Sterically induced .eta.2-acyl formation: syntheses and structures of TpMo(CO)2(.eta.2-COR) (R = Me, Ph) and TpMo(CO)3Br (Tp = hydridotrispyrazolylborate)

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NMR (CD_2Cl_2) at δ 2.27 and IR peaks [CH_2Cl_2, $\nu(CO)$] at 2110 and 2050 cm^{-1}. Clear colorless crystals of **2** can be obtained by slowly evaporating CH_2Cl_2/Et_2O solutions of cation **2**. These results are summarized in Scheme I.

Recent work has concentrated on the modeling of carbon monoxide hydrogenation by stoichiometric reduction of carbon monoxide on cationic metal centers. This kind of reaction has resulted in the observation of neutral formyl complexes[2c,d,8] and in the isolation of serveral α-hydroxy complexes such as (η-C_5H_5)Re(NO)(CO)CH_2OH[2b–d] and (η-C_5Me_5)Os(CO)$_2CH_2OH$.[2h] All reported reduction techniques[17] that produce hydroxymethyl complexes from coordinated CO [(1) $NaBH_4$/THF/H_2O;[2h] (2) NaH_2AlEt_2;[2d] (3) $NaBH_3CN$, $MeOH$[2g]] when utilized on [(η-C_5Me_5)Ru(CO)$_3$][BF_4] (**2**) produce (η-C_5Me_5)Ru(CO)$_2CH_2OH$ (**4**) in varying amounts; however, our best results are obtained in methanol with an excess of $NaBH_3CN$ as the reductant. In a typical experiment, [(η-C_5Me_5)Ru(CO)$_3$][BF_4] (0.50 g, 1.2 mmol) is added to a –50 °C solution of $NaBH_3CN$ (0.225 g, 3.6 mmol) in 20 mL of degassed MeOH. The resulting mixture is allowed to warm to room temperature. Then the mixture is stirred for 2 h, the methanol is stripped, and the residue is extracted with pentane (2 × 15 mL). After removal of solvent, a mixture of (η-C_5Me_5)Ru(CO)$_2$H (**3**),[9] (η-C_5Me_5)Ru(CO)$_2CH_2OCH_3$,[10] and (η-C_5Me_5)Ru(CO)$_2CH_2OH$ (**4**) remains. Pure, white, crystalline **4** (0.24 g, 60%) is afforded by recrystallization of the crude material from pentane at –78 °C: IR [C_6H_6, $\nu(CO)$] 1997, 1932 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.96 (d, J = 6 Hz, CH_2, 2 H), 1.68 (s, C_5Me_5, 15 H), 0.88 (t, J = 6 Hz, OH, 1 H).[12] An excess of $NaBH_3CN$ is required since the use of 1 mol equiv of reductant yields (η-C_5Me_5)Ru(CO)$_2CH_2OCH_3$ as the major isolated product. The reason for this behavior is not yet known.[13] Initial work with **4** indicates that it is not as robust as its osmium analogue.[2h] Analytically pure crystals of **4** turn dark after several hours of exposure to air; pentane solutions turn dark after several minutes of exposure to air. IR and ^{1}H NMR show that mixtures containing (η-C_5Me_5)Ru(CO)$_2$H and [(η-C_5Me_5)Ru(CO)$_2$]$_2$ are formed.[15]

That the decomposition is not related to thermal stability is evident because benzene-d_6 solutions of **4**, after being heated at 85 °C for several hours in the absence of air, do not show a significant loss of the α-hydroxy complex. However, at 127 °C (toluene-d_8) **4** undergoes a first-order decomposition which can be followed by ^{1}H NMR (k = 2.9 × 10^{-3} s^{-1}, $\Delta G^{\ddagger}_{400}$ = 28.3 kcal mol^{-1}). This can be compared with (η-C_5Me_5)Os(CO)CH_2OH that decomposes at 174 °C with a first-order rate constant of 9.0 × 10^{-5} s^{-1} ($\Delta G^{\ddagger}_{447}$ = 34.8 kcal mol^{-1}).[2h]

One of the key steps proposed in the formation of C_2 oxygenates with transition-metal catalysts is migration of an α-hydroxymethyl group to coordinate carbon monoxide. It is, therefore, of interest that not one of the isolated α-hydroxymethyl complexes has been reported to undergo carbon monoxide insertion. Complex **4** is thus far not unusual in this aspect. A THF solution of **4** heated to 80 °C under 5000 psi of carbon monoxide for 5 h results only in recovery of the starting compound. More intense thermal, as well as oxidative, conditions are being probed to attempt to induce CO insertion in **4** and other related ruthenium complexes.

