obtained were washed several times with hexane (50 ml) pre-cooled to −78°, then dried in vacuo below −30° for 1 day; yield, 20%. The product was hygroscopic, very sensitive to air and decomposed giving a green substance. (Found: Mn, 18.5; I, 45.2; THF, 37.4; ratio of Mn/I/THF = 1.00/1.05/1.54).

The reaction of (II) (50.9 mg) with decanol in a vacuum system released 3.82 ml of hydrogen (97.4% of the calculated value for $\text{MnHI(THF)}_{1.5}$). On heating (II) (75.1 mg) at the rate of 5°/min, (II) started to evolve gas at 30°. This gas evolution ceased at 80° with the change from light green through yellow to pink. The amount of hydrogen evolved was 1.45 ml (50.1% of the calculated value). Heating the complex at higher rate caused a decrease in the quantity of hydrogen evolved.

$MnAl_2(CH_3)_4I_4(THF)_4$ (III)

To (I) (90 g) in THF (70 ml) cooled at −78° was added 15 ml of trimethylaluminum with stirring. The suspension became a red homogeneous solution and methane together with a small amount of ethane were evolved. The solution was slowly brought to room temperature and stirred for several hours until it was almost colorless. Light green fine crystals deposited upon keeping the solution at −20° for one day. The complex was recovered by filtration, and was recrystallized from THF (100 ml) containing 3–5 ml of trimethylaluminum. The dissolution of the complex can be carried out at 50–70°. After two recrystallizations, the complex was washed several times with 50 ml aliquots of hexane and was dried in vacuo at 0 to −10° for 1 day. (Found: C, 24.1; H, 4.4; Al, 6.14; I, 52.2; Mn, 5.76; THF, 29.4; ratio of Mn/Al/I/C/H/THF 1.00/2.17/3.93/18.4/41.8/3.92. $C_{20}H_{44}Al_2I_4MnO_4$ calcd.: C, 24.9; H, 4.56; Al, 5.60; I, 52.8; Mn, 5.70%).

Decanolysis of (III) (59.6 mg) released 1.99 mmol of methane, (80.6% of the calculated value). Thermolysis of 73.8 mg of (III) gave 2.80×10^{-5} mol of methane.

The reaction of (III) in THF

(III) (5 g) was dissolved in 50 ml of THF to obtain a yellow homogeneous solution, which upon storage at −20° for 1 day deposited light orange plates. These crystals were washed with THF and dried at −10° in vacuo for 5 hours. No gas evolution was observed during the reaction. (Found: C, 26.5; H, 4.1; Al, 0 ; I, 49.7; Mn, 9.85; ratio of Mn/I/C/H 1.00/2.09/12.30/22.8.) The orange complex did not react with trimethylaluminum.

$MnAl_2(C_2H_5)_4I_4(THF)_4$ (IV)

When triethylaluminum (5 ml) was added to a cooled THF solution (50 ml) of (I) (18 g) at −78°, color changed from brown to red and a clear solution was obtained accompanied by gas evolution. Upon warming to room temperature the solution changed to pale yellow. After a few hours, the solution was concentrated to 20 ml and kept at −20° for 1 day to yield light green plates. These crystals were washed with hexane cooled at −20° and dried for one day in vacuo at −10°. The complex is more soluble in THF than is (III). (Found: C, 26.1; H, 4.75; I, 51.0; Mn, 5.33; $C_{24}H_{52}Al_2I_4MnO_4$ calcd.: C, 27.6; H, 5.09; I, 49.9; Mn, 5.39%), Decanolysis of (IV) (31.9 mg) released 0.0921 mmol of ethane (73.7% of the calculated value). (IV) dissociates in a THF solution giving the orange manganese diiodide complex.

$Mn_2AlH_4I_6(THF)_8$ (V)

Addition of complex (III) or (IV) (2 g) to THF (30 ml) containing 5% of triethylaluminum at −78° yielded a yellow homogeneous solution. Further addition of triethylaluminum (5 ml) caused a color change to orange. The solution was gradually warmed to room temperature and stirred for several hours until the first crop of light green crystals was formed. Ethane, ethylene and C_4 hydrocarbons were also formed in a ratio of 10/1/5 during the reaction. The solution was kept for 2 days at −20° in order to obtain further crops of light green crystals which were separated by filtration and recrystallized three times from THF at 50°. The complex was dried in vacuo at −10° for a day. (Found: Al, 1.84; I, 47.46; Mn, 7.06; THF, 36.7. Ratio of Mn/Al/I/THF 1.00/0.532/2.96/3.95). Complex (V) lost THF less readily than (II) or $MnI_2(THF)_m$ and is relatively stable in THF but readily decomposed evolving hydrogen in diethyl ether, pyridine, acrylonitrile and styrene.

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