interactions with Eu(II) ions relative to framework oxides, as indicated by the longer Eu(II)–H_2O bonds. The particularly long Eu(2)–$H_2O(2)$ bond may result in part from the strong hydrogen-bonding interactions between $H_2O(2)$ water molecules and framework O(3) oxide ions.

Only the angles O(3)–Eu(1)–$H_2O(2)$ and O(3)–Eu(2)–$H_2O(2)$, at 79.4 (5) and 84.7 (8)°, respectively, are near the ideal value of 77° which results when all atoms of a seven-coordinate complex are placed at equal distances from the metal ion so that all adjacent pairs of atoms make equal angles at the metal.[25] The O(3)–Eu(1)–O(3) and O(3)–Eu(2)–O(3) angles at 111° are considerably larger as a result of 6-ring constraints. All remaining angles about both Eu(1) and Eu(2) are smaller, nearly identical at 69°, somewhat less than the average value found in eight-coordinate square-antiprismatic complexes.[26] This suggests that the zeolite framework, which requires that three coordination angles of an ion associated with a 6-ring not be too much less than 120°, has kept the coordination number of these ions from being eight, or more.

Hydrated Eu_5Na_2-A has a remarkable structure. In no previous zeolite A structure has such an elaborate and well-ordered bonding network between cations, ligands, and the framework been found. The molecules at $H_2O(2)$ in the sodalite unit form a well-ordered hydrogen-bonded structure and, in addition and in different ways, participate in the coordination spheres of both Eu(1) and Eu(2).

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Registry No. Eu_5Na_2-A, 66551-62-0.

Supplementary Material Available: Listing of the observed and calculated structure factors, Supplementary Table I (4 pages). Ordering information is given on any current masthead page.

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Allylmanganese Phosphine and Phosphite Chemistry. Synthesis, Chemistry, and Catalytic Properties[1]

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A new family of compounds derived from η^3-$C_3H_5Mn(CO)_4$ by partial substitution of CO by trialkyl phosphites and trialkylphosphines has been synthesized and its catalytic chemistry explored. The disubstituted compounds η^3-$C_3H_5Mn(CO)_2(PR_3)_2$, with R = OCH_3, O-*i*-C_3H_7, and C_2H_5, catalyzed the hydrogenation of alkenes with rates that increased as the steric bulk of the phosphorus ligand increased and without detectable catalyst decomposition. These allylmanganese species selectively complexed acetylenes over olefins under hydrogenation conditions and thus they selectively hydrogenate an acetylene to an olefin. The trisubstituted compound η^3-$C_3H_5Mn(CO)[P(OCH_3)_3]_3$ was a rapid alkene hydrogenation catalyst precursor which underwent a rapid competitive loss of the allyl group as propene and concomitant catalyst death. The compound η^3-$C_3H_5Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$ reacted with CH_3SO_3H and with CF_3SO_3H through a formal displacement of the η^3-allyl by an alkanesulfonato group to give $(CH_3SO_3)Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$ and $(CF_3SO_3)Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$, respectively. The methanesulfonato complex was a catalyst precursor for the hydrogenation of 1-hexene, although less active than the corresponding allylmanganese complex. Unlike the formally analogous η^3-$C_3H_5Co[P(OR)_3]_3$ compounds, none of the above catalyzed the hydrogenation of benzene. Reaction of η^3-$C_3H_5Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$ with CF_3SO_3H in the presence of dienes gave $(\text{diene})Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+CF_3SO_3{}^-$ compounds. The norbornadiene derivative was obtained in good yield whereas only a low yield of the 1,5-cyclooctadiene analogue was isolated, the major product being $(CF_3SO_3)Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$. This new manganese chemistry appears to provide the first examples of a Mn(I)–Mn(III) couple in coordination catalysis.

Introduction

Designed control of the chemistry of a coordination or organometallic complex can be achieved by ligand modification. A ligand combination set that we have found especially effective for oxidative-addition reactions is the π-allyl ligand with either phosphine or phosphite ligands. The latter increase the electron density on the metal atom and thereby enhance the potential for an oxidative addition while the allyl ligand through generally facile π–σ transformations can provide the coordinately unsaturated intermediate. The efficacy of this ligand combination set is illustrated in the chemistry of the η^3-$C_3H_5Co[P(OR)_3]_3$ and η^3-$C_3H_5Co(PR_3)_3$ complexes which effect a unique, fully stereoselective catalysis of aromatic hydrocarbon hydrogenation.[2,3] By imposing this specific ligand design on manganese, we have generated the first examples of manganese coordination catalyst precursors that operate on a facile Mn(I)–Mn(III) couple and have obtained further basic information about hydrogenolysis of allyl–metal bonds in coordination chemistry.

