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The Preparation and Suggested Geometry for Bis(pentacarbonylmanganate)mercury(II) Monotetrahydrofuran Adduct, $[(CO)_5Mn]_2Hg\cdot THF$

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Treatment of $NaMn(CO)_5$(THF solution) with $(C_2H_5)_2AlCl\cdot THF$ in the presence of excess Na amalgam results in the formation of $[(CO)_5Mn]_2Hg\cdot THF$, (I), in good yield. Formation of (I) does not take place if any of the indicated reagents are omitted from the reaction system. Addition of pentane to a benzene solution of (I) results in precipitation of (I) leaving a yellow solution from which trace amounts of $Hg[Mn(CO)_5]_2$, (II), were isolated and characterized by comparison of its infrared [2] and mass [3] spectra with an authentic sample [4].

The mass spectrum of (I) was obtained and is a composite of that of (I) and THF. Apparently (I) undergoes decomposition to (II) and THF under the conditions of mass spectrum determination. In an effort to determine whether THF is adducted with (II) to afford (I) or (I) contains a hydrocarbon fragment which affords THF on pyrolysis, the ^1H nmr spectrum of (I) was obtained in d_8 THF. No ^1H signals were observed other than the weak signals due to the impurity, ^1H THF, in d_8 THF. From this result, one may infer no other ^1H environments are present in (I) other than THF. In addition, the ^1H nmr spectrum of (I) in d_6 acetone indicated only ^1H signals from THF.

In an effort to prepare (I) from (II), (II) was treated with THF in the temperature range 0–60 °C; no solution formation occurred and in no case was the green color of (I), detected. However, when a THF solution of (I) is allowed to stand at 25 °C for several days, (II) precipitates in small amounts.

With regard to the reactivity of the components of the reaction system affording (I), it was demonstrated that treatment of $(C_2H_5)_2AlCl$ with THF in the absence or presence of Na/Hg alloy, affords only $(C_2H_5)_2AlCl\cdot THF$, (III). III is a non-volatile (at 25 °C) clear liquid and was characterized by its ^1H NMR spectrum in benzene. This spectrum consisted of a quarted centered at 0.26 ppm from TMS, J = 8 Hz, and a complicated multiplet due to overlap of the C_2H_5Al triplet and the THF triplet with absorptions at 1.52, 1.35, 1.30, and 1.18 ppm from TMS. The β THF triplet, J = 7 Hz, was centered at 3.70 ppm from TMS (3.67 in pure THF). By way of comparison, $(C_2H_5)_2AlCl$ dissolved in benzene exhibits a quarter centered at 0.42 ppm from TMS, J = 8 Hz and a triplet centered at 1.29 ppm from TMS. Hydrolysis data associated with (III) are

$$(C_2H_5)_2AlCl\cdot THF + 2H_2O \longrightarrow 2C_2H_6 + Al(OH)_2^+ + Cl^- + THF \qquad (1)$$

and are consistent with the formulation based on ^1H NMR data. In the case of reaction of (III) with Na/Hg, the colorless nature of the 'product', (III), is also consistent with the absence of any aluminium–aluminium bonds [5], as is the absence of H_2 evolution during hydrolysis [6].

Possible Geometry for (I)

The infrared spectra of (II) and (I) (carbonyl region, KBr pellet) are presented in Figs. 1A and 2B, respectively, while the infrared spectra of (I), mull, and in THF are shown in Figs. 2A and 2B, respectively. As may be deduced from these respective infrared data, the spectra of (I) and (II) are virtually identical (KBr disk) while the solution spectrum of (I) in THF, Fig. 2B, indicates clear resolution of three absorptions at 2045 (m), 1970 (s), and 1900 (m) cm^{-1} and is consistent with C_{4v} symmetry about Mn [7]. In addition to the increased resolution for the solution data, (I), the δ M–C mode is very weak as compared to the strong absorption at 628 and 630

