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Preparation and Structure of Chiral Carbene Complexes of Manganese and Iron from Terminal Alkynes

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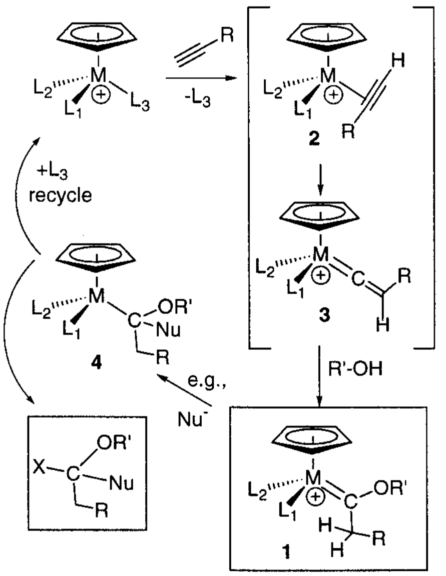
Summary: Chiral-at-the-metal Fischer carbene complexes are prepared by reaction of coordinatively unsaturated Cp(NO)(Ph$_3$P)Mn(+) or Cp(CO)(Ph$_3$P)Fe(+) by intramolecular rearrangement of hydroxyalkynes and the parallel reaction of methyl alcohol with TMS−acetylene.

Introduction

Chiral-at-the-metal carbene complexes (e.g., **1**, Scheme 1) have significant potential for asymmetric synthesis, as recognized by Gladysz,[1] Davies,[2] Brookhart,[3] and others.[4] The asymmetry at the metal center can be transmitted effectively in the creation of stereogenic centers at the carbene carbon and adjacent carbon sites, through reactions such as the addition of nucleophiles to the electrophilic carbene carbon. Such conversions would be particularly useful if the carbene−metal complex could be prepared in a direct way, compatible with succeeding steps and thereby allow a "one-pot" process or a catalytic sequence. Fischer-type carbene complexes have been prepared in numerous ways, but the more general procedure, addition of an organolithium reagent to a metal carbonyl followed by alkylation, does not lend itself to a catalytic cycle.[5] They are also prepared directly from terminal alkynes, via rearrangement to the vinylidene analogue and addition (intra- or intermolecular) of alkoxy (Scheme 1).[6] The process is initiated by generation of a coordinatively unsaturated intermediate, usually through photodissociation of a CO ligand,[7] by thermal dissociation of a weakly bound ligand,[8] or by ionization of an anionic ligand [e.g., iodide activated by Ag(I)]. Then coordination of the alkyne (in **2**) allows rearrangement to an electrophilic vinylidene complex (**3**). Addition of alkoxy and protonation gives the carbene complex **1**. In a second stage, addition of a nucleophile to **1** at the carbene carbon (or transformations adjacent to the carbene carbon) can occur stereoselectively (e.g., to give **4**). Further processing by various methods can cleave the organic ligand and allow recycling of the asymmetric metal unit.

Scheme 1. Catalytic Functionalization of Alkynesvia Carbene−Metal Intermediates



Results and Discussion

Here we report preparation of chiral Mn and Fe analogues of **1** by the direct reaction with alkynes. The first efforts toward an efficient synthesis of asymmetric Fischer carbene complexes involved photochemical activation of the known asymmetric manganese complex **5**. Photodissociation of racemic complex **5** leads to coordinatively unsaturated intermediate **6**, which is known to racemize only slowly, with a half-life time of >6 h at 25 °C,[9] a prerequisite for the synthesis of enantiopure carbene complexes from enantiopure **5**.

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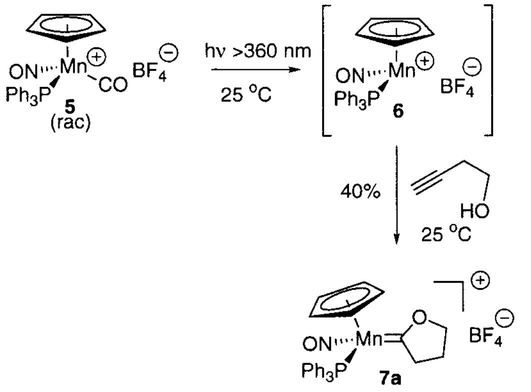
Scheme 2. Photoinitiation

