in solution[5] is most likely increased in comparison to the gas phase by higher solvation energies for the leaving group (I^-) compared to the larger Fp^-. Available thermodynamic data for $CH_3SO_3CF_3$ are inadequate to evaluate thermodynamics for reactions involving that substrate.

Further evaluation of thermochemistry and mechanisms in these organometallic reactions will be possible when further data for electron affinities of organometallic radicals and reverse reactions (i.e., $X^- + RML_x$) become available. Such gas-phase experiments can also provide data on fundamental quantities such as metal–carbon bond strengths for comparison to the expanding literature for solvated reactants.[24] Studies directed toward these goals are underway in our laboratories.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (D.E.R.). Additional support was also provided by Research Corp. (D.E.R.). Helpful discussions with J. Boncella are gratefully acknowledged.

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Synthesis of a Molybdenum-Substituted Furan from $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-Na^+$ and Epibromohydrin in the Presence of Triphenylphosphine: *trans*-$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)\text{-}2\text{-furan}]$

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Received March 2, 1987

Summary: The reaction between $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ Na^+ and epibromohydrin ($BrCH_2CHOCH_2$) in the presence of an excess of triphenylphosphine leads to the isolation of *trans*-$(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)$-2-furan. In the absence of phosphine a σ–π allyl ester complex is formed, $(\eta^5\text{-}C_5H_5)\overline{Mo(CO)_2{-}CO{-}O{-}CH_2CH{=}CH_2}$. The structure of the furan complex is provided along with a suggested mechanism of formation.

The chemistry of furans plays a pivotal role in modern heterocyclic chemistry, and this chemistry, along with the various modes of synthesis of these compounds have recently been reviewed.[1]

We wish to report the first example of the use of the simple molecule carbon monoxide as a reagent in the one-step synthesis of furans, namely, by coupling a coordinated CO with epibromohydrin. The reaction (eq 1) occurs in the coordination sphere of a molybdenum complex.

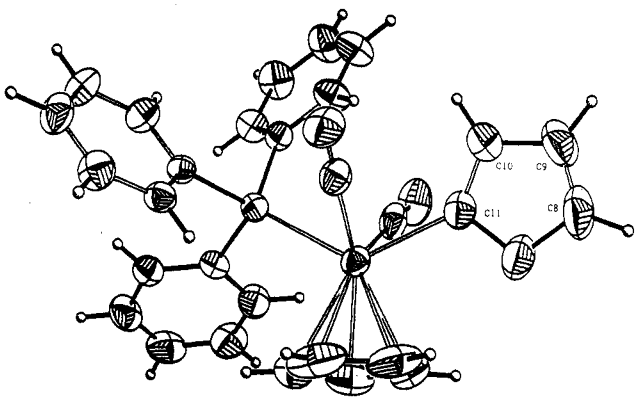
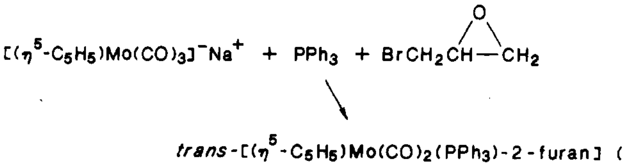


Figure 1. Crystal structure of $C_{29}H_{23}O_3PMo$: space group $P\bar{1}$ with a = 9.150 (5) Å, b = 12.028 (5) Å, c = 12.716 (8) Å, α = 112.67 (3) °, β = 100.97 (3) °, γ = 98.83 (8) °, and Z = 2. The data were collected on a Nicolet R3M four-circle diffractometer, and refinement using SHELXTL gave a final R of 0.0348. Selected bond lengths (Å): Mo–C_{11} = 2.233 (4), C_{10}–C_{11} = 1.331 (7), C_9–C_8 = 1.298 (9), C_{10}–C_9 = 1.414 (7).



$$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-Na^+ + PPh_3 + BrCH_2\underset{}{CH}\overset{O}{—}CH_2 \longrightarrow trans\text{-}[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)\text{-}2\text{-furan}] \quad (1)$$

