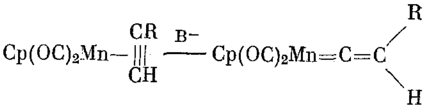
CHEMICAL REACTIONS OF 1-PROPYN-3-OL AND 1-BUTYN-3-OL WITHIN THE COORDINATION SPHERE OF MANGANESE

UDC 542.91:541.49:546.711:547.361:547.362.4:547.514.72

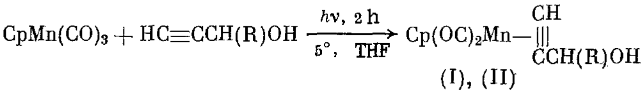
N. E. Kolobova and V. V. Derunov

Acetylene π-complexes of manganese containing electron acceptor (MeOOC) substituents on the acetylenic ligand are known to isomerize upon treatment with strong bases (PhLi) [1], whereas those with Ph and CPh_2OH substituents undergo isomerization upon chromatography on Al_2O_3 (pH 9-10) [2, 3].



$$Cp(OC)_2Mn-\overset{CR}{\underset{CH}{|||}} \xrightarrow{B^-} Cp(OC)_2Mn{=}C{=}C\begin{smallmatrix}R\\H\end{smallmatrix}$$

It was of interest to us to investigate the nature of the conversions of η^2-acetylenic ligands containing electron donating substituents (such as CH_2OH, CH(R)OH) within Mn complexes upon treatment with bases. Complexes (I) [4] and (II) were prepared for this purpose via photochemical reactions between cymmantrene and prop-1-yn-3-ol and but-1-yn-3-ol.



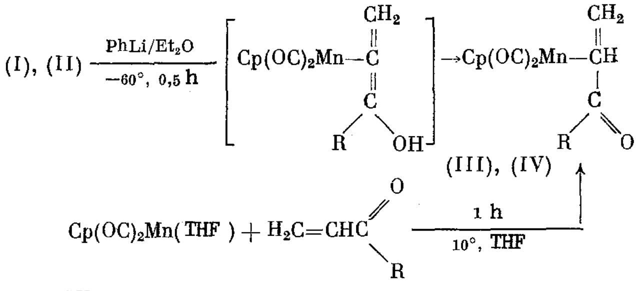
$$CpMn(CO)_3 + HC\equiv CCH(R)OH \xrightarrow[5°,\ THF]{h\nu,\ 2\,h} Cp(OC)_2Mn-\overset{CH}{\underset{CCH(R)OH}{|||}}$$

(I), (II)

R = H (I), Me (II).

Experiments designed to isomerize complexes (I) and (II) to the corresponding metal-allenyl complexes, via treatment with Al_2O_3 (pH 9-10), proved unsuccessful; the starting materials were recovered unchanged in nearly quantitative yields. In contrast to (I) and (II), acetylenic π-complexes with Mn in which the ligands contain tertiary carbinol substituents, such as $Cp(OC)_2Mn(\eta^2\text{-}HC\equiv CCR^1R^2OH)$, isomerize upon treatment with Al_2O_3 (pH 9-10) to give the corresponding η^1-vinylidene complexes [3].

Action of an ethereal solution of PhLi on (I) or (II) leads to cymmantrene complexes containing π-coordinated acrolein (III) and vinyl methyl ketone (IV), respectively. It is assumed that under these conditions complexes (I) and (II) undergo 1,3-hydrogen shifts, which result in the formation of unstable η^2-allenyl intermediates, which then undergo subsequent irreversible ketoenol tautomerization to give the corresponding π-olefin complexes.



R = H (III), Me (IV).

The formation of complexes (III) and (IV) via the isomerization reactions of π-coordinated acetylenic alcohols was confirmed by independent synthesis of the former.

