Hindered Ligand Movements in Transition-Metal Complexes, 46[+]

Facile Hapticity Changes in (1-Hydronaphthalene)manganese Complexes, Ligand Addition and Photochemical Ligand Cleavage

Andreas Georg[a] **and Cornelius G. Kreiter***[a]

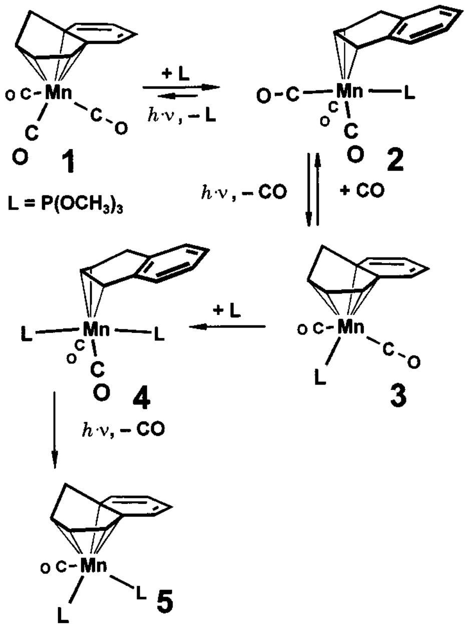
Keywords: Manganese / Coordination modes / 1-Hydronaphthalene complexes / Trimethylphosphite addition / Photochemistry

Tricarbonyl(2–4,4a,8a-η-1-hydronaphthalene)manganese (**1**) reacts readily with trimethyl phosphite to afford tricarbonyl(2–4-η-1-hydronaphthalene)(trimethyl phosphite)manganese (**2**), by a simultaneous η^5-η^3-hapticity change. Upon UV irradiation, one carbonyl ligand is preferentially cleaved from **2** to yield dicarbonyl(2–4,4a,8a-η-1-hydronaphthalene)(trimethyl phosphite)manganese (**3**), with a η^5-coordinated 1-hydronaphthalene ligand. In a similar fashion **3** also reacts with trimethyl phosphite and forms dicarbonyl(2–4-η-1-hydronaphthalene)bis(trimethyl phosphite)manganese (**4**), which loses carbon monoxide upon UV irradiation to afford carbonyl(2–4,4a,8a-η-1-hydronaphthalene)bis(trimethyl phosphite)manganese (**5**). All compounds were characterized by IR and NMR spectroscopy. The η^5-1-hydronaphthalene complexes **1**, **3** and **5** show hindered 1,4-H shifts of 1-H^{endo}. Considerable energy barriers were also found for the rotation of the 1-hydronaphthalene ligand in **2**–**5**.

Recently, the authors reported the formation of an η^5-1-hydronaphthalene manganese complex as a byproduct of the photochemical reaction of pentacarbonyl(μ-$\eta^{4:6}$-1,4-dimethylnaphthalene)dimanganese with 2-butyne.[2][3] Meanwhile it was found[4] that 1-hydronaphthalene complexes are also formed in high yields by the treatment of cationic tricarbonyl(η^6-naphthalene)manganese complexes[5] with $Li[BEt_3H]$. An analogous behaviour was already known in the case of the corresponding reaction of cationic (η^6-benzene)tricarbonylmanganese complexes.[6−11] In this work the reaction of tricarbonyl(2,3,4,4a,8a-η-1-hydronaphthalene)manganese (**1**) with potential ligands, such as trimethyl phosphite, has been studied in order to learn how the partially weakly coordinated 1-hydronaphthalene ligand influences the reactivity. Even at 203 K **1** adds one equiv. of trimethyl phosphite within seconds to form tricarbonyl(2−4-η-1-hydronaphthalene)(trimethyl phosphite)manganese (**2**).

The reaction can be carried out in coordinating solvents such as THF or ether, as well as in non-polar hydrocarbon solvents such as *n*-hexane or *n*-pentane. Simultaneously with the coordination of trimethyl phosphite, the C4a−C8a bond is decomplexed and the hapticity of the 1-hydronaphthalene ligand changes from η^5 to η^3.

