Organometallic Lewis Acids. 28. [1] Directed Synthesis of σ,π-Allyl-Bridged Metal Compounds via Nucleophilic Attack of Carbonylmetalates to Cationic π-Allyl Complexes $(\eta^5\text{-}C_5H_5)(OC)(ON)Mo(\sigma,\pi\text{-allyl})\text{-}M(CO)_5$ (M = Re, Mn)

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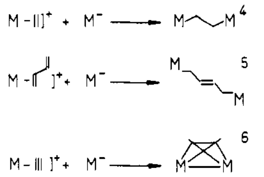
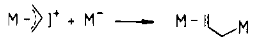
Summary: The reaction of the cationic allyl complex $[(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(allyl)]^+$ with $[M(CO)_5]^-$ (M = Re, Mn) leads to σ,π-allyl-bridged complexes $(\eta^5\text{-}C_5H_5)(OC)(ON)Mo(allyl)M(CO)_5$. The crystal structure of the rhenium complex—determined by X-ray diffraction analysis—is consistent with attack of $[Re(CO)_5]^-$ to the allyl group cis to NO in the exo conformer of $[(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(allyl)]^+$ as has been previously observed with organic nucleophiles.

Nucleophilic attack on unsaturated hydrocarbons which are coordinated to transition metals is one of the most important reactions in organometallic chemistry.[2] The addition of organometallic nucleophiles (e.g., $Re(CO)_5^-$) instead of common nucleophiles has led to hydrocarbon-bridged bimetallic complexes:[3]



Following this concept we have studied the reaction of cationic η^3-allyl complexes with carbonylmetalates which provides a directed synthesis of σ,π-allyl-bridged complexes:



The addition of organic nucleophiles to η^3-allyl complexes has found wide application in organic synthesis.[2,7]

A remarkable stereospecificity has been observed in the reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(allyl)]^+$ with nucleophiles.[8,9] Theoretical calculations[10] agree well with the experimental findings that in most cases the reactions of the exo and endo isomers of $[(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(allyl)]^+$ lead to a single product which results by addition of the nucleophile cis to the nitrosyl ligand in the exo conformer. As demonstrated by Faller,[9] the endo form is converted to the exo isomer before nucleophilic attack occurs.

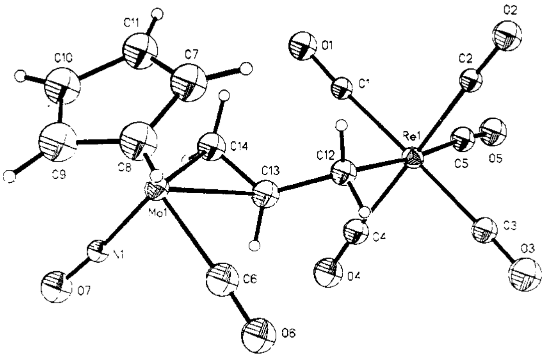
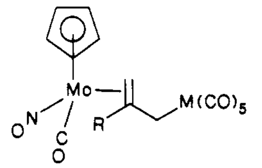


Figure 1. Molecular structure of **1a**. Some relevant bond lengths (Å): Re(1)–C(12), 2.31 (2); C(12)–C(13), 1.53 (2); C(13)–C(14), 1.37 (3); Mo(1)–C(14), 2.25 (2); Mo(1)–C(13), 2.43 (2); Mo(1)–N(1), 1.82 (1); Mo(1)–C(6), 1.97 (2); N(1)–O(7), 1.20 (2); C(6)–O(6), 1.15 (2). Some relevant bond angles (deg): Re(1)–C(12)–C(13), 108 (1); C(12)–C(13)–C(14), 126 (2); Mo(1)–C(14)–C(13) 80 (1); Mo(1)–C(13)–C(14), 66 (1); N(1)–Mo(1)–C(6) 90.5 (7).