Acetylene-η^2-allene rearrangements have been observed previously in complexes of the type $\eta^5\text{-}MeC_5H_4(OC)_2Mn(\pi\text{-}RC\equiv CCHR^1R^2)$ ($R = COOR^1$, COR^1, R^1R^2 = Alk) upon treatment with Al_2O_3

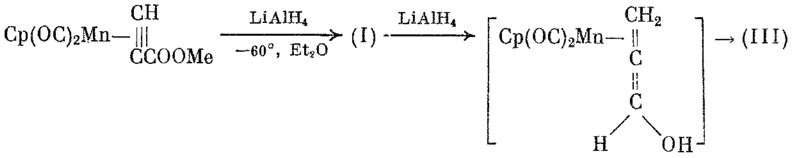
A. N. Nesmeyanov Institute of Heteroorganic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1626-1630, July, 1987. Original article submitted November 27, 1985.

0568-5230/87/3607-1504$12.50

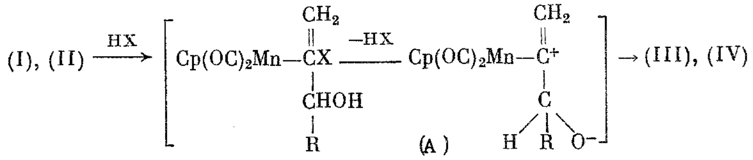
(pH 9-10), resulting in the formation of allenyl π-complexes of the type η^5-$MeC_5H_4(CO)_2Mn$-(η^2-$RHC{=}C{=}CR^1R^2$) [5].

The conversions of 1-propyn-3-ol and 1-butyn-3-ol are of additional interest as the first examples of π-acetylene-π-olefin rearrangements occurring within the coordination sphere of a transition metal; this has not been observed previously. Similar conversions could be of practical significance for the preparation of difficultly accessible organic compounds, such as unsaturated ketones of the type $H_2C{=}CHC(O)R$, from available acetylenic alcohols.

It should be noted that (III) could also be prepared by the reaction of the π-complex $Cp(OC)_2Mn(\pi\text{-}HC{\equiv}CCOOCH_3)$ with $LiAlH_4$. This conversion involves selective reduction of the ester group in the first stage of the reaction, resulting in the formation of the acetylenic complex (I), which then undergoes isomerization to the olefinic π-complex (III).

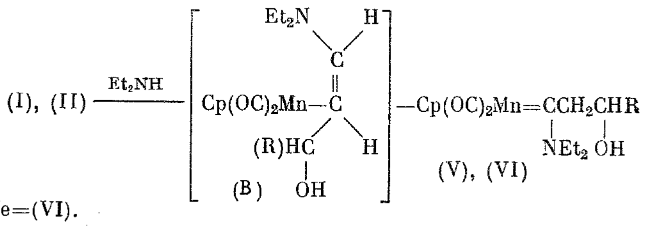


We have also found that, in contrast to $Cp(OC)_2Mn(\pi\text{-}HC{\equiv}CCOOPh)$ [6], $Cp(OC)_2Mn(\pi\text{-}HC{\equiv}CCOOMe)$ [7], and $Cp(OC)_2Mn(\pi\text{-}HC{\equiv}CPh)$ [8], complexes (I) and (II) react with protic acids to give (III) and (IV); the formation of these complexes is observed to occur after the addition of catalytic amounts of acids. It is assumed that the first stage of this conversion involves addition of HX to the triple bond of the π-ligand, in accordance with Markovnikov's Rule, and that this is followed by loss of HX to give a zwitterionic complex A, which then isomerizes to the olefinic π-complex.



$X = Cl^-, CH_3COO^-$; R = H, Me.

Reaction of (I) and (II) with Et_2NH leads to the formation of a mixture of (III) or (IV) and the aminocarbene complexes (V) or (VI), respectively; the latter were isolated in 21 to 54% yield by chromatography. The aminocarbene complexes are probably formed as a result of addition of the secondary amine to the triple bond of the coordinated ligand, and subsequent 1,2-hydrogen shift within the intermediate π-olefin complex B.



R=H(V), Me=(VI).

The secondary amine can thus act both as a Lewis base, leading to acetylene–allene rearrangement, and as a Bronsted acid, adding to the triple bond of the ligand. The aminocarbene complexes (V) and (VI) are unstable in air, and occur in the form of oils which are extremely soluble in polar organic solvents and only sparingly soluble in aliphatic hydrocarbons. Based on their IR spectra, complexes (V) and (VI) consist of aminocarbene complexes of cymmantrene [9].