One derivative of **4** has been synthesized. Treatment of crude reaction mixtures containing **4** with *N*,*N*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) results, after a normal workup, in the isolation of (η-C_5Me_5)Ru(CO)$_2CH_2OSiMe_3$ (**5**) as colorless air- and water-sensitive crystals.[16] Complex **5** exhibits ^{1}H NMR signals (C_6D_6) at δ 4.87 (s, CH_2, 2 H), 1.65 (s, C_5Me_5, 15 H), and 0.21 (s, $SiMe_3$, 9 H) and IR [CH_2Cl_2, $\nu(CO)$] at 1995 and 1935 cm^{-1}. This is a convenient derivative because it can be easily purified by column chromatography; unfortunately, we have been unable to regenerate **4** from the trimethylsilyl complex. Treatment of **5** with either tetrabutylammonium fluoride or the milder ammonium bifluoride[2a] results only in isolation of (η-C_5Me_5)Ru(CO)$_2$H in high yield.

In summary, several derivatives of the (η-C_5Me_5)Ru-(CO)$_2$ group including the hydroxymethyl complex (η-C_5Me_5)Ru(CO)$_2CH_2OH$, which is obtained by reduction of [(η-C_5Me_5)Ru(CO)$_3$][BF_4], have been isolated. Further studies are directed toward modeling carbon monoxide hydrogenation with (pentamethylcyclopentadienyl)ruthenium dicarbonyl complexes.[13]

(7) Anal. Calcd for $C_{13}H_{15}O_3RuBF_4$: C, 38.28; H, 3.68. Found: C, 38.40; H, 3.68.

(8) Wilson, T.; Lin, G.; Wong, W.; Kiel, W.; Wong, V.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141–152 and references therein.

(9) Hydride complex 3 is isolated as very air-sensitive colorless crystals and has thus far been identified by IR and NMR only: IR (C_6H_6) 2000, 1941 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.72 (s, C_5Me_5), –10.20 (s, Ru–H). 3 readily decomposes to [(η-C_5Me_5)Ru(CO)$_2$]$_2$ when exposed to air or to light.

(10) This compound is identified by the similarity of its IR and ^{1}H NMR to (η-C_5H_5)Ru(CO)$_2CH_2OCH_3$.[11] (η-C_5Me_5)Ru(CO)$_2CH_2OCH_3$-(CH_2Cl_2): IR 2000, 1935 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.60 (s, CH_2), 3.28 (s, CH_3), 1.65 (s, C_5Me_5).

(11) Moss, J. R.; Pelling, S. *J. Organomet. Chem.* **1982**, *236*, 221–227.

(12) Anal. Calcd for $C_{13}H_{18}O_3Ru$: C, 48.23; H, 5.56. Found: C, 48.34; H, 5.60.

(13) This behavior is possibly related to the chemistry of the assumed intermediate formyl complex (η-C_5Me_5)Ru(CO)$_2$(CHO). We have recently generated this complex by interaction of [Ph_3PCuH]$_6$[14] with 2. The formyl complex: IR (THF) 2015, 1964, 1645 cm^{-1}; ^{1}H NMR (C_6D_6) δ 14.0 (s, CHO), 1.5 (s, C_5Me_5). Surprisingly this complex only very slowly decomposes to 3 at room temperature in solution. The chemistry of this complex is being explored; details will be reported later; Sumner, C.; Nelson, G., in preparation.

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(15) Photolysis of 4 in benzene-d_6 also produces mixtures of 3 and [(η-C_5Me_5)Ru(CO)$_2$]$_2$. This reaction is similar to that observed with the osmium analogue[2h] except no [(η-C_5Me_5)Os(CO)$_2$]$_2$ is observed in that case, probably because (η-C_5Me_5)Os(CO)$_2$H is more stable than 3.

(16) Complex 5 is usually obtained as an oil that slowly crystallizes when stored at 7 °C. Anal. Calcd for $C_{16}H_{26}O_3RuSi$: C, 48.54; H, 6.58. Found: C, 48.58; H, 6.54.

(17) After this manuscript was submitted, a copy of the journal containing Astruc's report of (μ-C_5Me_5)Fe(CO)$_2CH_2OH$ was received in our library: Lapinte, C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1983**, 430.