Results and Discussion

Our initial objective was the synthesis of η^3-$C_3H_5Mn[P(OR)_3]_4$ or η^3-$C_3H_5Mn(PR_3)_4$ complexes. As there was no obvious intermediate for such a synthesis, the rather inelegant synthesis approach based on ligand displacement in the readily prepared η^3-$C_3H_5Mn(CO)_4$ was employed. Ligand replacement in this allylmanganese carbonyl proceeded with thermal and with photolytic activation to cleanly yield η^3-$C_3H_5Mn(CO)_2L_2$, with L = $P(OCH_3)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, and $P(C_2H_5)_3$, and η^3-$C_3H_5Mn(CO)[P(OCH_3)_3]_3$, eq 1–3.[4] No

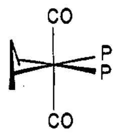
$$\eta^3\text{-}C_3H_5Mn(CO)_4 + 2L(\text{excess}) \xrightarrow{\Delta} \eta^3\text{-}C_3H_5Mn(CO)_2L_2 + 2CO \tag{1}$$

$$\eta^3\text{-}C_3H_5Mn(CO)_4 + 2L \xrightarrow{h\nu(\text{Pyrex})} \eta^3\text{-}C_3H_5Mn(CO)_2L_2 + 2CO \tag{2}$$

$$\eta^3\text{-}C_3H_5Mn(CO)_4 + 3P(OCH_3)_3 \xrightarrow[\text{argon flow}]{h\nu(\text{quartz}),\ 0\ ^\circ C} \eta^3\text{-}C_3H_5Mn(CO)[P(OCH_3)_3]_3 + 3CO \tag{3}$$

η^3-allylmanganese perphosphite or perphosphine complex was prepared but the two classes successfully isolated yielded chemistries that answered all the questions we posed concerning oxidative-addition reactions to Mn(I) and about allylmanganese hydrogenolysis reactions.

The phosphine and phosphite derivatives of η^3-$C_3H_5Mn(CO)_4$ may be considered as pseudo-six-coordinate complexes.[5,6] For the disubstituted derivatives, there are four possible stereoisomers **1**–**4**. A multinuclear NMR study of the allylmanganese compounds over a wide temperature range was not possible because of adverse relaxation effects from the quadrupolar manganese atoms. Proton spectra at 25 °C were characteristic of an η^3-allyl ligand with spectroscopic equivalence of syn protons and equivalence of anti protons. There was no evidence of a fast $\eta^3 \rightleftharpoons \eta^1$ allyl process. The $^{31}P\{^1H\}$ spectra at −69 °C were AB quartets which strictly ruled out only isomer **1** because allyl ligand rotation about the Mn–C_3 centroid axis could be fast on the NMR time scale even at very low temperatures. However, $^{13}C\{^1H\}$ spectra at −90 °C unambiguously established the stereoisomeric form as **2** for the isopropyl phosphite derivative. There was a triplet (P–C spin coupling) CO resonance and there were singlet resonances for the CH_2 and CH allyl carbon atoms. The ^{31}P spectrum of η^3-$C_3H_5Mn(CO)[P(OCH_3)_3]_3$ was an AB_2 pattern which was consistent with all three possible stereoisomeric forms, taking into account the possibility of fast allyl ligand rotation; if not fast, then a facial (phosphites) isomer is the dominant form. All the allymanganese carbonyl phosphine and phosphite derivatives were rapidly oxidized in solution by air as were the crystalline phosphite derivatives. Crystalline η^3-$C_3H_5Mn(CO)_2[P(C_2H_5)_3]_2$ has been exposed to the atmosphere for days without significant oxidation.



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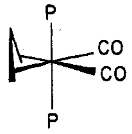

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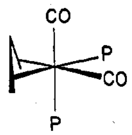

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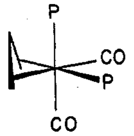

4

Protonation of the allylmanganese compound was invariably accompanied by allyl–manganese bond scission to give propylene. Interception of the $Mn(CO)_2[P(OR)_3]_2^+$ fragment with potentially bidentate ligands yielded a class of new manganese(I) derivatives. Thus, the protonation of η^3-$C_3H_5Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$ by CH_3SO_3H and CF_3SO_3H yielded $CH_3SO_3Mn(CO)_2[P(OR)_3]_2$ and $CF_3SO_3Mn(CO)_2[P(OR)_3]_2$, respectively. The methanesulfonate derivative showed an AB $^{31}P\{^1H\}$ NMR spectrum at −69 °C, a result consistent with the sulfonate analogues of the allyl stereoisomers **2**–**4**. Stereoisomer analogues **3** and **4** would probably interconvert in the solution state through an $\eta^2 \rightleftharpoons \eta^1$ process for the sulfonate ligand (vide infra), but we have no sound basis to estimate the rate for such a dynamic process.

An analogous protonation of η^3-$C_3H_5Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$ in the presence of unconjugated dienes, a more favorable form than a conjugated diene for a d^6 ML_4 fragment,[7] yielded $Mn(\text{diene})(CO)_2[P(OR)_3]_2^+$ complexes. The yield was high for norbornadiene and low for 1,5-cyclooctadiene, a result that was the reverse of the yields for a d^8 cobalt ML_3 fragment, $Co[P(OCH_3)_3]_3^+$.[8] Unlike the compounds above, infrared and ^{31}P NMR data for the norbornadiene complex were fully consistent with a trans CO arrangement.