EXPERIMENTAL

All operations were conducted under an Ar atmosphere. The solvents used in this paper were absolute (dry), and saturated with Ar. Photochemical reactions were carried out under irradiation with a PRK-4 (200 V) Hg lamp, in a quartz apparatus fitted with a cooling jacket.

Silica gel grade 40/100 μ (Chemapol, Czechoslovakia) was used for chromatography; IR spectra were recorded on a UR-20 spectrophotometer (Zeiss), while mass spectra were measured on an AEIMS-30 mass spectrometer (temperature of the ion source, 200°C; ionizing electron energy 70 eV; direct sample introduction). PMR spectra were obtained on a Bruker WP-200 (200 MHz) spectrometer. The synthesis of (I) has been reported previously [4].

$(\eta^5$-Cyclopentadienyl$)(\eta^2$-but-1-yn-3-ol)dicarbonylmanganese (II). A solution of 6 g (29.4 mmole) $CpMn(CO)_3$ in 180 ml THF was treated with 4 ml (69 mmole) 1-butyn-3-ol and the reaction mixture was irradiated with stirring for 3 h at 5°C. After evaporation of the solvent the red-orange crystalline residue was subjected to column chromatography on SiO_2 at 5°C. Elution with petroleum-ether—Et_2O (1:1) gave an orange band, which yielded 1.5 g (21%) of orange crystals of (II), mp 56-57°C. IR spectrum of (II) in CH_2Cl_2 (ν, cm^{-1}): 1973, 1900 ($C\equiv O$); 3500-3600 (OH). Mass spectrum of (II), m/z: 246 M^+, 218 $[M-CO]^+$, 190 $[M-2CO]^+$, 172 $[M-2CO, H_2O]^+$, 148 $[M-CO, C_4H_6O]^+$, 120 $[CpMn]^+$, 55 Mn^+. Found: C 53.81; H 4.79; Mn 22.30%. $C_{11}H_{11}O_3Mn$. Calc.: C 53.67; H 4.50; Mn 22.32%.

Complex (II) was prepared in 24% yield by the reaction of $Cp(OC)_3Mn(THF)$ with 1-butyn-3-ol (1 h at 20°C).

Reaction of (I) with PhLi. To 1 g (4.31 mmole) of (I) in 50 ml of ether at −60°C was added 8.62 ml (4.31 mmole) of a 0.5 N solution of PhLi in ether. The mixture was stirred 0.5 h at −60°C, 0.5h at −20°C, and then acidified with 4 ml 1 N HCL in ether. After filtration the mixture was chromatographed and the solvent evaporated to give 0.4 g (40%) of (III) as yellow crystals, mp 142-143°C (from pentane—ether, 1:1). IR spectrum (CH_2Cl_2, ν, cm^{-1}): 1984, 1926 ($C\equiv O$), 1677 (C=O), 1470 (C=C). PMR spectrum ($CDCl_3$, TMS, δ, ppm): 2.35 m, 3.113 m ($J_{HH\ avg}$ = 1.2 Hz), ($H_2C{=}C$), 3.485 m (C=C=H), 4.727 s (Cp), 8.209 s (HC=O), intensity ratio 1:1:1:5:1. Mass spectrum (m/z): 232 M^+, 186 $[M-CO, H_2O]^+$, 176 $[M-2CO]^+$, 148 $[CpMn(CO)]^+$, 120 $[CpMn]^+$, 93 $[MnC_3H_2]^+$, 80 $[MnC_2H]^+$, 55 Mn^+. Found: C 51.45; H 4.30; Mn 23.00%. $C_{10}H_9O_3Mn$. Calc.: C 51.74; H 3.91; Mn 23.67%.