Sterically Induced η^2-Acyl Formation: Syntheses and Structures of TpMo(CO)$_2$(η^2-COR) (R = Me, Ph) and TpMo(CO)$_3$Br (Tp = Hydridotris(pyrazolyl)borate)

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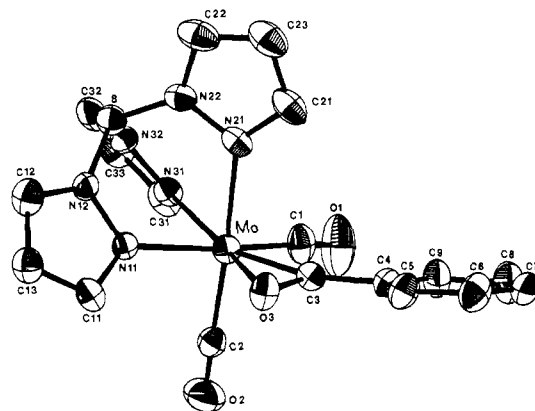*Department of Chemistry, The University of Michigan Ann Arbor, Michigan 48109*

Summary: The anion TpMo(CO)$_3$$^-$ (Tp = hydridotris(pyrazolyl)borate) reacts with MeI or Me_3OBF_4 or with

PhCOBr to give the η^2-acyl complexes TpMo(CO)$_2(\eta^2$-COR) (R = Me, Ph). These facile alkyl migration and decarbonylation reactions are ascribed in part to the steric demands of the Tp ligand, which are evident in the structure of TpMo(CO)$_3$Br, and in part to the electronic tendency of the Tp ligand to favor an octahedral coordination geometry.

η^2-Acyl complexes have been proposed as surface intermediates on catalysts in the reductive homologation of CO,[1] and this has led to increased activity in preparation and characterization of discrete η^2-acyl complexes. Most η^2-acyl complexes prepared to date have utilized an alkyl migration to coordinated CO promoted by the high oxophilicity[2] of group 4 or group 5 metals.[3-7] External Lewis acids have been used to promote the alkyl migration in the case of the less oxophilic late transition metals,[8-10] and metal oxidation induced alkyl to acyl migratory insertions have been reported recently.[11,12]

We wish to report here that the hydridotris(pyrazolyl)borate (Tp) ligand induces extremely facile decarbonylations and migratory insertions to give (η^2-acyl)molybdenum complexes. Prior to our beginning this work, only one η^2-acyl complex of Mo was known.[13] During the course of the work, Desmond et al.[14] reported the structure of the reaction product of Tp'Mo(CO)$_3^-$ (Tp' = hydridotris(3,5-dimethyl-1-pyrazolyl)borate) and aryl diazonium salts and showed these to be η^2-aroyl dicarbonyl complexes Tp'Mo(CO)$_2(\eta^2$-COAr). The work of Desmond et al. clearly shows the intermediacy of hydrocarbon radicals produced by a redox reaction between the Tp'Mo(CO)$_3^-$ anion and the species Ar$_2$I$^+$ or ArN$_2^+$. We wish to report here the formation of η^2-acyl complexes from TpMo(CO)$_3^-$ and RX via reactions that show no evidence for the intermediacy of radicals and to put forth some conclusions that may have general applicability in the synthesis of η^2-acyl complexes.
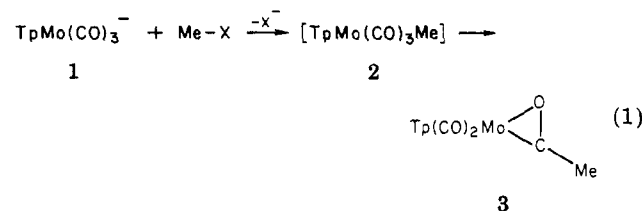
Trofimenko[15] originally reported that the reaction of TpMo(CO)$_3^-$ (1) and methyl iodide gave the methyl tricarbonyl complex TpMo(CO)$_3$Me (2). This brick-red product exhibits two sharp carbonyl bands at 1983 and 1856 cm^{-1}, a pattern not characteristic of C_s symmetry M(CO)$_3$X groups which typically have three (2A' + A'') ν_{CO} bands. Furthermore, we observed a very weak band at 1570 cm^{-1}, not present in other TpMo(CO)$_3$X (X = H, Br, I) complexes (this band was not reported previously).
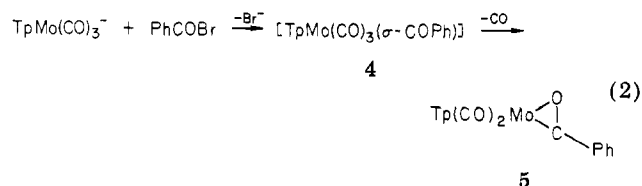

Figure 1. ORTEP plot for TpMo(CO)$_2(\eta^2$-COPh) (5). The η^2-acetyl complex 3 has essentially the same structure. Some selected parameters for 5 and 3 (in order) are as follows: Mo–C$_{acyl}$ = 2.021 (5), 2.022 (9) Å; Mo–O$_{acyl}$ 2.189 (3), 2.224 (6) Å; RC–O = 1.224 (6), 1.225 (11) Å; Mo–N$_{av}$ = 2.21 ± 0.03, 2.20 ± 0.02 Å; M–CO$_{av}$ = 1.99 ● 0.04, 1.96 ± 0.03 Å.