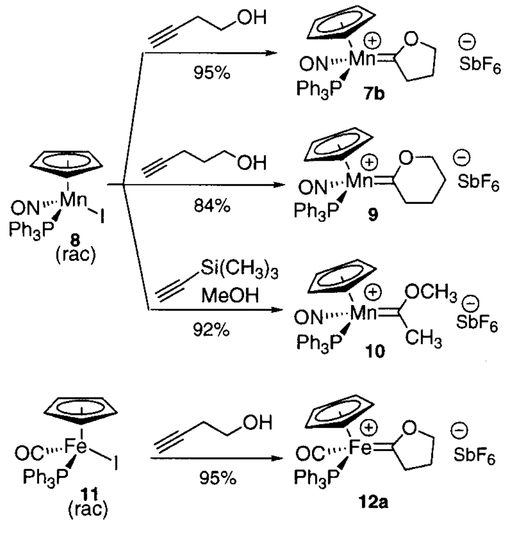


Irradiation was carried out with external radiation with a medium-pressure mercury arc (Hanovia 450) and a Uranium glass filter (λ 360 nm cutoff). Using various solvents and stoichiometric amounts of **5** and 3-butyn-1-ol led mainly to decomposition products of the starting manganese complex. Similar experiments using neat 3-butyn-1-ol were more successful. The desired complex **7a** was obtained in an optimized yield of 40% as a yellow-orange powder after a simple filtration through a short SiO$_2$ column (Scheme 2).

In an effort to increase the efficiency of the carbene complex formation, thermal reactions from different precursors were investigated. The known chiral complex **8** was prepared in racemic form by sequential replacement of CO ligands in [CpMn(CO)$_3$]$^+$BF$_4^-$ by PPh$_3$, NO, and I$^-$.[10] Complex **8** was dissolved in 3-butyn-1-ol, treated with 1 molar equiv of Ag(SbF$_6$) at −78 °C, and then allowed to warm slowly over 1 h to 23 °C. Dilution with dichloromethane, filtration, and concentration gave an essentially pure product, **7b**, in 95% yield. Recrystallization from THF/ether gave the analytical sample. Similarly, the six-membered ring analogue **9** was prepared by reaction in 4-pentyn-1-ol, in 84% yield after recrystallization; a longer reaction time (18 h) was required in this case. For an acyclic case, trimethylsilyl acetylene was used as an equivalent of acetylene, in methyl alcohol solution. Reaction with silver(I) for 1 h at 23 °C gave complex **10** in 92% yield. The analogous series with iron begins with the known[11] racemic iron complex **11**. Treatment as for the Mn complex with Ag(SbF$_6$) in neat 3-butyn-1-ol at −78 °C and then warming to 23 °C over 1 h gave the hexafluoroantimonate salt **12a** in 75% yield after recrystallization from THF/ether.

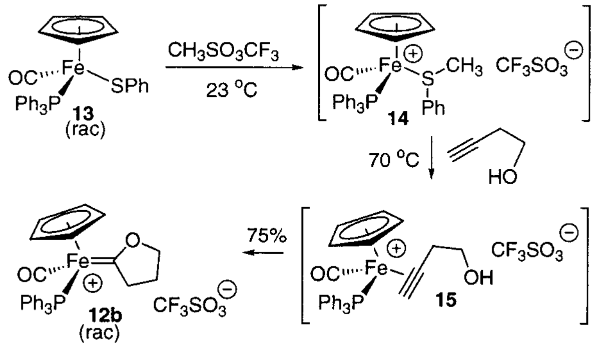
In an effort to avoid the requirement of stoichiometric amounts of Ag(I), the activation of a thiolate ligand as a leaving group was investigated. The approach is based on the work by Treichel et al., where a thiophenyl ligand was replaced by bromide, using ethylation of the sulfur as an activation process.[12] We prepared the thiophenyl complex **13** in racemic form and activated it by methylation with methyl triflate to give **14** (not isolated). Then reaction with 3-butyn-1-ol at 70 °C gave complex **12b** in 75% yield after recrystallization, presumably via the alkyne complex **15** produced by thermal ligand exchange.

Scheme 3. Formation of Chiral Mn and Fe Carbene Complexes



Conditions: AgSbF$_6$ -78 °C to 25 °C

Scheme 4. Replacement of a Thiophenyl Ligand



In complexes with an asymmetric ligand sphere, such as manganese complex **7**, the carbene ligand is forced into a plane with the nitrosyl ligand and the manganese center.[13] This orientation maximizes the orbital overlap between an empty p-orbital on the carbene ligand and a filled d-orbital on the transition metal. Nevertheless, two conformers are possible: synclinal and anticlinal. In the synclinal isomer, the larger carbene carbon substituent is placed gauche to the cyclopentadienyl and the triphenyl phosphine ligands. In the anticlinal isomer the larger substituent (R) is eclipsed with the linear nitrosyl ligand and unfavorable steric interactions of the cyclopentadienyl and triphenyl phosphine ligands with the large substituent are removed. This makes the anticlinal conformer typically about 0.5−5 kcal/mol more stable than the synclinal conformer.[1,14] The difference in stability depends directly on the difference in size of the two substituents. For example, in the

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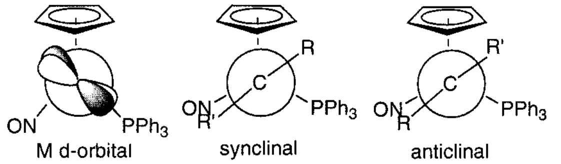

Figure 1. Relationship of the metal-centered d-orbital with respect to the carbene ligand in complexes such as **7**.