Reaction of (II) with PhLi. To 1 g (4.06 mmole) of (II) in 50 ml ether at −60°C was added 4.06 ml (4.06 mmole) of 1 N PhLi in ether. The mixture was stirred for 0.5 h at −60°C, 0.5 at −20°C, then acidified with 4 ml 1 N HCl in ether. The solution was filtered to remove LiCl and the solvent evaporated in vacuo. The residue (red-orange crystals) was chromatographed on a SiO_2 column at 5°C. Elution with hexane—ether (1:1) gave an orange zone, which consisted of 0.5 g of a mixture of cymmantrene and (II); elution with ether gave a yellow band. Yield 0.35 g (35%) of (IV) as yellow crystals, mp 75-76°C (pentane—ether, 1:1). IR spectrum (CH_2Cl_2, ν, cm^{-1}): 1985, 1926 ($C\equiv O$), 1670 (C=O), 1468 (C=C). Found: C 53.78; H 4.62; Mn 22.20%. $C_{11}H_{11}O_3Mn$. Calc.: C 53.67; H 4.50; Mn 22.32%.

$(\eta^5$-Cyclopentadienyl$)(\eta^2$-but-1-en-3-one)dicarbonylmanganese (IV). To solution of $CpMn(CO)_2THF$, prepared by irradiation of 3 g (14.7 mmole) $CpMn(CO)_3$ in 150 ml THF (2 h at 10°C), was added 2 ml (1.68 g, 30 mmole) acrolein, and the mixture was stirred for 1 h. After evaporation of the solvent under vacuum the yellow crystalline residue was chromatographed on SiO_2. Yield (hexane eluant) 2 g (67%) of unreacted cymmantrene and 0.93 g (80% based on reacted cymmantrene) (ether eluant) of (III) as yellow crystals, which was identified based on its TLC properties and IR and PMR spectra.

$(\eta^5$-Cyclopentadienyl$)(\eta^2$-but-1-en-3-one)dicarbonylmanganese (IV). To a solution of $CpMn(CO)_2THF$, prepared via irradiation of 3 g (14.7 mmole) $CpMN(CO)_3$ in 150 ml THF (2 h, 10°C), was added 2.4 ml (2.1 g, 30 mmole) methyl vinyl ketone; the mixture was stirred for 1 h. After removal of the solvent in vacuo the yellow crystalline residue was chromatographed on SiO_2. Yield (hexane eluant) 2 g (67%) unreacted cymmantrene and 0.89 g (72% based on reacted cymmantrene) (ether eluant) of (IV), as yellow crystals, which was identified based on its TLC properties and IR spectrum.

Reaction of $Cp(OC)_2Mn(\eta^2$-$HC\equiv CCOOMe)$ with $LiAlH_4$. A solution of 1 g (3.84 mmole) $Cp(OC)_2Mn(\pi$-$HC\equiv CCOOMe)$ in 50 ml ether was treated at −60°C with 15.2 ml (4 mmole) of a 0.263 N ethereal solution of $LiAlH_4$; the mixture was stirred for 0.5 h at −60°C and 0.5 h at −20°C, then neutralized with 4 ml 1 N HCl in ether (the course of the reaction was followed by IR spectroscopy). After filtration, chromatography, and solvent removal, the yield of (III), which was isolated as yellow crystals, was 0.26 g (26%) (pentane—ether eluant, 1:1); the material was identified by TLC and IR.

Reaction of (I) with HCl. To a solution of 1.51 g (6.5 mmole) (I) in 100 ml absolute ether was added 3 ml (2.8-fold excess) of HCl in ether (5.6 N). The resulting yellow crystalline precipitate was filtered, washed with pentane, and recrystallized from a mixture of ether and pentane (3:1). Yield 1.37 g (91%) of (III) as yellow crystals, identified by TLC and IR.

Treatment of MeCOOH and (I). To a solution of 0.58 g (2.5 mmole) (I) in 50 ml absolute ether was added 2.85 ml (5 mmole) glacial acetic acid; the mixture was stirred for 0.5 h at 20°C, evaporated in vacuo, and the residue was recrystallized from ether–pentane (3:1). Yield 0.2 g (35%) of (II) as yellow crystals, identified by TLC and IR.

Reaction of (II) with HCl. To a solution of 1.23 g (5.0 mmole) (II) in 50 ml absolute ether was added 5 ml of 1 N HCl in ether. The resulting yellow precipitate was filtered, washed with pentane, and recrystallized from ether–pentane (1:1). Yield 1 g (81%) of (IV) as yellow crystals, identified by TLC and IR.