The π or side-on bonding of unsaturated hydrocarbons to transition metals is described according to the Dewar−Chatt−Duncanson model[12][13] with a so called σ-donor and π-acceptor part. In Lewis formulas of π complexes the interaction between the π system of an unsaturated hydrocarbon and the metal center is normally characterized by an arrow or a (dotted) line from double bonds, circles or circular arches, which symbolize the π system, to the metal center. An alternative formalism, which seems to us more meaningful, uses thin lines between the coordinated carbon atoms and the metal center. It is justified by the bonding model in which each coordinated sp^2-carbon atom donates one electron to the metal center, which then contributes the same number of electrons for back donation. The thin lines in our formulae mark bonding interactions between carbon and metal atoms and do not symbolize localised σ bonds.



Scheme 1

Photolysis of **2** in hexane or THF at room temp. yields 78% of dicarbonyl(2−4,4a,8a-η-1-hydronaphthalene)(trimethyl phosphite)manganese (**3**), in addition to 8% of **1**.

[+] Part 45: Ref.[1]

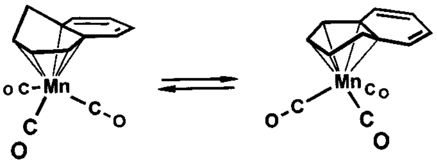
[a] Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany

The main reaction is the photochemical cleavage of one carbonyl ligand and the recoordination of the C4a−C8a bond, to afford complex **3**. Byproduct **1** is formed in a back reaction of the addition of trimethyl phosphite to **1**.

The reaction of **3** with CO effects the quantitative back reaction to **2** with decomplexation of the C4a−C8a bond. Treatment of **3** in ether with trimethyl phosphite yields dicarbonyl(2−4-η-1-hydronaphthalene)bis(trimethyl phosphite)manganese (**4**). Due to the steric bulk of the two trimethyl phosphite ligands, this bright yellow complex is only stable at temperatures below 268 K.

By photolysis of **4** one CO ligand is cleaved. The C4a−C8a bond is coordinated again to form the dark red carbonyl(2−4,4a,8a-η-1-hydronaphthalene)bis(trimethyl phosphite)manganese (**5**).

For the η^5-1-hydronaphthalene complexes **1**, **3** and **5** hindered 1,4-H shifts of 1-H^{endo} are observed in the temperature-dependent ^{1}H-NMR spectra. The activation parameters were determined by line-shape analysis (**1**: ΔH^{+} = 78.6 kJ·mol^{-1}, ΔS^{+} = 14.9 J·mol^{-1}·K^{-1}; **3**: ΔH^{+} = 66.7 kJ·mol^{-1}, ΔS^{+} = 0.1 J·mol^{-1}·K^{-1}; **5**: ΔH^{+} = 43.7 kJ·mol^{-1}, ΔS^{+} = 26.9 J·mol^{-1}·K^{-1} with maximum errors of ± 3 kJ·mol^{-1}, and ± 20 J·mol^{-1}·K^{-1}, respectively).