Catalytic Chemistry of Allylmanganese Complexes

We sought in the phosphine and phosphite derivatives of η^3-$C_3H_5Mn(CO)_4$ activity in the catalytic hydrogenation of unsaturated organic compounds despite the fact that a manganese catalytic cycle based on the +1 and +3 oxidation states was unknown prior to our studies. The parent carbonyl compound η^3-$C_3H_5Mn(CO)_4$ was inactive as a catalyst for the hydrogenation of 1-hexene at 20–110 °C. Also virtually inactive under these conditions was the bis(trimethyl phosphite) derivative. However, at 20 °C, the bis(triethylphosphine) and triisopropyl phosphite derivatives were active catalysts for the hexene hydrogenation with the former the more active of the two with a turnover rate of 2.3 per hour. These results suggest the intervention of a manganese(III) complex, specifically an allylmanganese dihydride, which could be either a seven- or six-coordinate complex, e.g., either η^1-$C_3H_5MnH_2(CO)_2(P{<})_2$ or η^1-$C_3H_5MnH_2(CO)_2(P{<})$. A "radical" intermediate based on a Mn(II) derivative is rather cleanly eliminated from consideration by the observation that η^3-$C_3H_5Mn(CO)_2[P(C_2H_5)_3]_2$ did not catalyze H–D exchange in H_2–D_2 mixtures.

Olefin hydrogenation requires a ligand dissociation step *at some point* in the catalytic cycle to give the seven-coordinate intermediate η^1-$C_3H_5MnH_2(CO)_2(P{<})(\text{olefin})$. This required ligand dissociation step probably explains the lack of catalytic activity in the bis(phosphite) complex based on the less sterically demanding trimethyl phosphite ligand. Of special note was the lack of detectable allyl ligand loss as propylene in this hydrogenation sequence on the time scale of the hydrogenation reaction unlike the allylcobalt, -rhodium, and -iron systems previously investigated in our laboratories.[2b,6,9]

η^3-$C_3H_5Mn(CO)[P(OCH_3)_3]_3$ was a very active catalyst for the hydrogenation of 1-hexene with a minimal turnover rate of two per minute. However, the complex suffered a rapid loss of the allyl ligand to give propylene, a catalytically inactive (or much less active) octahedral complex, *trans*-$HMn(CO)[P(OCH_3)_3]_4$, and other undefined manganese complexes. In the catalytic hydrogenation sequence with η^3-$C_3H_5Mn(CO)[P(OCH_3)_3]_3$, hydrogen addition appeared to be the first step. This allylmanganese complex and hydrogen showed a noticeable color change within 5 min and a deep brown coloration within 20 min in the presence and the absence of a reducible olefin substrate. However, attempts to spectroscopically detect allylmanganese(III) hydrides in such systems were unsuccessful at pressures of 1–3 atm and temperatures in the range of +25 to −80 °C; no allylmanganese hydride proton resonance was observed for these reaction systems even in FT NMR experiments.

Catalytic hydrogenation of acetylenes has also been effected with the allylmanganese complexes. Hydrogenation rates were, however, demonstrably lower than for olefins. For example, the η^3-$C_3H_5Mn(CO)_2[P(O$-*i*-$C_3H_7)_3]_2$ catalyst precursor effected a transformation of 3-hexyne to a 200:1 3-hexene to hexane mixture but at only a 2% conversion with a 100:1 hexyne to catalyst ratio within 24 h. At a 5:1 substrate to catalyst ratio, 2-butyne was completely hydrogenated in 48 h, but the product consisted of only 11% butane; the remainder comprised 54% *trans*-2-butene, 31% *cis*-2-butene, and 4% 1-butene. This accumulation of olefinic products in the hydrogenation of acetylenes despite the substantially larger rate of olefin hydrogenation with these allylmanganese catalyst precursors suggested a preferential binding of acetylenes. This was experimentally confirmed in competitive hydrogenations of 1:1 mixtures of 1-hexene with both 1-hexyne and 3-hexyne where the yields of hexane were essentially identical with those obtained with the hexyne alone and were substantially lower than for the pure hexene.

Unfortunately, the scenario that has developed for these allylmanganese complexes in hydrogenation reactions closely parallels that for the allylcobalt system.[2b] As the level of the catalytic activity is raised, typically by employing phosphine or phosphite ligands of increasing steric bulk, the rate of hydrogen atom transfer to the allyl ligand to give propylene and concomitant rate of destruction of the catalyst increases. Thus, allylmetal complexes seem intrinsically flawed as hydrogenation catalysts. This statement should not be construed to infer that all allylmetal catalysts will be so flawed because there may be an allylmetal coordination system which could yield a relatively stereochemically rigid allylmetal dihydride intermediate with a nonadjacent arrangement of the allyl and hydride ligands—although this is a feature geometrically impossible in five- or six-coordinate species and unlikely (stereochemical rigidity issue) in seven-coordinate species.