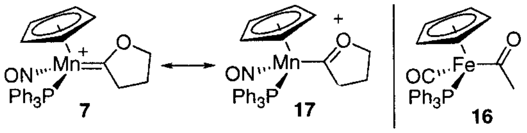

Figure 2. Relationship with acyl complexes.

$[\mathrm{CpRe(PPh_3)(NO)({=}CHPh)}]^+\mathrm{PF_6}^-$ system, the synclinal isomer was obtained exclusively at −78 °C as the kinetic product. Upon warming to 25 °C equilibration to the anticlinal isomer occurred to give a >99:1 anti:syn mixture.[15] For systems such as manganese complexes **7**, **9**, and **10**, the picture is not as clear. Conformational preferences for the tetrahydrofuryl ligand on a steric basis alone are not likely to be strong.

To establish the conformations preferred at least in the solid state, suitable crystals of carbene complexes **7b** and **10** were grown,[16] and diffraction studies provided structures that are shown as ORTEP representations in Figure 3. Both complexes adopt the anticlinal conformation. Torsion angles for N(1)−Mn(1)−C(6)−O(2) are measured at −177.3(3)° and −172.4(3)°, respectively. These results are in accordance with acyl complexes, such as complex **16**. For such systems it was found that the orientation with the acyl oxygen anti to the carbonyl ligand is preferred over the synclinal conformation.[17] The relationship is clear from inspection of resonance structure **17** (Figure 2).[18]

The M−C bond length is 1.898(4) Å for manganese tetrahydrofuryl carbene **7** and 1.901(4) Å for the acyclic complex **10**. This is well in agreement with previously reported bond lengths for similar Fischer carbene complexes[19,20] and slightly longer than the 1.872(1) Å measured for the manganese/carbene distance in the alkylidene complex $\mathrm{CpMn(CO)_2C(Me)_2}$,[21] again consistent with a contribution from the resonance structure **17**. Stereoselectivity issues in 1,2-addition reactions of nucleophiles to carbene complexes **7** and **10** are currently under study.

Experimental Section

Preparation of $[\mathrm{CpMn(PPh_3)(NO)(}\overline{\mathrm{CCH_2CH_2CH_2O}}\mathrm{)}]^+\mathrm{X}^-$ ($\mathrm{X}^- = \mathrm{PF_6}^-$, 7a). Method A. A Schlenk tube, equipped with a magnetic stirbar, was charged with $[\mathrm{CpMn(NO)(PPh_3)(CO)}]\mathrm{PF_6}$ (**8**, 0.150 g, 0.285 mmol). The reaction was placed under argon, and 3-butyn-1-ol (1.0 mL) was added. Then irradiation (medium-pressure Hg lamp, Uranium glass filter) was carried out at 25 °C. The irradiation was stopped when all starting material had dissolved. Evaporation of the dark brown solution gave a residue, which was taken up in dichloromethane. The dichloromethane solution was filtered through a plug of Celite on a fritted Büchner funnel. Carbene complex **7a** (0.067 g, 0.117 mmol, 40%) was obtained as a yellow solid after removal of the solvent from the filtrate.

Method B ($\mathrm{X}^- = \mathrm{SbF_6}$, 7b). In a 10 mL two-neck round-bottom flask equipped with a stirbar and a gas inlet, cyclopentadienyl manganese nitrosyl triphenylphosphine iodide (0.200 g, 0.370 mmol) was placed under argon. Via syringe, neat 3-butyn-1-ol (0.5 mL) was added, and the reaction mixture was stirred for 5 min at 25 °C to give a brown suspension. The suspension was cooled to −78 °C (stirring ceases due to high viscosity of the 3-butyn-1-ol), and under an argon stream, silver hexafluoro antimonate (98%, 0.143 g, 0.415 mmol) was added. The cooling bath was removed, and the reaction mixture was allowed to warm to 25 °C. Stirring at this temperature was continued for an additional 45 min. Upon warming, the reaction brightened (grayish yellow-brown), and an off-white precipitate formed. The solvent was removed under oil pump, and the residue was extracted with portions of dichloromethane (3 × 10 mL). The combined dichloromethane solution was filtered through a plug of Celite on a fritted Büchner funnel, and the solvent was then removed on a rotary evaporator. This leads to a yellow-orange product (**7b**, 0.252 g, 0.351 mmol, 95%). The product is usually already >95% pure by ^{1}H NMR. Trituration with tetrahydrofuran gave an analytically pure sample, mp 219−221 °C dec.