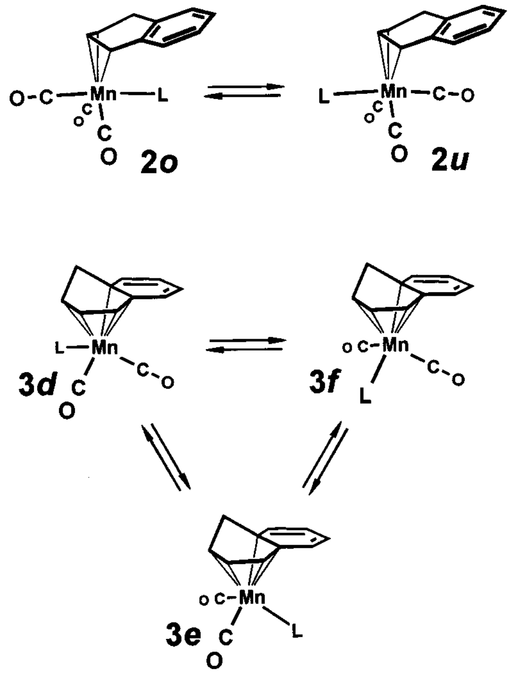
Scheme 2

The low-temperature ^{1}H- and ^{31}P-NMR spectra of **2** show the presence of two isomers with populations of 81:19. They differ due to the position of the trimethyl phosphite ligand in the pseudo-trigonal-bipyramidal coordination sphere of manganese. In [Mn(η^3-enyl)L(CO)$_3$] complexes donor ligands occupy exclusively axial positions from which the *o*-position relative to the enyl ligand is normally more favoured than the *u*-position. In case of sterically demanding enyl ligands the preference of the isomers is inverted. For the η^3-1-hydronaphthalene ligand such a sterical hindrance has to be expected as the trimethyl phosphite ligand is in the *o*-position. For that reason we assign the predominant isomer to **2*u***, and the other to **2*o***, with the trimethyl phosphite close to C-8a of the aromatic ring. In the predominant isomer the trimethyl phosphite shows no sterical interaction with the 1-hydronaphthalene ligand. This assignment is supported by a $^3J_{H,P}$ coupling of 3-H of 15.5 Hz in **2*u***. The isomer **2*o*** shows only a small, unresolved H,P coupling of 3-H. The interconversion of **2*u*** and **2*o*** affords an activation energy of ΔH^{+} = 65.0 kJ·mol^{-1} with ΔS^{+} = 36.0 J·mol^{-1}·K^{-1}.

A comparable ligand movement is found for **4**. The two trimethyl phosphite ligands both occupy axial positions. At 183 K the rotation of the η^3-1-hydronaphthalene ligand is slowed down and two ^{31}P-NMR signals appear. The activation energy was determined to be ΔH^{+} = 51.1 kJ mol^{-1}, ΔS^{+} = 15.5 J K^{-1} mol^{-1}.

The η^5-1-hydronaphthalene complexes **3** and **5** also show a hindered rotation. The ^{31}P-NMR of **3** shows an intense signal at 183 K which is assigned to the less hindered isomer **3*d*** (0.92), a weaker signal is assigned to **3*f*** (0.08). Although a separate signal for the third, strongly hindered isomer is not observed, it can not be excluded with certainty. The activation parameters for the **3*d*/3*f*** isomerization were found to be ΔH^{+} = 47.7 kJ mol^{-1} and ΔS^{+} = 21.0 J K^{-1} mol^{-1}. For **5** all three possible isomers give separate ^{31}P-NMR signals, from which the relative populations 0.89:0.06:0.05 are determined. They were assigned according to the sterical interactions between the trimethyl phosphite ligands and the 1-hydronaphthalene. The activation parameters for the isomerization are $\Delta H^{\neq}$ = 37.6 kJ mol^{-1} and $\Delta S^{\neq}$ = −37.0 J K^{-1} mol^{-1}.

A similar hindered H-shift and ligand rotation was already detected for dicarbonyl($\eta^{4:(2)}$-1,5-*H*-benzocyclohept-ene)(trimethyl phosphite)chromium(0).[14]



Scheme 3

Experimental Section

All reactions were carried out under dry nitrogen using common Schlenk techniques. THF was dried with potassium, diethyl ether with sodium, *n*-pentane with P_4O_{10} and *n*-hexane with CaH_2. Silica gel for column chromatography was heated to 413 K in vacuo, deactivated with 4% of degassed water and stored under nitrogen. A high-pressure mercury lamp TQ 150 (Heraeus-Noblelight, Kleinostheim) was used for the photolysis reaction. It was immersed in a 120-mL photoreactor of Duran® with a cooling jacket, wrapped with aluminium foil. The photoreactor and the chromatography column were cooled with a cryostat RUL 80 (Lauda), with methanol as the coolant. − IR: Perkin Elmer FT-IR 16 PC. − NMR: Bruker AMX 400 (^{1}H, 400.13 MHz, ^{13}C, 100.62 MHz, ^{31}P, 162.12 MHz), ^{1}H and ^{13}C chemical shifts are given relative to TMS, using the solvent signals as internal reference ($C_6D_5CHD_2$: $\delta_H = 2.03$, $C_6D_5CD_3$: $\delta_C = 20.40$, C_6HD_5: $\delta_H = 7.20$, C_6D_6: $\delta_C = 128$), ^{31}P chemical shifts are relative to external 85% phosphorous acid. − Elemental analyses: Perkin Elmer microanalyser 240. − Tricarbonyl(2−4,4a,8a-η-1-hydronaphthalene)manganese (**1**) was synthesized according to the literature[4] using $Li[BEt_3H]$ instead of $Na[BH_3CN]$ as the reducing agent. The activation parameters for the hindered 1,4-H shift of 1-H^{endo} in **1** were determined from the temperature dependence of the ^1H-NMR signals of 1-H−4-H; T [K], k [s^{-1}]: 328, 2; 348, 15; 358, 40; 368, 70; 378, 100. The trimethyl phosphite (Fluka) was used as purchased.