(η^5-Cyclopentadienyl)(diethylamino-2-hydroxyethyl)carbenedicarbonylmanganese (V). a) A solution of 0.93 g (4 mmole) (I) in 50 ml hexane was treated with 0.6 g (8 mmole) Et_2NH. The mixture was stirred 0.5 h at 0-5°C. After evaporation of the solvent the resulting orange-yellow crystalline residue was chromatographed on SiO_2. Yield (hexane–ether, 5:1, eluant) 0.3 g (25%) of (V) as an orange oil, and 0.5 g (54%) (ether eluant) (III), yellow crystals, identified by TLC and IR. IR spectrum of (V) (CH_2Cl_2, $\nu C\equiv O$): 1915, 1835 cm^{-1}.

b) Reaction of (I) (0.93 g, 4 mmole) with Et_2NH (0.3 g, 4 mmole) led to the formation of (V) and (III) in yields of 0.14 g (11.5%) and 0.3 g (32%), respectively.

(η^5-Cyclopentadienyl)(diethylamino-2-hydroxypropyl)carbenedicarbonylmanganese (VI). a) A solution of 0.98 g (4 mmole) (II) in 50 ml hexane was treated with 0.6 g (8 mmole) Et_2NH. The mixture was stirred for 0.5 h 0-5°C. After solvent evaporation the orange yellow crystalline residue was chromatographed on SiO_2. Yield (hexane–ether, 6:1, eluant) 0.27 g (21.0%) of (VI) as an orange oil, and 0.49 g (50%) (ether eluant) of (IV), yellow crystals. IR spectrum of (VI) (CH_2Cl_2, $\nu C\equiv O$): 1918, 1840 cm^{-1}.

b) Reaction of (II) (0.98 g, 4 mmole) and Et_2NH (0.3 g, 4 mmole) led to the formation of (VI) and (IV) in yields of 0.13 g (10%) and 0.27 g (28%), respectively.

CONCLUSIONS

1. Acetylenic π-complexes $Cp(OC)2Mn(\pi\text{-}HC\equiv CCH_2OH)$ and $Cp(OC)_2Mn(\pi\text{-}TC\equiv CCH(CH_3)OH)$ have been demonstrated to react with bases and acids and to undergo conversion to the π-olefinic complexes $Cp(OC)_2Mn(\pi\text{-}H_2C{=}CHC(H){=}O)$ and $Cp(OC)_2Mn(\pi\text{-}H_2C{=}CHC(CH_3){=}O)$.

2. Treatment of acetylenic π-complexes $Cp(OC)_2Mn(\pi\text{-}HC\equiv CCH_2OH)$ and $Cp(OC)_2Mn(\pi\text{-}HC\equiv CCH\text{-}(CH_3)OH)$ with Et_2NH gives aminocarbene and π-olefinic manganese complexes.

LITERATURE CITED

1. N. E. Kolobova, L. L. Ivanov, and O. S. Zhvanko, Izv. Akad. Nauk SSSR, Ser. Khim., 478 (1980).
2. A. N. Nesmeyanov, A. B. Antonova, N. E. Kolobova, and K. N. Anisimov, Izv. Akad. Nauk, SSSR, Ser. Khim., 2873 (1974).
3. N. E. Kolobova, L. L. Ivanov, O. S. Zhdanov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2632 (1982).
4. N. E. Kolobova, L. L. Ivanov, Yu. A. Chernykh, and V. V. Derunov, Izv. Akad. Nauk SSSR, Ser. Khim., 1395 (1982).
5. M. Frank-Newmann and F. Brion, Angew. Chem. Inter. Ed. Engl., 18, 688 (1979).
6. N. E. Kolobova, T. V. Rozantseva, and P. V. Petrovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2063 (1979).
7. N. E. Kolobova, L. L. Ivanov, and O. S. Zhdanov, Izv. Akad. Nauk SSSR, Ser. Khim., 2646 (1980).
8. G. G. Aleksandrov, A. B. Antonova, N. E. Kolobova, et al., Koord. Khim., 5, 279 (1979).
9. H. Berke, G. Huttner, and J. Seyerl, Z. Naturforsch., 36B, 1277 (1981).