We have found that the reactions of $[(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^3\text{-allyl})]^+$ with $[Re(CO)_5]^-$ and $[Mn(CO)_5]^-$, respectively, give the σ,π-allyl-bridged complexes **1** and **2**.[11] According to the IR and ^1H NMR data[12] only a single

$$[(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^3\text{-allyl})]^+PF_6^- + Na^+[M(CO)_5]^- \xrightarrow[-NaPF_6]{}$$



1a: M = Re; R = H
b: M = Re; R = Me
2: M = Mn; R = H

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[11] Experimental procedure: All reactions were carried out in Schlenk tubes under argon. To a suspension of $[(\eta^5\text{-}C_5H_5)Mo(NO)(CO)(\eta^3\text{-}C_3H_5)]PF_6$[8c] (314 mg, 1.03 mmol) in 25 mL of tetrahydrofuran, cooled at −78 °C, was added a cooled (−15 °C) solution of $NaRe(CO)_5$ (prepared from 560 mg (0.85 mmol) of $Re_2(CO)_{10}$ and 2 mL 0.8% sodium amalgam in 3 mL of THF at 0 °C, reaction time 90 min). The obtained pale yellow suspension was stirred for 30 min at −50 °C. Evaporation of the solvent leads to a bright yellow powder from which $NaPF_6$ was separated by washing with 3 mL of water (three times). The remaining solid was dissolved in 10 mL of THF, and the clear orange solution was centrifuged and transferred into another Schlenk tube by using Teflon needles. Evaporation of the solvent gave a bright yellow powder of **1a** (430 mg, 72%) which can be recrystallized from CH_3NO_2/THF (1:2). **1b** and **2** are less stable than **1a** and were purified chromatographically at 20 °C (silica gel 60, for **1b** with ether and for **2** with CH_2Cl_2).

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isomer of **1a** and **1b** is formed. The structure of **1a**, which was determined by X-ray analysis, is consistent with attack of pentacarbonylrhenate to the coordinated allyl group cis to NO in the exo isomer as has been observed with organic nucleophiles.

The Re–C(12) distance (Figure 1) of 2.31 Å clearly shows a rhenium–carbon σ-bond (for comparison Re–C in $H_3C\text{-}Re(CO)_5$[14] and $(OC)_5ReCH_2CH_2Re(CO)_5$[4c] are 2.31 and 2.30 Å, respectively). The C(12)–C(13) bond length (1.53 Å) is a typical C–C single bond which also conforms with the Re–C(12)–C(13) bond angle of 108°. The C–C distances of the allyl bridge are similar to that in the σ,π-allyl-bridged $[(acac)Pt(allyl)_2Pt(acac)]$[15] and in the products from $[(CpMo(CO)(NO)(allyl)]^+$ and different nucleophiles.[8b,c] In contrast to these complexes the Mo–C(allyl) distances in **1a** (2.25 (2) and 2.43 (2) Å) are significantly different, which is probably due to the bulkiness of the $Re(CO)_5$ moiety. The small torsion angle C(13)C(14)Mo-C(6) of 10° in **1a** shows that the olefin carbon–carbon bond is almost colinear with the direction of the metal carbonyl bond (Mo–C(6)) as has been also found for the products of $[CpMo(CO)(NO)(allyl)]^+$ with an enamine,[8b] but the olefinic ligand is rotated by 180° about the metal–olefin bond. To our knowledge up to now only a few σ,π-allyl-bridged complexes, $[Cp(OC)_2Fe(allyl)Fe(CO)_2Cp]^+$,[16] $[(acac)Pt(allyl)_2Pt(acac)]_n$, and $[Pt(allyl)Cl]_4$,[15] have been described. In contrast to the fluxional $[Cp(OC)_2Fe(C_3H_5)Fe(CO)_2Cp]^+$ [16] the ^1H NMR spectrum shows that the σ,π-allyl bridge of **1** is rigid also in solution which is certainly due to the very stable Re–C σ-bond.

We believe that attack of organometallic nucleophiles to π-bonded unsaturated hydrocarbons in cationic complexes may be of broad scope for the preparation of various hydrocarbon-bridged bimetallic compounds, and work is in progress in our laboratory to extend this chemistry.

Acknowledgment. Generous support by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged. We thank one of the reviewers for a most crucial comment.

Registry No. **1a**, 105502-18-9; **1b**, 105502-20-3; **2**, 105502-19-0; $[(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^3\text{-allyl})]^+$, 54438-51-6; $[(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(CH_2{=}C(CH_3)CH_2)]^+$, 72068-96-3; $[Mn(CO)_5]^-$, 14971-26-7; $[Fe(CO)_5]^-$, 14971-38-1.

Supplementary Material Available: Listings of positional and thermal atomic parameters and bond lengths and angles for 1 (2 pages); a listing of observed and calculated structure factors for 1 (17 pages). Ordering information is given on any current masthead page.