Tricarbonyl(2−4-η-1-hydronaphthalene)(trimethyl phosphite)manganese (2): 175 mg (0.66 mmol) of tricarbonyl(2−4,4a,8a-η-1-hydronaphthalene)manganese (**1**) was dissolved in THF (20 mL). When 0.1 mL (0.85 mmol) of trimethyl phosphite was added dropwise to the orange-red solution the color changed immediately to bright yellow. After 2 min of stirring, $MgSO_4$ (2 g) was added to the solution and the solvent removed in vacuo. Chromatography of the residue on a column packed with silica gel gave two fractions. An orange fraction was eluted with hexane/diethyl ether (50:1). It contained only a small amount of the starting material. **2** was eluted as a bright yellow fraction with *n*-hexane/diethyl ether (20:1). Removal of the solvent and crystallization from *n*-hexane at 243 K gave 158 mg (62%) of **2** as yellow crystals. − IR (*n*-hexane): $\tilde{\nu}$ = 2010 (s) cm^{-1} (CO), 1950 (s), 1944 (sh), 1918 (sh), 1911 (s). The shoulders of the ν_{CO} bands are probably due to the rotamer **2o**. − ^1H NMR ([D_8]toluene, 333 K): δ = 6.85 (dd, J = 7.3, 0.9 Hz, 1 H, 5-H), 6.78 (dd, J = 7.3, 6.8 Hz, 1 H, 6-H), 6.70 (ddd, J = 7.3, 6.8, 1.3 Hz, 1 H, 7-H), 6.55 (d, 7.3 Hz, 1 H, 8-H), 4.73 (ddd, J = 9.5, 6.8, 5.8 Hz, 1 H, 3-H,), 4.15 (d, J = 5.8 Hz, 1 H, 4-H), 4.05 (dddd, J = 6.8, 4.9, 1.6, 1.6 Hz, 1 H, 2-H), 3.31 (dd, J = 21.1, 4.9 Hz, 1 H, 1-H^{endo}), 3.17 [d, J = 11.2 Hz, 9 H, $P(OCH_3)_3$], 3.17 (d, J = 21.1 Hz, 1 H, 1-H^{exo}) . − ^1H NMR ([D_8]toluene, 233 K): **2*u*** (81%): δ = 6.90 (d, J = 7.5 Hz, 1 H, 5-H), 6.83 (dd, J = 7.5, 6.8 Hz, 1 H, 6-H), 6.77 (dd, J = 7.3, 6.8 Hz, 1 H, 7-H), 6.60 (d, 7.3 Hz, 1 H, 8-H), 4.76 (ddd, J = 15.5, 6.7, 6.1 Hz, 1 H, 3-H,), 4.27 (d, J = 6.1 Hz, 1 H, 4-H), 4.02 (br. m, 1 H, 2-H), 3.31 (dd, J = 21.8, 7.4 Hz, 1 H, 1-H^{endo}), 3.17 (d, J = 21.8 Hz, 1 H, 1-H^{exo}), 3.05 [d, J = 10.7 Hz, 9 H, $P(OCH_3)_3$]; **2*o*** (19%): δ = 6.72 (dd, J = 6.9, 6.9 Hz, 1 H, 6-H), 6.58 (dd, J = 6.9, 6.9 Hz, 1 H, 7-H), 6.52 (d, J = 7.1 Hz, 1 H, 8-H), 4.65 (br. dd, J = 6.6, 5.6 Hz, 1 H, 3-H), 4.16 (d, J = 5.6 Hz, 1 H, 4-H), 3.14 [d, J = 10.1 Hz, 9 H, $P(OCH_3)_3$]. − The activation parameters for the hindered interconversion of **2*u*** and **2*o*** were determined from the temperature dependence of the ^1H-NMR signals of 3-H of both isomers; T [K], k [s^{-1}]: 233, 1; 243, 5; 253, 15; 273, 100; 283, 500; 293, 1000; 313, 10000; 333, 30000. − ^{13}C NMR ([D_8]toluene, 293 K): δ = 225 (s, 3 C, CO), 143.10 (s, C-4a), 129.01 (s, C-8a), 127.77 (d, J = 153 Hz, C-5), 126.54 (d, J = 158 Hz, C-6), 125.65 (d, J = 158 Hz, C-8), 125.09 (d, J = 145 Hz, C-7), 83.84 (d, J = 168 Hz, C-3), 61.81 (d, J = 180 Hz, C-4 or -2), 59.91 (br. d, J = 160 Hz, C-2 or -4), 51.96 (dq, $^1J_{C,H}$ = 147, $^2J_{C,P}$ = 5 Hz, OCH_3), 34.32 (t, J = 127 Hz, C-1) . − ^{31}P NMR ([D_8]toluene, 233 K): δ = 194.4 (s, 0.81 P), 185.4 (s, 0.19 P). − $C_{16}H_{18}MnO_6P$ (392.23): calcd. C 49.00, H 4.63; found C 48.9, H 4.4.