Interestingly, $CH_3SO_3Mn(CO)_2[P(O$-*i*-$C_3H_7)_3]_2$, which has a bidentate ligand that should be resistant to elimination on protonation, unlike the formally analogous allyl ligand, is a long-lived catalyst although of relatively low activity (0.3 turnovers/h), for the hydrogenation of 1-hexene. An $\eta^2 \rightleftharpoons \eta^1$ (bidentate to monodentate) sulfonato ligand process might be a key step in the hydrogenation sequence. Curiously, the CF_3SO_3 analogue was not an active hydrogenation catalyst.

None of the above described allylmanganese and alkylsulfonatomanganese complexes was an active catalyst for arene hydrogenation.

Experimental Section

Reagents and Procedure. All procedures were carried out in an argon atmosphere, either in a Vacuum Atmospheres drybox equipped with a Model HE 493 Dri Train or by conventional Schlenk techniques. Solution ^1H NMR spectra were measured in benzene-d_6 on a Varian EM-390 spectrometer with tetramethylsilane as internal lock and reference unless otherwise indicated. ^{31}P NMR spectra were recorded on a Bruker HX-90 instrument with a Digilab FTS Fourier transform unit and were relative to external trimethyl phosphite; ^{13}C spectra were obtained with a Varian CFT-20. Upfield shifts are reported as positive. Infrared spectra were recorded on a Perkin-Elmer 337 instrument. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by the Pascher Mikroanalytisches Laboratorium (Bonn, Germany).

Dimanganese decacarbonyl (Pressure Chemical Co.) and triethylphosphine (Aldrich) were used as received. Trimethyl phosphite (Aldrich) was dried by storage over sodium, followed by vacuum distillation. Triisopropyl phosphite (Strem) was dried by storage over 13X molecular sieves. All other reagents were purchased in their purest commercially available form and used as obtained.

Allylmanganese tetracarbonyl was prepared by literature procedures[10] and purified by repeated trap-to-trap sublimation (−78 °C receiver) at 0.005–0.02 Torr.

Hexane, acetonitrile, olefins, acetylenes, and deuterated solvents were dried over calcium hydride. Olefins and acetylenes were distilled from activated alumina. Ethers and aromatic solvents were dried with sodium–benzophenone. All solvents, acetylenes, and olefins were distilled and degassed on a high-vacuum line.

Photolyses were carried out using an aged 450-W Hanovia medium-pressure mercury arc lamp in a quartz water-cooled immersion well.

Hydrogenation reactions at room temperature were carried out in reaction tubes of approximately 100-mL volume fitted with Teflon vacuum stopcocks and joints for attachment to a high-vacuum line. Reactions were run using a 1:100 ratio of catalyst to unsaturated compound, typically with 30 mg of catalyst (no solvent). The reaction mixture was prepared and loaded into the reaction vessel in the inert-atmosphere box and then degassed on the high-vacuum line. Hydrogen was admitted to 1 atm while the reaction tube was immersed in liquid N_2, giving an estimated 3–3.5 atm of H_2 at room temperature allowing for probable incomplete thermal equilibration of the H_2 during the filling procedures. Reactions at elevated temperature were run similarly in sealed Carius tubes. Product analysis was by gas chromatography on a Perkin-Elmer 990 instrument equipped with a flame ionization detector and the following columns: 12 ft × $^1/_8$ in., 15% 2,4-dimethylsulfolane on Chromosorb P; 6 ft × $^1/_8$ in., 3% OV-225 on Gas-Chrom Z; 12 ft × $^1/_8$ in., 15% Carbowax 20 M on Chromosorb W; 12 ft × $^1/_8$ in., 3% squalane on Chromosorb P, joined to 7 ft × $^1/_8$ in., 20% ethyl *N,N*-dimethyloxamate on Chromosorb P.

η^3-$C_3H_5Mn[P(OCH_3)_3]_2(CO)_2$. η^3-$C_3H_5Mn(CO)_4$ (0.7 g, 3.4 mmol) was placed in a Pyrex reaction tube with a stopcock at the top and $P(OCH_3)_3$ (4 mL, ~32 mmol) was added. The tube was capped, brought out of the drybox, and placed next to the quartz photolysis well. The stopcock of the reaction tube was attached to a mineral oil bubbler, and the well and reaction tube were wrapped with aluminum foil. The photolysis was run for 2 h. Excess $P(OCH_3)_3$ was removed under vacuum. The remaining yellow oil was dissolved in hexane and the solution was cooled to −40 °C to give yellow crystals which melted below room temperature. Repeated recrystallization increased the melting point to 45 °C (occasionally the compound oiled on attempted recrystallization in which case the solution was diluted). This compound was also prepared by thermal methods. A 50-mL Schlenk flask containing 0.5 g (2.4 mmol) of η^3-$C_3H_5Mn(CO)_4$ dissolved in 5 mL of $P(OCH_3)_3$ was heated on a steam bath for 11 h. Excess $P(OCH_3)_3$ was removed under high vacuum, and the resultant yellow oil was dissolved in hexane. The solution was filtered and the solid recrystallized from hexane as above: mp 45.5–46.1 °C; IR (ν_{CO}, hexane) 1940, 1870 cm^{-1}; ^1H NMR δ −1.78 (quartet, 2), −2.44 (doublet, 2), −3.44 (triplet, 18), −4.90 (multiplet, 1). Anal. Calcd for $MnC_{11}H_{23}O_8P_2$: C, 33.01; H, 5.79; Mn, 13.72. Found: C, 33.59; H, 5.90; Mn, 13.45.

