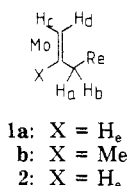


isomer of **1a** and **1b** is formed. The structure of **1a**, which was determined by X-ray analysis, is consistent with attack of pentacarbonylrhenate to the coordinated allyl group cis to NO in the exo isomer as has been observed with organic nucleophiles.

The Re-C(12) distance (Figure 1) of 2.31 Å clearly shows a rhenium-carbon σ -bond (for comparison Re-C in $\text{H}_3\text{C-Re}(\text{CO})_5^{14}$ and $(\text{OC})_5\text{ReCH}_2\text{CH}_2\text{Re}(\text{CO})_5^{4c}$ 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(C₃H₅)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.

(12) **1a**: IR (CH₂Cl₂) 2125 (m), 2044 (m), 2009 (vs), 1979 (s), 1950 (sh), 1897 (sh, w), 1590 (s) cm⁻¹. ¹H NMR (CD₂Cl₂) δ 5.55 (Cp), 4.50 (m, H_a), 2.53 (dd, H_d), 2.22 (m, H_e), 0.85 (d, H_a), 0.71 (d, H_b); mp >138 °C dec. Anal. Calcd for C₁₄H₁₀MoNO₇Re: C, 28.67; H, 1.72; N, 2.38. Found: C, 28.77; H, 1.83; N, 2.44. For spectroscopic data of (OC)₅ReCH₂CH=CH₂ see: Brisdon, B. J.; Edwards, D. A.; White, J. W. *J. Organomet. Chem.* 1979, 175, 113. **1b**: IR (CH₂Cl₂) 2125 (m), 2046 (m), 2012 (vs), 1982 (s), 1938 (m), 1607 (s) cm⁻¹; ¹H NMR (CD₂Cl₂) δ 5.56 (Cp), 2.55 (s, H_d), 2.31 (s, H_e), 2.01 (s, Me), 1.06 (s, H_a), 0.94 (s, H_b); mp >81 °C dec. Anal. Calcd for C₁₅H₁₂MoNO₇Re: C, 30.00; H, 2.01; N, 2.33. Found: C, 29.81; H, 2.10; N, 2.19. **2**: IR (CH₂Cl₂) 2103 (m), 2045 (s), 2008 (vs), 1986 (s), 1935 (m), 1593 (s) cm⁻¹; ¹H NMR (CD₂Cl₂) δ 5.56 (Cp), 4.20 (m, H_e), 2.53 (dd, H_d), 2.30 (m, H_a), 0.96 (d, H_a), 0.83 (d, H_b); mp >130 °C dec. ¹³C data could not be obtained because of the instability of complexes **1** and **2** in solution.



Anal. Calcd for C₁₄H₁₀MnMoNO₇: 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 C₁₄H₁₀MoNO₇Re (**1a**): Nicolet R3 diffractometer, Mo K α radiation; space group P2₁/c, a = 21.426 (6) Å, b = 6.080 (2) Å, c = 12.967 (4) Å, β = 97.43 (2)°; V = 1675.0 (9) Å³; Z = 4; scan mode ω ; T = 310 K; θ range = 4-50°; measured reflections, 11156 ($\pm h, \pm k, \pm l$); 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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(15) Raper, G.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* 1972, 265. Gracey, B. P.; Mann, B. E.; Spencer, C. M. *J. Organomet. Chem.* 1985, 297, 375.

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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; [(η^5 -C₅H₅)Mo(CO)(NO)(η^3 -allyl)]⁺, 54438-51-6; [(η^5 -C₅H₅)Mo(CO)(NO)(CH₂=C(CH₃)CH₂)]⁺, 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.

Reduction of a Coordinated Carbon Monoxide to an Oxymethyl-Bridging Group: Synthesis and X-ray Characterization of the Dianion [Re₃(μ -H)₃(μ_3 - η^2 -CH₂O)(CO)₉]²⁻

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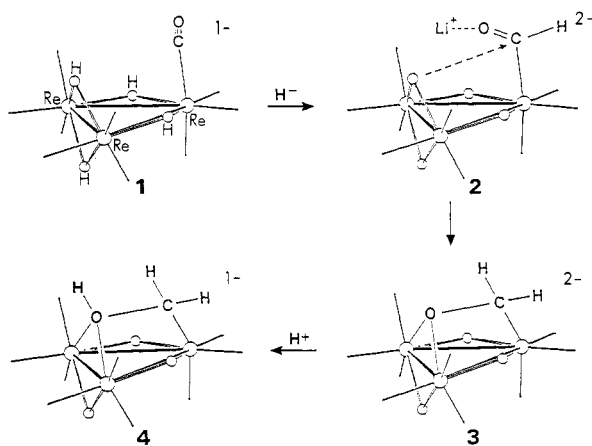
Received July 17, 1986