Photoreaction of Tricarbonyl(2−4-η-1-hydronaphthalene)(trimethyl phosphite)manganese (2): 106 mg (0.27 mmol) of **2** was dissolved in 100 mL of *n*-hexane in a photoreactor. The yellow solution was irradiated with UV light at room temp. After 10 min, the carbon monoxide bands of **2** had disappeared and the color of the solution turned to orange. The irradiation was stopped, 2 g of $MgSO_4$ added and the solvent removed in vacuo. The orange residue was separated into three fractions by column chromatography on silica gel at 253 K. A bright yellow fraction was obtained with *n*-pentane/toluene (10:1) as eluent. It contained 6 mg (0.02 mmol, 8%) of **1**. The second fraction was eluted with *n*-pentane/diethyl ether (20:1) from which 73 mg (0.21 mmol) of dicarbonyl(2−4,4a,8a-η-1-hydronaphthalene)(trimethyl phosphite)manganese (**3**) was obtained (78%). − IR (*n*-hexane): $\tilde{\nu}$ = 1947 (s) cm^{-1} (CO), 1889 (s). − ^1H NMR ([D_8]toluene, 293 K): δ = 7.03 (d, J = 7.3 Hz, 1 H, 5-H), 6.78 (dd, J = 7.5, 7.3 Hz, 1 H, 6-H), 6.72 (d, J = 8.2 Hz, 1 H, 8-H), 6.64 (dd, J = 8.2, 7.5 Hz, 1 H, 7-H), 5.93 (d, J = 5.0 Hz, 1 H, 4-H), 4.85 (ddd, J = 5.0, 5.5, 7.0 Hz, 1 H, 3-H), 3.2 [d, J = 11.4 Hz, 9 H, $P(OCH_3)_3$], 3.13 (dd, J = 13.6, 5.6 Hz, 1 H, 1-H^{endo}), 2.83 (ddd, J = 5.8, 5.5, 2.7 Hz, 1 H, 2-H), 2.50 (dd, J = 13.6, 2.7 Hz, 1 H, 1-H^{exo}) . − The activation parameters for the hindered 1,4-H shift of 1-H^{endo} in **3** were determined from the temperature dependence of the ^1H-NMR signals of 1-H−4-H; T [K], k [s^{-1}]: 303, 20; 313, 50; 323, 100; 343, 500; 353, 1000. − ^{13}C NMR ([D_8]toluene, 293 K): δ = 232.1 (s, CO), 224.5 (s, CO), 134.0 (d, J = 161 Hz, C-5), 129.9 (d, J = 162 Hz, C-6), 128.3 (d, J = 169 Hz, C-7), 126.6 (d, J = 162 Hz, C-8), 109.3 (s, C-4a), 96.6 (d, J = 164 Hz, C-4), 90.7 (s, C-8a), 72.4 (d, J = 173 Hz, C-3), 51.2 [dd, $^1J_{C,H}$ = 145, $^3J_{C,P}$ = 4 Hz, $P(OCH_3)_3$], 46.3 (d, J = 165 Hz, C-2), 30.6 (t, J = 131 Hz, C-1) . − ^{31}P NMR ([D_8]toluene, 183 K): **3*d***: δ = 212.3 (s, 0.92 P), **3*f***: δ = 207.4 (s, 0.08 P). − The activation parameters for the hindered isomerization of **3*d*−3*f*** were determined from the temperature dependence of the ^{31}P-NMR signals of **3*d*** and **3*f***; T [K], k [s^{-1}]: 183, 1; 203, 30; 223, 500; 233, 1000; 253, 10000; 273, 50000. − $C_{15}H_{18}MnO_5P$ (364.22): calcd. C 49.47, H 4.98; found: C 49.2, H 4.9. − A third red fraction could be eluted with diethyl ether. Removal of the solvent yielded less than 1 mg of a red oil. − IR (*n*-pentane, 293 K): $\tilde{\nu}$ = 1970 (m) cm^{-1},1948 (s), 1889 (m), 1868 (vs).