η^3-$C_3H_5Mn(CO)[P(OCH_3)_3]_3$. A 200-mL photochemical reaction vessel fitted with a quartz water-cooled immersion well, a 450-W Hanovia medium-pressure Hg arc lamp, and a magnetic stirring bar was filled with a solution containing 0.75 g (3.6 mmol) of η^3-$C_3H_5Mn(CO)_4$ and 3 mL (24 mmol) of $P(OCH_3)_3$ in 145 mL of hexane and then placed in an ice bath. A gentle stream of argon was passed through the solution through a cannula while photolyzing for 1.25 h. The solution, along with some solid that had formed, was transferred into a Schlenk flask under argon, briefly degassed, and brought into the glovebox where it was filtered and the solvent and excess phosphite were removed under vacuum. The remaining tan-yellow oil was dissolved in a minimum amount of hexane. The solution was filtered and then cooled to −40 °C to yield air-sensitive yellow crystals. An analytical sample was prepared by three recrystallizations from hexane. The reaction was repeated using 1.50 g (7.21 mmol) of η^3-$C_3H_5Mn(CO)_4$ and 3.6 mL (29 mmol) of $P(OCH_3)_3$ as above photolyzing for 2.25 h; this gave 2.54 g (71%) of triply recrystallized product: mp 137.0–138.5 °C; IR (ν_{CO}, hexane) 1855 cm^{-1}; ^1H NMR δ −1.60 (partially resolved quintet, 2), −2.37 (broad, 2), −3.57 (partially resolved multiplet, 27), −4.88 (multiplet

1); $^{31}P\{^1H\}$ NMR (-80 °C) AB_2: $\delta_{P_A} = -66.1$, $\delta_{P_B} = -49.3$ ($J = 105$ Hz). Anal. Calcd for $MnC_{13}H_{32}P_3O_{10}$: C, 31.46; H, 6.50; Mn, 11.07; P, 18.72. Found: C, 31.91; H, 6.51; Mn, 10.54; P, 19.52.

η^3-$C_3H_5Mn[P(OCH(CH_3)_2)_3]_2(CO)_2$. This compound was prepared in a manner analogous to the photolytic preparation of η^3-$C_3H_5Mn[P(OCH_3)_3]_2(CO)_2$ starting from 0.52 g (2.5 mmol) of η^3-$C_3H_5Mn(CO)_4$, 2.08 g (10 mmol) of $P[OCH(CH_3)_2]_3$, and 20 mL of hexane solvent. The photolysis was run for 24 h. Hexane and excess phosphite were removed by distillation on a high-vacuum line to yield a pale yellow solid, 1.25 g, an 88% yield of crude product. The compound was recrystallized from hexane at -40 °C to give yellow, air-sensitive crystals. An analytical sample was purified by two further recrystallizations. The reaction was repeated on a fourfold scale using 40 mL of solvent and otherwise as above; this gave a 64% yield of twice recrystallized products: mp 104.6–106 °C; IR (ν_{CO}, hexane) 1930, 1850 cm^{-1}; ^1H NMR δ -1.23 (broad singlet, 36), -2.00 (quartet, 2), -2.60 (doublet, 2), -4.8 (broad, 7); $^{31}P\{^1H\}$ NMR (-69 °C) δ -41.4, -45.4, -47.3, -51.3 (AB quartet: $\delta_{P_A} = -48.5$, $\delta_{P_B} = -44.2$, $J = 143$ Hz); $^{13}C\{^1H\}$ NMR (-90 °C, Me_4Si reference) δ 22.97 (t, $J = 40$ Hz, *C*O), 93.3 (allyl *C*H), 68.6 (phosphite *C*H), 43.0 (allyl *C*H_2), 24.2 (phosphite *C*H_3). Anal. Calcd for $MnC_{23}H_{47}O_8P_2$: C, 48.59; H, 8.33; Mn, 9.66; P, 10.90. Found: C, 49.00; H, 8.44; Mn, 9.44; P, 10.71.