Summary: The reaction of [Re₃(μ -H)₄(CO)₁₀]⁻ with Li-[BH(s-Bu)₃] gives in high yields the novel anion [Re₃(μ -H)₃(CH₂O)(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 [Re₃(μ -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) → M_n(CHOH) → M_n(CH₂OH)] 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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Scheme I



hydroxymethylene [$M_n(\text{CHOH})$] intermediate is some kind of formaldehyde [$M_n(\text{CH}_2\text{O})$] complex. Compounds of this type, containing π -bonded CH_2O ligands, have been obtained (i) by direct reaction of formaldehyde with a proper precursor,³ (ii) by oxidation of a $\text{Re}=\text{CH}_2$ system with iodosobenzene,⁴ (iii) by dehydrogenation of methanol.⁵ Moreover, by reaction of organometal-hydride complexes of the early transition metals and of actinides with CO or carbonyl complexes, species containing bridging $\eta^2\text{-CH}_2\text{O}$ can be obtained.⁶ Sometimes, in reactions of this type, unstable dinuclear $\mu\text{-}\eta^2\text{-oxymethyl M-O-CH}_2\text{-M}$ intermediates are postulated, evolving to various final products.⁷

We have now synthesized and characterized by NMR spectroscopy and X-ray analysis a species containing an intermediate of CO hydrogenation with two H atoms bound to carbon, which can be considered as an oxymethyl group $\mu_3\text{-}\eta^2$ -coordinated to a triangle of rhenium atoms, namely, the dianion $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CH}_2\text{O})(\text{CO})_9]^{2-}$.

The novel compound has been obtained in high yields upon treatment of the unsaturated cluster anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ (**1**)⁸ with stoichiometric $\text{Li}[\text{BH}(\text{s-Bu})_3]$, at room temperature.⁹ Its formation (see Scheme I) implies as the

(2) Rare examples of hydroxycarbene complexes, obtained by protonation of a formyl precursor, are $[\text{CpRe}(\text{NO})(\text{CHOH})(\text{PPh}_3)]^+$ (Tam, W.; Lin, G. Y.; Wong, W. K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141) and *trans*- $[\text{IrX}(\text{CHOH})(\text{dppe})_2]^{2+}$ (X = H, Cl) (Lilja, M. A.; Ibers, J. A. *Organometallics* **1985**, *4*, 590).

(3) Compounds of this class are $\text{Os}(\text{CO})_2(\eta^2\text{-CH}_2\text{O})(\text{PPh}_3)_2$ [C-O = 1.59 (1) Å] (Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503), $\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2\text{O})[\text{P}(\text{OMe})_3]_2$ [C-O = 1.32 (2) Å] (Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353), $\text{Cp}_2\text{V}(\eta^2\text{-CH}_2\text{O})$ [C-O = 1.353 (10) Å] (Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019), and $\text{Cp}_2\text{Mo}(\eta^2\text{-CH}_2\text{O})$ [C-O = 1.360 (9) Å] (Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985).

(4) (a) Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A.; McCormick, F. B.; Etter, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 1056. (b) Buhro, W. E.; Georgiou, S.; Fernandez, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956.

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(6) Structurally characterized examples, in which the CH_2O groups are $\eta^2\text{-}\pi$ -bonded to a metal atom and act as bridging toward another metal via the oxygen atom (mean C-O = 1.43 Å), are the dinuclear $[\text{Cp}_2\text{ZrCl}_2(\text{CH}_2\text{O})]$ (Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690) and the trimeric species $[\text{Cp}_2\text{Zr}(\eta^2\text{-CH}_2\text{O})_3]$ (Kropp, K.; Skibbe, V.; Erker, G.; Kruger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353). Other examples include $\text{Cp}_2(\text{CO})\text{Nb}(\text{CH}_2\text{O})\text{Zr}(\text{H})\text{Cp}_2$ (Wolczananski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218) and $\text{Cp}(\text{PMe}_3)_2\text{M}(\text{CH}_2\text{O})\text{Zr}(\text{H})\text{Cp}^*_2$ (M = Fe, Ru) (Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278).

(7) Manriquez, J. M.; McAlister, D. R.; Sanner, D. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716; Katahira, D. A.; Moloy, K. G.; Marks, T. *J. Organometallics* **1982**, *1*, 1723.