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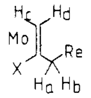
(12) **1a**: IR (CH_2Cl_2) 2125 (m), 2044 (m), 2009 (vs), 1979 (s), 1950 (sh, m), 1897 (sh, w), 1590 (s) cm^{-1}. ^1H NMR (CD_2Cl_2) δ 5.55 (Cp), 4.50 (m, H_e), 2.53 (dd, H_d), 2.22 (m, H_c), 0.85 (d, H_a), 0.71 (d, H_b); mp >138 °C dec. Anal. Calcd for $C_{14}H_{10}MoNO_7Re$: C, 28.67; H, 1.72; N, 2.38. Found: C, 28.77; H, 1.83; N, 2.44. For spectroscopic data of $(OC)_5ReCH_2CH{=}CH_2$ see: Brisdon, B. J.; Edwards, D. A.; White, J. W. *J. Organomet. Chem.* **1979,** *175,* 113. **1b**: IR (CH_2Cl_2) 2125 (m), 2046 (m), 2012 (vs), 1982 (s), 1938 (m), 1607 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 5.56 (Cp), 2.55 (s, H_d), 2.31 (s, H_c), 2.01 (s, Me), 1.06 (s, H_a), 0.94 (s, H_b); mp >81 °C dec. Anal. Calcd for $C_{15}H_{12}MoNO_7Re$: C, 30.00; H, 2.01; N, 2.33. Found: C, 29.81; H, 2.10; N, 2.19. **2**: IR (CH_2Cl_2) 2103 (m), 2045 (s), 2008 (vs), 1986 (s), 1935 (m), 1593 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 5.56 (Cp), 4.20 (m, H_e), 2.58 (dd, H_d), 2.30 (m, H_e), 0.96 (d, H_a), 0.83 (d, H_b); mp >130 °C dec. ^{13}C data could not be obtained because of the instability of complexes **1** and **2** in solution.



1a: X = H_e
b: X = Me
2: X = H_e

Anal. Calcd for $C_{14}H_{10}MnMoNO_7$: C, 36.94; H, 2.21; N, 3.07. Found: C, 36.31; H, 2.63; N, 3.25.

(13) X-ray diffraction data for $C_{14}H_{10}MoNO_7Re$ (**1a**): Nicolet R3 diffractometer, Mo Kα radiation; space group $P2_1/c$, a = 21.426 (6) Å, b = 6.080 (2) Å, c = 12.967 (4) Å, β = 97.43 (2)°; V = 1675.0 (9) $Å^3$; Z = 4; scan mode ω; T = 310 K; θ range = 4–50°; measured reflections, 11 156 ($\pm h$, $\pm k$, $\pm l$); unique reflections, 2934; observed reflections, 2766 ($I > 2\sigma(I)$); empirical absorption correction; Patterson methods to locate the metal atoms; all calculations with SHELXTL system; cyclopentadienyl as regular pentagon; hydrogen atoms calculated; number of variables, 98; R = 0.074, R_w = 0.078; residual electron density = 2.0 e·$Å^{-3}$ (weak disorder of cyclopentadienyl group).

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Reduction of a Coordinated Carbon Monoxide to an Oxymethyl-Bridging Group: Synthesis and X-ray Characterization of the Dianion $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}\eta^2\text{-}CH_2O)(CO)_9]^{2-}$

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Summary: The reaction of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with $Li[BH(s\text{-}Bu)_3]$ gives in high yields the novel anion $[Re_3(\mu\text{-}H)_3(CH_2O)(CO)_9]^{2-}$, which contains a μ_3-η^2-oxymethyl ligand, representing a type of intermediate of CO hydrogenation never previously fully characterized. Protonation at -80 °C leads to an unstable hydroxymethyl derivative, characterized by NMR, which under CO, at room temperature, converts in fair yields to $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ and methanol.

The reductive hydrogenation of carbon monoxide is a subject of both technological and scientific relevance. The mechanism most commonly accepted,[1] especially in homogeneous catalysis, involves a stepwise sequence $[M_n(CHO) \rightarrow M_n(CHOH) \rightarrow M_n(CH_2OH)]$ for which model compounds have been identified in organometallic chemistry. Particularly difficult, however, is the isolation of the species containing two H atom:[2] an alternative to the

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