η^3-$C_3H_5Mn[P(C_2H_5)_3]_2(CO)_2$. This compound was prepared analogously to the phosphite compounds starting with 0.52 g (2.5 mmol) of η^3-$C_3H_5Mn(CO)_4$ and 1.47 mL (1.0 mmol) of $P(C_2H_5)_3$ in 20 mL of hexane. The photolysis was run for 18 h. Workup was similar to that used for the isopropyl phosphite analogue; by repeated concentration of mother liquors on recrystallization, a total of 0.65 g (67% yield) of three-times recrystallized material was obtained as yellow crystals, a sample of which was unaffected by air and water for 2 days but began to darken after 1 week's exposure. An analytical sample was prepared by recrystallizing a portion of this material once more. In scaling up this reaction, it was found advantageous to attach the reaction tube to an argon supply and a mineral oil bubbler via a glass tee and slowly pass argon through the system to purge CO and to monitor the course of the reaction by IR spectroscopy as it sometimes went more slowly than above: mp 87.5–88.2 °C; IR (ν_{CO}, hexane) 1905, 1840 cm^{-1}; ^1H NMR δ -0.7 to +1.7 (complex multiplet, 32), -2.26 (doublet with unresolved fine structure, 2), -3.67 to -4.27 (multiplet, 1). Anal. Calcd for $MnC_{17}H_{37}O_2P_2$: C, 52.58; H, 9.08; Mn, 14.15; O, 8.24; P, 15.95. Found: C, 52.76; H, 9.19; Mn, 13.91; O, 8.22; P, 16.09.

$(CH_3SO_3)Mn[P(OCH(CH_3)_2)_3]_2(CO)_2$. A solution of 45 μL (~0.7 mmol) of CH_3SO_3H in 10 mL of diethyl ether was poured with stirring into 0.4 g (0.7 mmol) of η^3-$C_3H_5Mn[P(OCH(CH_3)_2)_3]_2(CO)_2$ dissolved in 10 mL of diethyl ether; there was a rapid color change from yellow to orange. The solution was concentrated under vacuum to ~$^1/_3$ volume and allowed to return to room temperature. Hexane was then slowly added until precipitation began and then the solution was cooled to -40 °C. A small amount of waxy yellow solid precipitated out and was removed by filtration. The filtrate was concentrated to a small volume and cooled to -40 °C to yield very air-sensitive orange crystals. Alternatively, the filtrate was evaporated to dryness and the resulting orange oil crystallized from hexane at -40 °C, with a greater product recovery. An analytical sample was prepared by recrystallizing the product three times from hexane at -40 °C: mp 75 °C dec; IR (ν_{CO}, Nujol) 1960, 1885 cm^{-1}; there was a strong band at 1270 cm^{-1} which is presumably a sulfonate stretch; ^1H NMR (Varian A-60A) δ -1.42 (doublet, 36), -2.73 (broad singlet, 3), -5.16 (broad multiplet, 6); $^{31}P\{^1H\}$ NMR (-69 °C) δ -11.5, -20.2, -22.0, -30.7 (AB quartet: $\delta_{P_A} = -24.0$, $\delta_{P_B} = -18.2$, $J = 315$ Hz). Anal. Calcd for $MnC_{21}H_{45}P_2SO_{11}$: C, 40.52; H, 7.29; Mn, 8.82; P, 9.95. Found: C, 40.96; H, 7.50; Mn, 9.13; P, 10.23. When run at twice the above scale, this procedure gave a 62% yield.

$\{(norbornadiene)Mn(CO)_2[P(OCH(CH_3)_2)_3]_2\}CF_3SO_3$. To a Schlenk vessel was added 0.57 g (1.0 mmol) of η^3-$C_3H_5Mn[P(OCH(CH_3)_2)_3]_2(CO)_2$, 20 mL of diethyl ether, and 0.4 mL (4 mmol) of norbornadiene (bicyclo[2.2.1]heptadiene) (Aldrich) which had been freshly distilled, degassed, and dried by passage through an activated alumina column in the drybox. Ninety microliters (1 mmol) of CF_3SO_3H (Aldrich) was added through a syringe with stirring of the reaction mixture. The initially yellow solution rapidly turned orange and a crystalline solid began to precipitate. The reaction mixture was allowed to stand without stirring for 30 min to promote crystal growth and then was taken into a drybox. The orange-yellow crystals were collected by filtration and washed with diethyl ether until the washings were colorless. The crystals were recrystallized twice from tetrahydrofuran–diethyl ether at -40 °C to give 0.47 g (61% yield). An additional 0.05 g was recovered from the supernatant, giving a total yield of 68%: mp 119–121 °C dec; IR (ν_{CO}, KBr pellet) 2020 (m), 1955 (vs); ^1H NMR δ -1.37, -1.39 (overlapping doublets, 38), -3.78 (multiplet, 2), -4.45, -4.68 (overlapping multiplets, 10); $^{31}P\{^1H\}$ NMR (-81 °C, relative to external room temperature $P(OCH_3)_3$) δ -20.2. Anal. Calcd for $MnC_{28}H_{50}O_{11}P_2SF_3$: C, 43.75; H, 6.56; P, 8.06; S, 4.17. Found: C, 43.81; H, 6.62; P, 8.06; S, 4.24.