(8) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A. *Inorg. Chem.* **1985**, *24*, 2666.

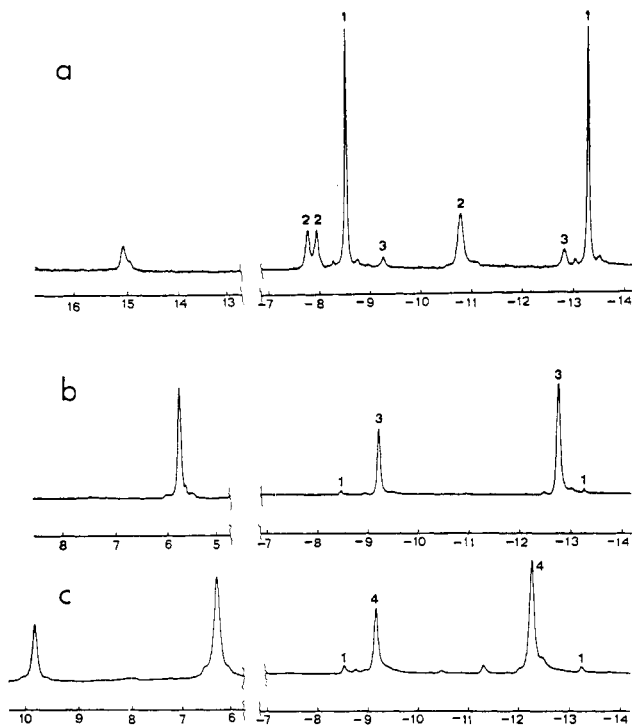


Figure 1. ^1H NMR spectra (80.13 MHz) of different reaction mixtures, containing the products of successive hydrogenation of the coordinated CO. Each hydric resonance is labeled by the number of the corresponding compound. (a) The reaction mixture containing the formyl intermediate (-40°C). (b) A typical reaction mixture (room temperature) containing **3** as the main species. (c) The reaction mixture after the protonation of **3**, at -80°C : **4** is the main product formed.

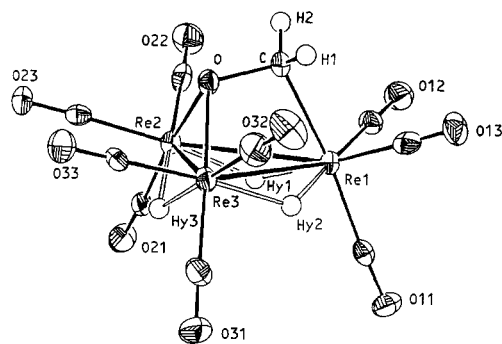


Figure 2. A view of the anion $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CH}_2\text{O})(\text{CO})_9]^{2-}$. The carbonyls are labeled by their oxygen atoms. The hydrides are in calculated positions. Relevant bond distances (Å) are as follows: $\text{Re1-Re2} = 3.221$ (1), $\text{Re1-Re3} = 3.201$ (1), $\text{Re2-Re3} = 2.950$ (1), $\text{Re1-C} = 2.214$ (13), $\text{Re2-O} = 2.139$ (8), $\text{Re3-O} = 2.152$ (8), $\text{C-O} = 1.467$ (12), $\text{C-H1} = 1.03$ (10), $\text{C-H2} = 1.07$ (10), $\text{Re-C}(\text{carbonyl})$ (mean) = 1.885, $\text{C-O}(\text{carbonyl})$ (mean) = 1.18.

first stage the attack of the hydride on one apical CO group of the $\text{Re}(\text{CO})_4$ moiety, giving an unstable formyl intermediate (compound **2**), which could acquire some stabi-

(9) The reaction was performed under N_2 , using Schlenk techniques, in THF distilled over Na/benzoketyl, directly into the reaction vessel, previously oven dried. In a typical preparation, 100 mg (0.103 mmol) of the $[\text{NEt}_4]^+$ salt of **1**, in 5 mL of THF, was treated at room temperature with 135 μL of a 1 M solution of $\text{Li}[\text{BH}(\text{s-Bu})_3]$ in THF (0.135 mmol). After ca. 20 min, $[\text{Re}_3\text{H}_3(\text{CH}_2\text{O})(\text{CO})_9][\text{NEt}_4]_2$ was precipitated as a cream solid (105 mg, 0.095 mmol, 92% isolated yield) by addition of an excess of a concentrated aqueous solution of NEt_4Br . Anal. Calcd for $\text{C}_{26}\text{H}_{45}\text{N}_2\text{O}_{10}\text{Re}_3$: C, 28.28; H, 4.11; N, 2.54. Found: C, 28.73; H, 4.21; N, 2.45. Crystals suitable for X-ray analysis were grown at -20°C from THF/*n*-pentane. Spectroscopic data for the anion: IR (THF) $\nu(\text{CO})$ 1982 (s), 1970 (s), 1884 (vs), 1870 (vs) cm^{-1} ; ^1H NMR (THF- d_6) δ 5.75 (t, $J = 2$ Hz, 2 H), -9.19 (t, $J = 2$ Hz, 1 H), -12.74 (q, $J = 2$ Hz, 2 H); ^{13}C NMR (THF- d_6) δ 204.5 (2), 201 (2), 200 (1), 194 (2), 191.4 (2), 52.5 (1).