Reaction of Dicarbonyl(2−4,4a,8a-η-1-hydronaphthalene)(trimethyl phosphite)manganese (3) with Carbon Monoxide: 20 mg of dicarbonyl(2−4,4a,8a-η-1-hydronaphthalene)(trimethyl phosphite)manganese (**3**) was dissolved in 50 mL of diethyl ether. While stirring, carbon monoxide was bubbled through the solution for 5 min, then the reaction solution stirred for another 5 min. The original orange-colored solution changed to bright yellow. In the control IR spectra a quantitative reaction of **3** to **2** was observed. ^1H-NMR-spectroscopic measurements confirmed this observation.

Reaction of Dicarbonyl(2−4,4a,8a-η-1-hydronaphthalene)(trimethyl phosphite)manganese (3) with Trimethyl Phosphite: 200 mg (0.55 mmol) of dicarbonyl(2−4,4a,8a-η-1-hydronaphthalene)(trimethyl phosphite)manganese (**3**) was dissolved in 20 mL of *n*-hexane at 243 K. With a syringe 0.2 mL of $P(OMe)_3$ was slowly added dropwise to the solution. Within 10 min the color of the reaction solution changed to a lemon yellow. From the IR control spectra it was seen that **3** had reacted to a dicarbonyl complex nearly quantitatively. This was very temperature-sensitive and decomposed in solution even at 268 K. The solution was concentrated in vacuo at 243 K to about 5 mL and stored for 48 h at 198 K. Bright yellow dicarbonyl(2−4-η-1-hydronaphthalene)bis(trimethyl phosphite)manganese (**4**) separated as a microcrystalline powder. At 233 K the solvent was removed with a pipette and the residue washed with *n*-pentane (5 ×) and cooled to 233 K. The solid was dried for several days at 243 K in high vacuum. − IR (diethyl ether): $\tilde{\nu}$ = 1947 (s) cm^{-1}, 1848 (vs). − ^1H NMR ([D_8]toluene, 233 K): δ = 6.99 (d, J = 8.3 Hz, 1 H, 5-H), 6.92 (d, J = 8.1 Hz, 1 H, 8-H), 6.81 (dd, J = 8.3, 6.2 Hz, 1 H, 6-H), 6.74 (dd, J = 8.1, 6.2 Hz, 1 H, 7-H), 4.97 (dd, J = 6.2, 6.0 Hz, 1 H, 3-H), 4.17 (m, 1 H, 4-H), 4.04 (m, 1 H, 2-H), 3.36 (d, J = 12.4 Hz, 1 H, 1-H^{endo}), 3.32 [d, J = 11.0 Hz, 18 H, P(OCH$_3$)$_3$], 3.18 (d, J = 12.4 Hz, 1 H, 1-H^{exo}). − ^{31}P NMR ([D$_8$]toluene, 183 K): δ = 200.45 (s), 198.25 (s). − $C_{18}H_{27}MnO_8P_2$ (488.30): calcd. C 44.28, H 5.57; found C 45.0, H 5.5.