$(CF_3SO_3)Mn[P(OCH(CH_3)_2)_3]_2(CO)_2$. A solution of 0.40 g (0.70 mmol) of η^3-$C_3H_5Mn[P(OCH(CH_3)_2)_3]_2(CO)_2$ in 20 mL of diethyl ether was placed in a 50-mL Schlenk vessel with a magnetic stirring bar and then 70 mL (40.77 mmol) CF_3SO_3H was added through a glass syringe with a Teflon needle. The initially pale yellow solution immediately became dark orange. The reaction mixture was allowed to stir 5 min and then the solvent was removed under vacuum. The product was brought into the drybox and then was extracted with hexane. The extracts were filtered through a fine glass frit to give a clear orange solution and a small amount of yellow solid on the frit. The orange solution was reduced in volume under vacuum and then cooled to -40 °C. Soft orange-red crystals which formed under these conditions were recrystallized once from hexane to give 80 mg (17%) of product: mp ~91 °C dec; IR (hexane) ν_{CO} 1980 (s), 1965 (m), $\nu_{CF_3SO_3}$ 1230, 1200, 1175 cm^{-1}; ^1H NMR δ -1.27 (doublet $J = 6$ Hz, 36), δ 4.85 (partially resolved multiplet, 1). Anal. Calcd for $MnC_{21}H_{42}O_{11}P_2SF_3$: C, 37.28; H, 6.26; P, 9.16; S, 4.74. Found: C, 36.95; H, 6.03; P, 8.79; S, 4.61.

The yellow, hexane-insoluble solid from the above reaction was recrystallized twice from tetrahydrofuran–hexane to give 25 mg of off-white crystals which gave no ν_{CO} in the infrared. The analysis was consistent with $Mn(OSO_2CF_3)_2 \cdot 2O(CH_2)_4$. Anal. Calcd for $MnC_{10}H_{16}O_8S_2F_6$: C, 24.15; H, 3.24; P, 0.0; S, 12.89. Found: C, 23.73; H, 3.15; P, <0.5; S, 12.98.

Reaction of η^3-$C_3H_5Mn(CO)[P(OCH_3)_3]_3$ with H_2. Isolation of $HMn(CO)[P(OCH_3)_3]_4$. A solution of 0.60 g (1.2 mmol) of η^3-$C_3H_5Mn(CO)[P(OCH_3)_3]_3$ in 25 mL of C_6H_{14} was placed in a 500-mL round-bottom flask fitted with a vacuum line adapter. The solution was cooled to -198 °C and the vessel was evacuated on a high-vacuum line. The reaction vessel was then allowed to warm to room temperature and hydrogen was admitted to 1 atm. The reaction mixture was stirred for at least 48 h at which time it was brown with solids present, and then the reaction vessel was evacuated and brought into the drybox. An additional 25 mL of *n*-hexane was added and the mixture was stirred and filtered through a fine frit. The solids remaining undissolved were extracted with two 15-mL portions of *n*-hexane. The extracts were filtered and then combined with the reaction solution. The solution was concentrated under vacuum until crystallization began. It was then allowed to warm to room temperature and placed in the drybox freezer (≤-40 °C). The resulting crystals were recrystallized twice more from C_6H_{14}, washed with a little C_6H_{14}, and dried in vacuo to give 0.12 g (17%) of pale brownish pink crystals which dissolved in benzene and polar solvents to give yellow solutions: IR (ν_{CO}, benzene) 1860 cm^{-1}; ^1H NMR (HX-90) δ +8.40 (quintet, $J_{H-P} = 50$ Hz, 1), -3.55 (broad singlet, 36); ^{31}P NMR (-76.5 °C, relative to external room temperature $P(OCH_3)_3$) δ -60.0 (doublet, $J_{P-H} = 46$ Hz). Anal. Calcd for $MnC_{13}H_{37}O_{13}$: C, 26.91; H, 6.43; P, 21.35; Mn, 9.47. Found: C, 27.28; H, 6.51; P, 21.39; Mn, 8.90.

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Registry No. η^3-$C_3H_5Mn[P(OCH_3)_3]_2(CO)_2$, 66562-83-2; η^3-$C_3H_5Mn(CO)[P(OCH_3)_3]_3$, 66562-84-3; η^3-$C_3H_5Mn[P(OCH(CH_3)_2)_3]_2(CO)_2$, 66562-85-4; η^3-$C_3H_5Mn[P(C_2H_5)_3]_2(CO)_2$, 66562-86-5; $(CH_3SO_3)Mn[P(OCH(CH_3)_2)_3]_2(CO)_2$, 66562-87-6; $\{(norbornadiene)Mn(CO)_2[P(OCH(CH_3)_2)_3]_2\}CF_3SO_3$, 66562-89-8; $(CF_3SO_3)Mn[P(OCH(CH_3)_2)_3]_2(CO)_2$, 66562-90-1; $HMn(CO)[P(OCH_3)_3]_4$, 66562-91-2; η^3-$C_3H_5Mn(CO)_4$, 33307-28-7; H_2, 1333-74-0.