lization by interaction with the Li^+ cation. A hydride ligand of the $\text{Re}(\mu\text{-H})_2\text{Re}$ moiety (which has a marked H^- polarization⁸) then migrates from the cluster to the formyl carbon atom, giving the CH_2O group, stabilized by the μ -coordination of the oxygen atom on a cluster edge.

Two experiments gave support to this mechanism. (i) On performing the reaction on a sample of **1** selectively enriched (ca. 45%) in ^{13}C at the carbonyls mutually trans of the $\text{Re}(\text{CO})_4$ moiety,¹⁰ the two by far most intense signals in the ^{13}C NMR spectrum were at δ 52.5 (t, $^1J_{\text{CH}} = 134$ Hz) and 200, due to the CH_2O group and to the carbonyl trans to it, respectively. (ii) The formyl intermediate was observed on performing the reaction in a NMR tube at -40 °C:¹¹ a signal at δ 15.3 was detected, together with the hydridic resonances expected for a $[\text{Re}_3(\mu\text{-H})_4(\text{CHO})(\text{CO})_9]^{2-}$ unsaturated species (Figure 1a).

The structure of $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CH}_2\text{O})(\text{CO})_9]^{2-}$ (**3**), as the $[\text{NEt}_4]^+$ salt, has been investigated by X-ray analysis.¹² The dianion (Figure 2) contains an isosceles Re_3 triangle and shows an overall idealized C_s - m symmetry, the mirror plane passing through Re_1 , the C and O atoms of the bridging group, and the middle point of the Re_2 - Re_3 edge. Each rhenium atom bears three terminal carbonyls, and three hydrides, not directly located, are supposed to bridge the three triangular edges on the basis of the values of the M-M bond lengths and of the ligand stereochemistry. Within the CH_2O group the value of the C-O bond distance [1.467 (12) Å] is close to that expected for a single bond, and the value of the Re_1 -C-O angle [106.0 (8)°] and of the other angles at carbon, involving the H atoms and therefore affected by high uncertainties [range 100 (6)-117 (5)°, mean 110°], are indicative of an sp^3 hybridization.

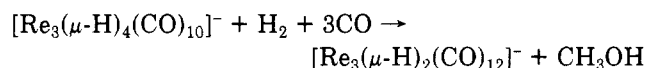
This dihydrogenated CO ligand, clearly stabilized by interaction with different metal centers, confirms the previous suggestions of the intermediate role of a bridging oxymethyl group in the reductive hydrogenation of CO in homogeneous catalytic systems and can also represent a valid model of intermediates on metal surfaces.

Treatment of the oxymethyl complex with stoichiometric $\text{CF}_3\text{SO}_3\text{H}$, at -80 °C, in anhydrous THF, gives almost quantitatively a species identified by NMR analysis as the anion $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CH}_2\text{OH})(\text{CO})_9]^-$ (**4**), in which the hydroxymethyl group maintains the same coordination mode as the parent ligand (see Scheme I).¹³ The resonances of the hydrides (at δ -9.15 (1) and -12.25 (2), values close to those of **3**) indicate in fact a C_s symmetry for the anion. The hydroxylic hydrogen gives a signal at δ 9.78 (which exchanges with D_2O), while the resonances of the CH_2 group are downfield shifted with respect to **3**, due to

the protonation of the oxygen atom [^1H NMR δ 6.27 (2); ^{13}C NMR δ 74 (t, $^1J_{\text{CH}} = 139$ Hz)].