An X-ray structure[16] of this product revealed that it is in fact the η^2-acetyl complex TpMo(CO)$_2(\eta^2$-COMe) (3). That this structure is maintained in solution is shown by the gated ^{13}C NMR spectrum of 3: the two terminal carbonyls give a singlet at δ 236, the acyl carbon signal is a quartet ($^2J_{CH}$ = 6 Hz) at δ 265, and the methyl carbon resonates at δ 28 ($^1J_{CH}$ = 131 Hz).

In an effort to detect an intermediate σ-methyl complex, we allowed TpMo(CO)$_3^-$ to react with (Me$_3$O)(BF$_4$). At −78 °C, there was no apparent reaction, but as the solution warmed gradually to room temperature, the η^2-acyl complex 3 formed without producing detectable quantities of the σ-methyl complex 2. Thus, if 2 is formed at all, it rearranges as rapidly as it is formed to complex 3 (eq 1).

$$\text{TpMo(CO)}_3^- + \text{Me-X} \xrightarrow{-X^-} [\text{TpMo(CO)}_3\text{Me}] \longrightarrow$$

$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{2}$$

$$\text{Tp(CO)}_2\text{Mo} \begin{array}{c} \diagup O \\ \diagdown C \diagdown Me \end{array} \qquad (1)$$

$$\mathbf{3}$$

The reaction of TpMo(CO)$_3^-$ with benzoyl bromide at room temperature in acetonitrile or CH$_2$Cl$_2$ also follows an unusual course. The product, as determined spectroscopically (δ(C(acyl)) 254, δ(C(carbonyl)) 239) and by X-ray analysis[17] (Figure 1), is the η^2-benzoyl complex 5 (eq 2).

$$\text{TpMo(CO)}_3^- + \text{PhCOBr} \xrightarrow{-Br^-} [\text{TpMo(CO)}_3(\sigma\text{-COPh})] \xrightarrow{-CO}$$

$$\mathbf{4}$$

$$\text{Tp(CO)}_2\text{Mo} \begin{array}{c} \diagup O \\ \diagdown C \diagdown Ph \end{array} \qquad (2)$$

$$\mathbf{5}$$
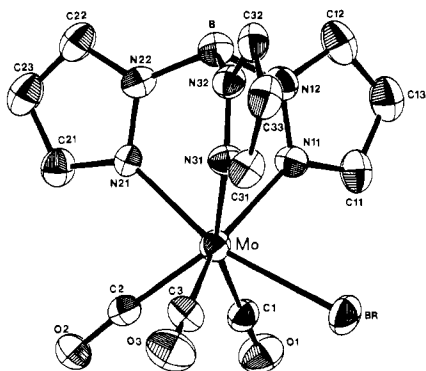
Such facile alkyl migrations and decarbonylations as rep-

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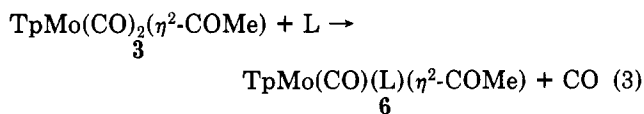
(17) The structure of 5 was refined with anisotropic temperature factors for all non-hydrogen atoms using 2360 reflections with $I \geq 3\sigma(I)$: R = 0.038, R_w = 0.063, a = 9.405 (2) Å, b = 12.504 (3) Å, c = 9.025 (2) Å, α = 114.59 (2)°, β = 92.85 (2)°, γ = 95.45 (2)°, V = 9560 (4) Å^3, Z = 2, space group $P\bar{1}$ (No. 2).