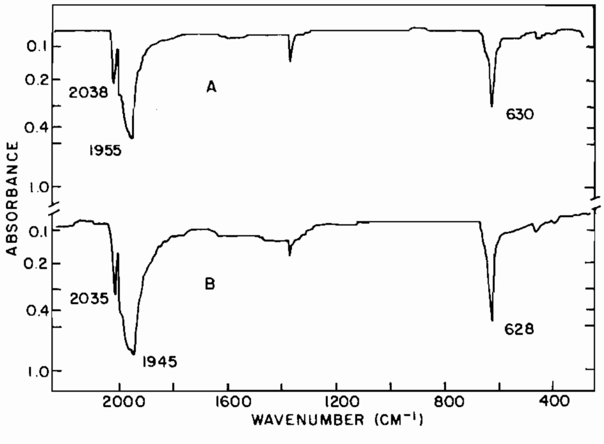

Figure 1. Solid state (KBr) infrared spectra; A) $[(CO)_5Mn]_2Hg$, B) $[(CO)_5Mn]_2Hg\cdot THF$.

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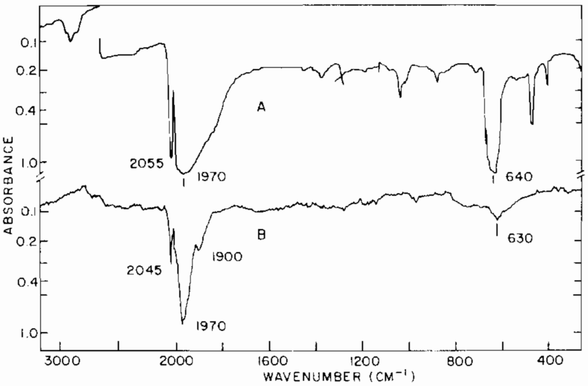

Figure 2. Infrared spectra of $[(CO)_5Mn]_2Hg{\circ}THF$: A) mull, B) In THF.

cm^{-1} for (I) and (II), respectively, in KBr, Fig. 2. Another surprising feature of the infrared spectrum for (I) (KBr, Fig. B) is the complete lack of infrared absorptions associated with THF (2980s, 2860s, 1450w, 1375w, 1175s, 915s, 640w(br) cm^{-1}). We have observed this same absence of infrared absorptions for coordinated THF in $HgBr_2{\cdot}THF$ by comparison of the infrared spectra of $HgBr_2$ and $HgBr_2{\cdot}THF$. In addition, the infrared spectra of these two species are virtually identical with respect to frequencies and absorption band shapes. One possible explanation is displacement of THF by Br^- during KBr disk formation.

At this time the mechanism associated with the formation of $[Mn(CO)_5]_2Hg{\cdot}THF$ remains clear. We have established the necessity for the presence of both $(C_2H_5)_2AlCl$ and Na amalgam, in addition to $NaMn(CO)_5$. Furthermore, we have determined that $(C_2H_5)_2AlCl$ only forms a Lewis acid–base complex with THF, and that the latter is inert toward Na amalgam under the employed reaction conditions. $[Mn(CO)_5]_2Hg{\cdot}THF$ is stable at 25 °C and decomposes only very slowly in solution to afford $Hg[Mn(CO)_5]_2$. Finally, treatment of $Hg[Mn(CO)_5]_2$ with THF does not afford $[Mn(CO)_5]_2Hg{\cdot}THF$.

Experimental

Equipment

All handling of reagents was in either a vacuum line, maintained at 10^{-5} torr, or in a nitrogen atmosphere dry box operating at <10 ppm O_2 and H_2O. Infrared spectra of gases were obtained in a 10 cm gas cell fitted with KBr plates, while spectra of solids were obtained from Nujol and/or Fluorolube mulls, KBr disks or in solution employing matched cells. All infrared spectra were obtained with a Perkin-Elmer Model 457 grating spectrophotometer. Noncondensable gases were collected and measured by means of a volume calibrated Toepler pump system and subsequently identified by selective combustion over CuO (CO, 150 °C; CH_4, 800 °C). NMR spectra were recorded with either Varian Associates A-60 or A-60-A spectrometers. Melting points were measured with a Mel-Temp melting point apparatus from Laboratory Devices, Cambridge, Massachusetts. In all cases samples were sealed in Kimax-51 capillary tubes; all melting points are uncorrected.

Analytical

Aluminum and chloride analyses were performed by quinoline precipitation and titration with $AgNO_3$, respectively, while Mn, Hg, C, and H analyses were performed by Galbraith Labs, Knoxville, Tennessee.