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Reaction of Ammonia with Platinum Dichloride: A Synthesis of Monoamminedichloroplatinum(II) and Diamminedichloroplatinum(II)

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β-$PtCl_2$ reacts with ammonia from the gas phase to form solid products of varying composition and structure. The products have the composition $PtCl_2{\cdot}xNH_3$, where x varies from 1 to 4. The reaction from $x = 0$ to $x = 1$ is highly exothermic, and the product has an X-ray diffraction pattern indistinguishable from that of β-$PtCl_2$.

Recently, Pilbrow reported the preparation of clathrate adducts of β-$PtCl_2$ with several small molecules.[1] These adducts have the stoichiometry $Pt_6Cl_{12}{\cdot}nA$ ($n = 1$ or 0.75) where A was reported as Br_2, C_6H_6, CS_2, CCl_4, $CHCl_3$, or CH_2Cl_2. The addition changed the X-ray diffraction pattern of the parent β-$PtCl_2$ by changing the unit cell geometry. The adducts all decomposed thermally to give the starting materials.

Results and Discussion

We effected reaction of β-$PtCl_2$ with ammonia at various ammonia partial pressures. At 1 atm of ammonia and 25 °C, β-$PtCl_2$ reacts very rapidly and exothermally to give metallic platinum and ammonium chloride:

$$3\beta\text{-}PtCl_2 + 8NH_3 \rightarrow 3Pt + 6NH_4Cl + N_2$$

The heat of the reaction is sufficient to vaporize the ammonium chloride from the platinum metal.

At ammonia pressures of 0.1 atm or less, the β-$PtCl_2$ sorbs ammonia without decomposition. The quantity of ammonia sorbed was determined by weighing the solid phase. Samples with the composition $PtCl_2{\cdot}NH_3$ were obtained. The X-ray diffraction pattern of this substrate is identical with that of β-$PtCl_2$.[2] Careful powder diffraction measurements of both the lattice parameters and intensities of the diffraction lines showed no change in position to ±0.01 Å or 5% in intensity.

Heating $PtCl_2{\cdot}NH_3$ at 473 K for 16 h produced no change in composition or structure. Heating above 503 K results in decomposition according to the reaction

$$2PtCl_2{\cdot}NH_3 \rightarrow 2Pt + N_2 + 4HCl + H_2$$

Exposing $PtCl_2{\cdot}NH_3$ to NH_3 vapor up to 1 atm does not result in a strongly exothermic reaction. A slow addition of ammonia occurs, which ultimately yields $Pt(NH_3)_4Cl_2$.[5]

These observations indicate the $PtCl_2{\cdot}NH_3$ still retains the basic Pt_6Cl_{12} structure found in β-$PtCl_2$, with the ammonia fitting into that structure. Since reaction of only one NH_3 per platinum is highly exothermic, we think one ammonia molecule is coordinated with each platinum(II) ion. This suggests that we have prepared a compound of empirical formula $Pt(NH_3)Cl_2$ different from the earlier reported monoammine.[6] The water-insoluble material reported here is probably a cluster compound with the individual unit $Pt_6Cl_{12}(NH_3)_6$.

Upon further addition of ammonia to $PtCl_2{\cdot}NH_3$ we have obtained solids which have the compositions $PtCl_2{\cdot}2NH_2$ and $PtCl_2{\cdot}3NH_3$.

The solid $PtCl_2{\cdot}2NH_3$ from all of our preparations is X-ray amorphous. We have tried without success to obtain crystalline products by heating the solid slightly and slurrying in water. This amorphous material represents a new structure for the composition $Pt(NH_3)_2Cl_2$, in addition to the known *cis*- and *trans*-diamminedichloroplatinum(II) complexes. The new compound with the empirical formula $Pt(NH_3)_2Cl_2$ reacts with gaseous ammonia, which distinguishes it from the cis and trans isomers as these crystalline solids are inert in gaseous NH_3.[7]

The solid $PtCl_2{\cdot}3NH_2$ appears to be a mixture of crystalline $Pt(NH_3)_4Cl_2$ and another unidentified crystalline solid phase.[8]

Experimental Section

β-$PtCl_2$ was prepared from hydrated hexachloroplatinic acid (Matthey Bishop) as needed. The reactions were also observed on β-$PtCl_2$ (Alfa Inorganics) prepared by other methods. The reactions with ammonia were studied on a du Pont Model 950 thermogravimetric analyzer modified as described earlier.[9] Larger quantities of products, up to 5 g, were prepared by reaction in a tube furnace. X-ray diffraction data were obtained with a Siemens powder diffractometer using Ni-filtered Cu Kα radiation. *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ were prepared by standard recipies.[10]

Registry No. $Pt(NH_3)Cl_2$, 66454-21-5; $Pt(NH_3)_2Cl_2$, 26035-31-4; $PtCl_2$, 10025-65-7; NH_3, 7664-41-7.

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