Figure 2. ORTEP plot for TpMo(CO)$_3$Br: Mo–C1 = 1.989 (7) Å, Mo–C2 = 1.957 (7) Å, Mo–C3 = 2.000 (8) Å, Mo–Br = 2.6546 (9) Å, Mo–N = 2.213 (5)–2.231 (5) Å; Br–Mo–C1 = 76.0 (2)°, Br–Mo–C2 = 118.5 (2)°, Br–Mo–C3 = 73.2 (2)°, C1–Mo–C2 = 71.7 (3)°, C1–Mo–C3 = 107.0 (3)°, C2–Mo–C3 = 68.5 (3)°.

resented in eq 1 and 2 are unprecedented in CpMo(CO)$_3$R chemistry.[18,19]

The η^2-acetyl complex **3** readily forms adducts with phosphines and phosphites (eq 3). The crystal structure

$$\text{TpMo(CO)}_2(\eta^2\text{-COMe}) + \text{L} \rightarrow$$
$$\mathbf{3}$$

$$\text{TpMo(CO)(L)}(\eta^2\text{-COMe}) + \text{CO} \quad (3)$$
$$\mathbf{6}$$

of the adduct **7** (L = (MeO)$_3$P) has been determined.[20] The Mo–C(acyl) and Mo–O(acyl) distances in **7** are each about 0.02 Å *shorter* than in **3** which suggests that backbonding from Mo to the π^* orbital of the η^2-COR moiety is an important factor in the bonding.

Since it is unlikely that a Mo–O bond in **3** or **5** is considerably stronger than this bond in the unknown CpMo(CO)$_2$(η^2-COMe), we are left with the question: why is M(η^2-COR) more stable than M(CO)(σ-R) in the TpMo complexes whereas the reverse stability is evident for the corresponding CpMo complexes?

We suggest that the η^2-acyl isomers are stabilized in the Tp complexes by a combination of steric and electronic effects that strongly favor octahedral coordination in TpMo complexes. The cone angle of the Tp ligand is near 180°, discouraging high coordination numbers, and the localized N$_3$–Mo bonding in the TpMo fragment "hybridizes" the fragment MO's into an octahedral array more efficiently than does the diffuse C$_5$–Mo bonding in the CpMo fragment.[21] If the η^2-COR group is considered to occupy one coordination site, then an isomerization, e.g., **2** → **3** or **4** → **5**, lowers the coordination number from seven to six, relieves steric congestion, and allows for a quasi-octahedral structure about the metal.[22]

The importance of steric factors in facilitating decarbonylation finds support in the facile formation of the π-allyl complexes XMo(CO)$_2$(η^3-C$_3$H$_5$) (X = indenyl,[23] Tp[15,24]) from XMo(CO)$_3^-$ and allyl halides. In contrast, CpMo(CO)$_3^-$ with allyl chloride gives the σ-allyl complex that is decarbonylated to the π-allyl dicarbonyl only under UV photolysis.[25]

In order to obtain a benchmark for a seven-coordinate TpMo complex, we have determined the structure of the previously unreported bromide TpMo(CO)$_3$Br (**6**).[26] The ligands are arranged in a version of the four-legged piano stool geometry (Figure 2). In a vertical projection, the Br lies between two pyrazolyl rings which causes the trans-carbonyl to eclipse the third pyrazolyl ring. The net effect is to bend the trans-carbonyl down (Br–Mo–CO$_t$ = 118.5 (2)° vs. ~132° in CpMo(CO)$_3$X complexes)[27] and generally to compress the "legs" of the piano stool. Such compression in a TpMo(CO)$_3$R complex would force the alkyl and cis-CO groups into close proximity, facilitating alkyl migration to form the η^2-acyl structure.

The use of sterically demanding, σ-bonded ligands to facilitate the formation of η^2-acyl or η^2-formyl complexes may have general synthetic applicability and investigations on this aspect are in progress.

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(26) The structure of TpMo(CO)$_3$Br was refined with anisotropic temperature factors for all non-hydrogen atoms to final R values of R = 0.036 and R_w = 0.058 using 1902 reflections with $I \geq 3\sigma(I)$: a = 8.305 (1) Å, b = 12.032 (1) Å, c = 8.570 (2) Å, α = 104.39 (1)°, β = 93.42 (1)°, γ = 92.03 (1)°, V = 826.9 (2) Å^3, Z = 2, space group $P\bar{1}$ (No. 2).

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(21) To our knowledge, the only seven-coordinate TpMo(CO)$_3$X complexes known are TpMo(CO)$_3$H,[15] the new halides TpMo(CO)$_3$X (X = Br, I), and the related TpMo(CO)$_2$(CS)I: Greaves, W. W.; Angelici, R. J. *J. Organomet. Chem.* **1980**, *191*, 49.

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A New Route to the Synthesis of Highly Alkylated Cyclic Chlorophosphazenes

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Summary: The reactions of hexachlorocyclotriphosphazene with trimethylaluminum have been examined. These reactions lead to good yields of a new series