Chemicals

Acetone, C_3H_6O, Anal. Reagent, Mallinckrodt Chemical Works, was dried over molecular sieves. *Benzene,* C_6H_6, Anal. Reagent, Chemical Samples Co., was dried over $LiAlH_4$ and distilled from the hydride prior to use. *Benzene*-d_6, C_6D_6, 99.5%, ICN Corporation, was used as received. *Ceric Ammonium Nitrate,* $(NH_4)_2Ce(NO_3)_6$, Reagent (A.C.S.), G. Frederick Smith Chemical Co., was used as received. *Pentane,* C_5H_{12}, Anal. Reagent, Chemical Samples Co., was stored over $LiAlH_4$ and distilled prior to use. *Diethyl aluminum chloride,* $(C_2H_5)_2AlCl$, Alfa Products, was used as received. *8-Hydroxyquinoline,* C_9H_7NO, Aldrich Chemical Co., was used as received. *Lithium Aluminum Hydride,* $LiAlH_4$, Alfa Inorganic, Inc., was used without further purification. *Dimanganese Decacarbonyl,* $Mn_2(CO)_{10}$, Strem Chemicals, was used as received. *Mercury,* Triple distilled, Bethlehem Apparatus Co., was used as received. *Osmium Tetroxide,* OsO_4, Reagent Grade, Fisher Scientific Co., was used as received. *Sodium,* ingot, 99%, Research Organic/Inorganic Chemical Corp., was used as received. *Tetrahydrofuran,* C_4H_8O, Certified, Fisher Scientific Co., was dried over $LiAlH_4$ and distilled from the hydride prior to use. *Toluene,* C_7H_8, Reagent Grade, Chemical Samples Co., was dried over $LiAlH_4$ and distilled from the hydride prior to use. *Sodium Manganese Pentacarbonyl,* $NaMn(CO)_5$, was prepared by Na/Hg cleavage of $Mn_2(CO)_{10}$ [8]. The reaction product was used in situ, and also $NaMn(CO)_5$ was purified by vacuum filtration employing THF to removed finely divided Hg and/or amalgam. The THF was distilled under vacuum and the remaining $NaMn(CO)_5$ was pumped on for 4 hours at 50 °C to remove any remaining $Mn_2(CO)_{10}$.

Preparation of $(C_2H_5)_2AlCl{\cdot}THF$

A 100 ml bulb containing 3 ml of $(C_2H_5)_2AlCl$ was frozen to –196 °C and approximately 10 ml of

THF condensed into the bulb. The vessel was allowed to warm to 25 °C and stirred for 1 hr. The system was pumped on to remove excess THF, leaving a clear non-volatile liquid, $(C_2H_5)_2AlCl\cdot THF$. Treatment of a 0.4269 g sample of $(C_2H_5)_2AlCl\cdot THF$ (2.22 mmol) with *ca.* 4 ml of H_2O for 4 hr at 25 °C afforded 4.40 mmol of C_2H_6. *Anal.* Calcd. for $(C_2H_5)_2AlCl\cdot THF$: Cl, 18.42; Found, 18.76%.

Reaction of $(C_2H_5)_2AlCl$ with Na/Hg in THF

A 100 ml bulb containing 3 ml of $(C_2H_5)_2AlCl$ was frozen to −196 °C and approximately 10 ml of THF were condensed into the bulb. Approximately 1 g of Na/Hg was added to the reaction system and the contents warmed to 60 °C with stirring for 3 days. The excess THF was pumped off leaving a clear liquid and Na/Hg alloy. The ^1H NMR spectrum and analyses of the clear liquid were identical to those of the product form the reaction of THF with $(C_2H_5)_2AlCl$.

Attempted Reaction Between $NaMn(CO)_5$ and $(C_2H_5)_2AlCl$

A 100 ml bulb was charged with 2 g of $NaMn(CO)_5$ which had been purified by repeatedly filtrating with THF in order to remove any occluded Na/Hg. The bulb was frozen to −196 °C, 30 ml of THF condensed into the flask, and subsequently warmed to 25 °C with solution of $NaMn(CO)_5$. Next the contents of the flask were frozen to −196 °C and 3 ml of $(C_2H_5)_2AlCl$ added followed by heating at 60 °C and stirring for 3 days. During the 3 days there was no color change nor evolution of any noncondensable gas. Subsequent examination of the reaction mixture indicated only the presence of starting materials.