Photolysis of Dicarbonyl(2−4,4a,8a-η-1-hydronaphthalene)bis(trimethyl phosphite)manganese (5): In a photolysis vessel 100 mg (0.02 mmol) of dicarbonyl(2−4-η-1-hydronaphthalene)bis(trimethyl phosphite)manganese (**4**) was dissolved at 223 K in 120 mL of diethyl ether. The bright yellow solution was irradiated for 60 min with UV light. One CO ligand was cleaved and an orange-colored monocarbonyl complex formed. The crude product was absorbed at 253 K on 2 g of Na_2SO_4 and placed on a column filled with silica gel. First an orange-colored fraction was eluted with *n*-pentane/diethyl ether (25:1) which contained 10 mg of **1**. A red-brown fraction was eluted with *n*-pentane/diethyl ether (10:1) into a precooled Schlenk tube at 253 K. Removal of the solvent in vacuo at the same temp. yielded carbonyl(2−4-η-1-hydronaphthalene)bis(trimethyl phosphite)manganese (**5**) as a dark, red-brown oil. − IR (*n*-pentane): $\tilde{\nu}$ = 1869 cm^{-1}. − ^{1}H NMR ([D$_8$]toluene, 183 K): δ = 7.26 (br. s, 1 H, 5-H), 6.91 (br. s, 1 H, 6-H), 6.79 (br. s, 1 H, 8-H), 6.65 (br. s, 1 H, 7-H), 5.88 (br. s, 1 H, 4-H), 5.22 (br. s, 1 H, 3-H), 3.38 [m, 18 H, P(OCH$_3$)$_3$], 3.17(br. s, 1 H, 1-H^{endo}), 3.05 (br. s, 1 H, 2-H), 2.62 (br. s, 1 H, 1-H^{exo}). − ^{31}P NMR ([D$_8$]toluene, 183 K): ***5d,f***: δ = 215.3 (d, J = 82 Hz, 0.89 P), 214.1 (d, J = 82 Hz, 0.89 P); ***5d,e***: δ = 206.7 (br. s, 0.06 P), 193.7 (br. s, 0.06 P); ***5e,f***: δ = 201.5 (br. s, 0.05 P), 198.8 (br. s, 0.05 P). − The activation parameters for the hindered isomerization of ***5d,f***, ***5d,e***, ***5e,f*** were determined from the temperature dependence of the ^{31}P-NMR signals of ***5d***, ***5d,e***, and ***5e,f***; T [K], k [s^{-1}]: 183, 1; 233, 150; 273, 1000. − $C_{17}H_{27}MnO_7P_2$ (460.28): calcd. C 44.36, H 5.91; found C 45.4, H 6.1.

Acknowledgments

Financial support from the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft and the Land Rheinland-Pfalz (Graduate Stipend) are gratefully acknowledged.

---

[1] S. Özkar, C.G. Kreiter, M. Kotzian, *J. Organomet. Chem.* **1995**, *494*, 115−121.
[2] C. G. Kreiter, A. Georg, G. J. Reiß, *Chem. Ber.* **1997**, *130*, 1197−1200.
[3] S. Sun, C. A. Dullaghan, G. B. Carpenter, A. L. Rieger, P. H. Rieger, D. A. Sweigart, *Angew. Chem.* **1995**, *107*, 2734−2737; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2540−2542.
[4] S. Sun, C. A. Dullaghan, G. B. Carpenter, D. A. Sweigart, S. S. Lee, Y. K. Chung, *Inorg. Chim. Acta* **1997**, *262*, 213−217.
[5] S. Sun, L. K. Yeung, D. A. Sweigart, T.-Y. Lee, S. S. Lee, Y. K. Chung, S. R. Switzer, R. D. Pike, *Organometallics* **1995**, *14*, 2613−2615.
[6] D. Jones, L. Pratt, G. Wilkinson, *J. Chem. Soc.* **1962**, 4458−4462.
[7] P. J. C. Walker, R. J. Mawby, *Inorg. Chim. Acta* **1973**, *7*, 621−625.
[8] P. L. Pauson, J. A. Segal, *J. Chem. Soc., Dalton Trans.* **1975**, 1683−1686.
[9] Y. K. Cung, D. A. Sweigart, N. G. Connelly, J. B. Sheridan, *J. Am. Chem. Soc.* **1985**, *107*, 2388−2393.
[10] D. B. Snyder, S. J. Schauer, D. P. Eyman, J. L. Moler, J. J. Weers, *J. Am. Chem. Soc.* **1993**, *115*, 6718−6729.
[11] K. Woo, P. G. Willard, D. A. Sweigart, N. W. Duffy, B. H. Robinson, J. Simpson, *J. Organomet. Chem.* **1995**, *487*, 111−118.
[12] M. J. S. Dewar, *Bull. Soc. Chim. Fr.* **1951**, *18*, C79.
[13] J. Chatt, L. A. Duncanson, *J. Chem. Soc.* **1953**, 2939.
[14] C. G. Kreiter, G. Michael, J. Kaub, *J. Organomet. Chem.* **1988**, *355*, 149−162.

Received September 18, 1998
[I98317]