Preparation of $[\mathrm{CpMn(PPh_3)(NO)(}\overline{\mathrm{CCH_2CH_2CH_2CH_2O}}\mathrm{)}]^+\mathrm{SbF_6}^-$, 9. In a 10 mL two-neck round-bottom flask, equipped with a stirbar and a gas inlet, cyclopentadienyl manganese iodo nitrosyl triphenyl phosphine (**8**, 0.100 g, 0.186 mmol) was placed under argon. Via syringe was then added neat 4-pentyne-1-ol (0.5 mL), and the reaction mixture was stirred for 5 min at 25 °C to give a brown suspension. The suspension was then cooled to −78 °C, and silver hexafluoro antimonate (98%, 0.080 g, 0.23 mmol) was added under an argon stream. The cooling bath was removed, and reaction mixture was allowed to warm to 25 °C. Stirring was continued for an additional 14 h at 25 °C. The solvent was removed under oil pump vacuum, and the residue was extracted with portions of dichloromethane (3 × 10 mL). The combined dichloromethane solution was filtered through a fritted Büchner funnel with a plug of Celite. Concentration by rotrary evaporation gave a yellow-brown solid, which was recrystallized from THF and diethyl ether to give pure complex **9** (0.114 g, 0.155 mmol, 84%), mp >300 °C dec.

Preparation of $[\mathrm{CpMn(PPh_3)(NO)(C(OCH_3)CH_3}]^+\mathrm{SbF_6}^-$, 10. A 10 mL two-neck round-bottom flask equipped with a stirbar and a gas inlet was charged with cyclopentadienyl manganese nitrosyl triphenyl phosphine iodide (**8**, 0.100 g, 0.186 mmol) and placed under argon. Trimethylsilylacetylene (0.5 mL) and methanol (0.024 g, 0.03 mL, 0.744 mmol) were added via syringe. Then the stirred solution was cooled to −78 °C. Under an argon stream, solid silver hexafluoroantimonate (98%, 0.080 g, 0.23 mmol) was added, and stirring was continued at −78 °C for 3 h. Then the cooling bath was removed, and the reaction was allowed to slowly warm to 25° C and was stirred for an additional 1 h. The solvent was removed under oil pump vacuum, and the residue was extracted with acetone (3 × 10 mL). The combined acetone extracts was filtered through a plug of Celite on a fritted Büchner funnel. Concentration by rotary evaporation followed by drying under vacuum for 12 h yielded an orange solid (0.121 g, 0.171 mmol). This was already sufficiently pure for further experiments. For elemental analysis, the product was recrystalized from THF and diethyl ether at −30 °C to give analytically pure complex **10** (0.105 g, 0.148 mmol), mp 195 °C dec.