Attempted Reaction of $NaMn(CO)_5$ with $(C_2H_5)_2AlCl$ in the Presence of Hg

A 100 ml bulb was charged with 2 g of $NaMn(CO)_5$, which had been filtered to remove any Na/Hg, and 3 ml $(C_2H_5)_2AlCl$. The bulb was frozen to −196 °C and 30 ml of THF condensed into the flask. Approximately 4 g of Hg was added and the vessel warmed to 60 °C with stirring for 3 days. There was no color change nor evolution of non-condensable gases during the reactive period. The adduct, $(C_2H_5)_2AlCl\cdot THF$, was subsequently isolated and characterized by ^1H NMR spectroscopy and its physical properties.

Preparation of $[(CO)_5Mn]_2Hg\cdot THF$

An excess of $(C_2H_5)_2AlCl$ was added to a solution of 3.0 g of $NaMn(CO)_5$ (containing excess Na amalgam) in 50 ml of THF at −196 °C followed by warming at 60 °C with stirring for 72 hr. During this reaction time the solution color changed from clear yellow to dark green, (red to transmitted light) and a pale yellow solid precipitated from solution. At the end of the reaction period, the vessel was cooled to −196 °C, and checked for the presence of noncondensable gases; none were found. The system was vacuum filtered affording a dark green solution and a white solid which proved to be NaCl. THF was removed from the system under vacuum and after pumping on the system overnight at 25 °C, 50 ml of fresh THF were condensed onto the dark green solid and the mixture stirred for 1 hr. The resulting system was vacuum filtered, again affording a dark green solution and NaCl. Benzene was added to the THF solution inducing further precipitation of NaCl, which was removed by filtration. This addition of benzene, followed by filtration, was repeated until no further NaCl precipitated. The solvent was slowly vaporized from the dark green solid. No more precipitation of NaCl was evident during this process. Approximately 50 ml of cyclopentane was condensed onto the green solid, at −196 °C, warmed to 25 °C and stirred for 30 min. Vacuum filtration afforded the green solid, 3.3 g (insoluble in the cyclopentane) and a light yellow solution from which trace amounts of $[(CO)_5Mn]_2Hg$ were subsequently isolated and identified. This filtration procedure was repeated until the cyclopentane came through the frit clear. The green solid (I) was pumped on at 25 °C for 8 hr. *Anal.* Calcd. for $[(CO)_5Mn]_2Hg\cdot THF$: Hg, 27.37; Mn, 16.59; C, 25.36; H, 1.20. Found: Hg, 27.07; Mn, 17.18; C, 24.92; H, 1.18%. The infrared spectrum of $[(CO)_5Mn]_2Hg\cdot THF$ (fluorolube and nujol mulls) contains absorptions at: 2908w(b), 2055s, 1970s(b), 1840(sh), 1374w, 1042m, 1020w(sh), 883w, 715w, 675m, 640s(b), 474m, and 406w, cm^{-1}.

THF Analysis for $[(CO)_5Mn]_2Hg\cdot THF$

A sample of (I) 0.0265 g, was heated to 95 °C *in vacuo* for 24 hr to afford 3.99×10^{-2} mmol THF, which was subsequently identified by comparison of its infrared and mass spectrum with an authentic sample. Additional analyses: a 0.0243 g sample afforded 3.67×10^{-2} mmol THF, and a 0.0112 g sample afforded 1.6×10^{-2} mmol THF. *Anal.* Calcd. for $[(CO)_5Mn]_2Hg\cdot THF$: THF, 10.8. Found: 10.8, 10.9, and 10.7%.

CO Analysis for $[(CO)_5Mn]_2Hg\cdot THF$

Ten ml of an acetone solution of $Ce(NH_4)_2(NO_3)_6$ and a crystal of OsO_4 were added to 0.0201 g of (I). The system was stirred at 25 °C for 8 hr followed by cooling to −196 °C. 3.04×10^{-4} mmol of a noncondensable gas was collected and shown to be CO by combustion to CO_2. An infrared spectrum of the remaining solid, after removal of solvent, was blank in the metal–CO region indicating complete loss of CO from the green solid. Similar treatment of an acetone blank afforded no CO. *Anal.* Calcd. for $[(CO)_5Mn]_2Hg\cdot THF$: CO 42.40. Found, 42.34%.

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