This anion is stable in solution up to -40 °C. At higher temperatures it decomposes to unidentified products. When the temperature is raised under CO flow, however, the main species formed (40-60%) is the anion $[\text{Re}_3(\mu\text{-H})_2(\text{CO})_{12}]^-$, which is also the principal component of the reaction mixtures obtained on performing the protonation reaction directly at room temperature under CO.¹⁴ A possible pathway to this species involves reductive elimination of CH_3OH from an unstable η^1 -bonded hydroxymethyl intermediate. The presence of methanol, in concentration corresponding to that of $[\text{Re}_3(\mu\text{-H})_2(\text{CO})_{12}]^-$, has been ascertained by gas chromatographic analysis.¹⁵ Moreover, when a sample of **3** selectively enriched in ^{13}C at the oxymethyl carbon was used, ^{13}C -enriched methanol was obtained.

The speculation that H_2 could replace the successive action of H^- and H^+ , according to the overall reaction



is, at present, an attractive working hypothesis.

Acknowledgment. We thank the Italian CNR "Progetto strategico: Dinamica molecolare e catalisi" for financial support.

Supplementary Material Available: Crystallographic experimental details and tables of positional and thermal parameters and bond lengths and angles (7 pages); a listing of structure factors (12 pages). Ordering information is given on any current masthead page.

(14) This species, identified spectroscopically, was also isolated by crystallization from the reaction mixture. Churchill, M. R.; Bird, P. H.; Kaesz, H. D.; Bau, R.; Fontal, B. *J. Am. Chem. Soc.* **1968**, *90*, 7135. The only other known hydridic species present in significant concentration (10-30%) was the anion $[\text{Re}_3(\mu\text{-H})_3(\mu\text{-OCH}_3)(\text{CO})_{10}]^-$, identified spectroscopically. Ciani, G.; Sironi, A.; D'Alfonso, G.; Romiti, P.; Freni, M. *J. Organomet. Chem.* **1983**, *254*, C37.

(15) After completion of the reaction, the solvent was removed under vacuum, trapped, and analyzed on a Porapak QS column, at 150 °C.

Synthesis, CO Substitution, and Structure of Tricarbonyl(η^5 -3,4-dimethylpyrrolyl)manganese(I). Evidence for Slippage toward Nitrogen of the N-Heterocycle

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Summary: The compound tricarbonyl(η^5 -3,4-dimethylpyrrolyl)manganese(I) (**2**) and its corresponding 2,5-dimethylpyrrolyl (**3**) compound were synthesized for the first time, and the X-ray structure of **2** and kinetic data support a mechanism which involves $\eta^5 \rightarrow \eta^3$ slippage toward N for CO substitution reactions.

(1) (a) Northwestern University. (b) University of Delaware.

(10) Such a sample was obtained by treating with ^{13}C (ca. 90%) a solution of the anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{NCMe})]^-$, in which a labile nitrile replaced one of the two trans diaxial CO ligands of compound **1**. Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A. *J. Chem. Soc., Dalton Trans.*, in press.

(11) A 25-mg (0.026-mmol) sample of $[\text{Re}_3\text{H}_4(\text{CO})_{10}][\text{NEt}_4]$ in a 5-mm NMR tube, dissolved in THF- d_6 (distilled over Na/benzokethyl), was treated at -80 °C with 40 μL of a 1 M solution of $\text{Li}[\text{BH}(s\text{-Bu})_3]$ in THF. ^1H NMR spectra (-40 °C) showed the appearance of signals at δ 15.3 (1), -7.75 (1), -7.95 (1), and -10.79 (2). When the formyl concentration reached ca. 40% of the starting compound (ca. 2 h), the resonances of compound **3** appeared and increased in intensity.

(12) Crystal data: $\text{C}_{26}\text{H}_{45}\text{N}_5\text{O}_{10}\text{Re}_3$, M , 1104.3; crystal size $0.14 \times 0.33 \times 0.39$ mm; orthorhombic, space group $P2_12_12_1$ (No. 19), with $a = 9.676$ (3), $b = 16.348$ (5), $c = 21.709$ (5) Å; $U = 3433.9$ Å³; $Z = 4$, $D_{\text{calc}} = 2.13$ g cm^{-3} ; $\mu(\text{Mo K}\alpha) = 107.0$ cm^{-1} ; Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å); diffractometer Enraf-Nonius CAD4. The refinements were carried out by full-matrix least-squares, on the basis of 2374 significant [$I > 3\sigma(I)$] unique data. The final values of the agreement indices for the correct enantiomorph are $R = 0.027$ and $R_w = 0.031$.

(13) The only other alternative consistent with the C_s symmetry—namely, protonation on the oxygen atom of the carbonyl trans to the CH_2O group—seems most unlikely for the low shift (less than 2 ppm upfield) undergone by the ^{13}C resonance of this carbonyl.