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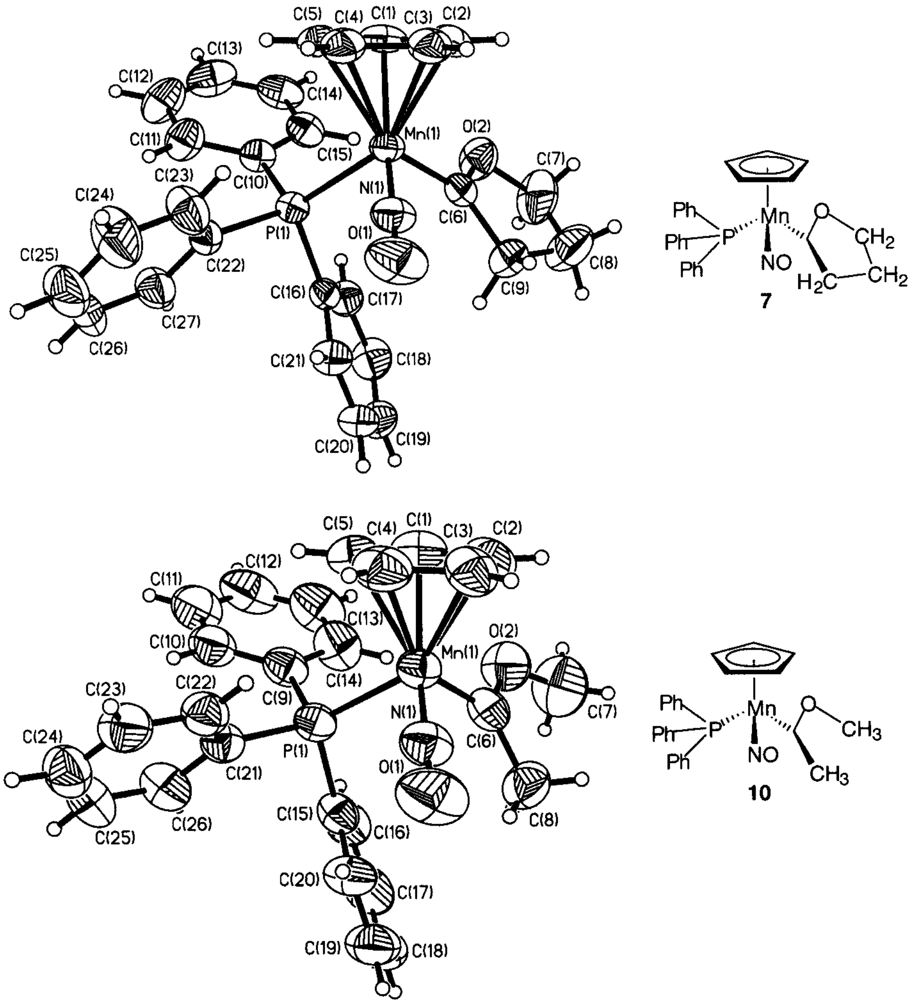

Figure 3. ORTEP drawing of the cations in **7** and **10** with thermal ellipsoids at 50% probability level.

Preparation of $[\mathrm{CpFe(PPh_3)(NO)(}\overline{\mathrm{CCH_2CH_2CH_2O}}\mathrm{)]^+X^-}$ ($\mathrm{X = SbF_6^-}$, 12a). In a 10 mL two-neck round-bottom flask, equipped with a stirbar and a gas inlet, cyclopentadienyl iron carbonyl triphenyl phosphine iodide (**11**, 0.500 g, 0.929 mmol) was placed under argon. Via syringe, 3-butyn-1-ol (1.5 mL) was added all at once. The reaction mixture was stirred for 5 min at 25 °C to give a suspension and was then cooled to −78 °C. Under an argon stream, solid silver hexafluoroantimonate (0.399 g, 1.161 mmol) was added. The reaction mixture was allowed to warm slowly to 25 °C by removing the cooling bath. Stirring was continued at 25 °C for an additional 1 h. The solvent was evaporated under oil pump vacuum, and the residue was extracted with dichloromethane (3 × 10 mL). The combined dichloromethane extract was filtered through a fritted Büchner funnel containing a plug of Celite, and the solvent was then removed on a rotary evaporator. This led to carbene complex **12a** (0.490 g, 0.683 mmol, 95%) as a yellow brown solid, which was >95% pure by ^{1}H NMR. For elemental analysis the product was recrystallized from tetrahydrofuran and diethyl ether.

Method B ($\mathrm{X = CF_3SO_3^-}$, 12b). A 10-mL two-neck round-bottom flask, equipped with a stirbar and a gas inlet, was charged with cyclopentadienyl iron carbonyl triphenylphosphine thiophenylate **13** (0.025 g, 0.049 mmol). The flask was placed under argon, and dichloromethane (1 mL) was added. Via syringe, methyl triflate (0.048 g, 0.033 mL, 0.29 mmol) was added at 25 °C. The reaction mixture was stirred for 15 min at 25 °C followed by removal of all volatiles under oil-pump vacuum. Then 3-butyn-2-ol (0.4 mL) was added via syringe. The reaction mixture was heated on an oil bath to 70 °C and stirred at that temperature for 1 h. The mixture was cooled to 25 °C, the solvent was evaporated under oil-pump vacuum, and the residue was extracted with dichloromethane (3 × 10 mL). The combined dichloromethane extract was filtered through a Celite plug on a fritted Büchner funnel. Rotary evaporation of the solvent yielded carbene complex **12b** (0.020 g, 0.031 mmol, 75%) as a yellowish brown solid, mp 247 °C dec.

Supporting Information Available: Experimental procedures and characterization of complexes **7b**, **9**, **10**, and **12a**. Crystallographic data for structures **7** ($\mathrm{PF_6}$ salt) and **10** ($\mathrm{SbF_6}$ salt). This material is available free of charge via the Internet at http://pubs.acs.org.

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