In a typical reaction, 1.0 g (3.8 mmol) of $Mo(CO)_6$ was heated at reflux in 100 mL of THF with an equivalent of NaC_5H_5 for 24 h. After this time period, infrared monitoring indicated that a high yield of the molybdenum carbonylate had formed.[2] To this solution at room temperature was added initially 1.4 g (5.3 mmol) of triphenylphosphine (infrared monitoring showed that no chemical reaction took place at this stage) and then 3.0 g (17 mmol) of epibromohydrin. The resulting mixture was stirred for 12 h during which period the solution slowly changed color from clear yellow to brown-orange. After removal of the solvent a waxy solid was obtained from which unreacted $Mo(CO)_6$ was removed by sublimation at 45 °C and 10^{-1} mmHg. The residue was dissolved in the minimum of a 30:70 methylene chloride/hexane mixture and placed upon a neutral alumina column, 20 × 2.5 cm. Initial elution with hexane removed any residual phosphine and $Mo(CO)_6$, and subsequent elution with a 70:30 methylene chloride/hexane mixture led to the slow elution of a yellow band of the title complex (0.4 g, 0.7 mmol, 20%). The product was recrystallized from the same solvent mixture.

A single crystal X-ray structural determination was performed, and the resulting structure is illustrated in Figure 1 together with some of the pertinent bond lengths. The spectral data of the complex are in accord with the structure.[3]

The mechanism of this reaction appears to be related to the acid-catalyzed transformation of epoxide acetates

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(3) The initial structure solution, with the furan O atom regarded as C, gave an isotropic thermal parameter of 0.15, which was reduced to 0.12 upon changing to O, clearly distinguishing the unique O atom. No intramolecular H-bonding interactions were observed in the structure: orange-red solid; mp 178 °C dec; IR (CH_2Cl_2) ν(CO) 1955 (m), 1870 (s) cm^{-1}; ^{13}C NMR (ppm, C_6D_6) 92.4 (C_5H_5), 111.7, 148.6, 126.7 128.3, 128.7, 130.3, 133.6, 133.8, 148.6 (furan, phenyl), 199.3 (CO); ^1H NMR (ppm, C_6D_6) 4.69 (d, J = 0.7 Hz, C_5H_5), 7.12, 7.61 (C_6H_5), 6.70, 7.23, 7.30, 8.13 (m, C_4H_3O). Anal. Found (Calcd): C, 64.2 (63.8); H, 4.46 (4.20).

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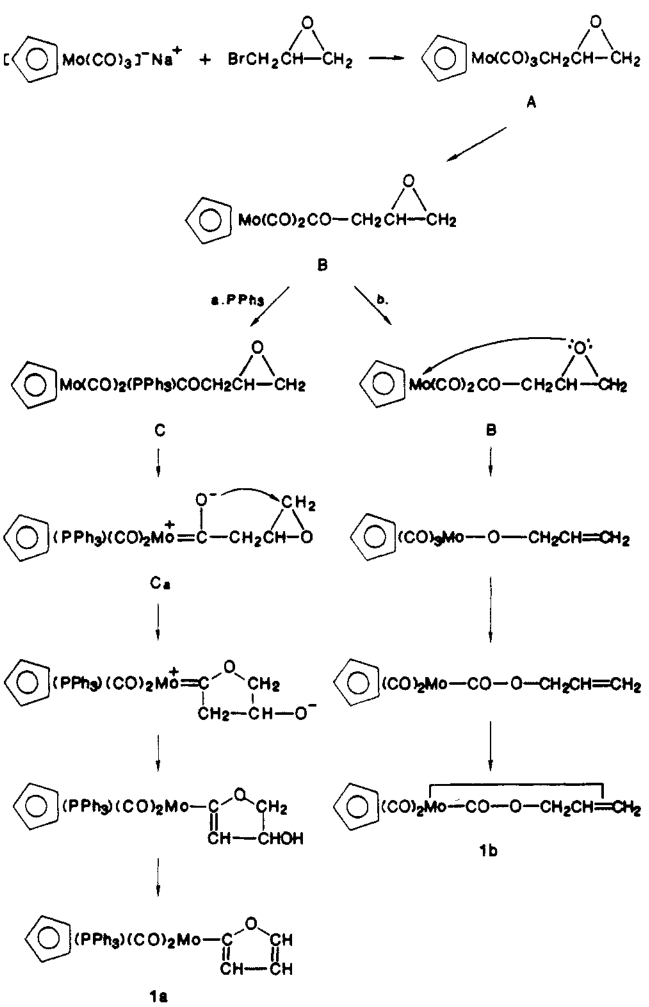
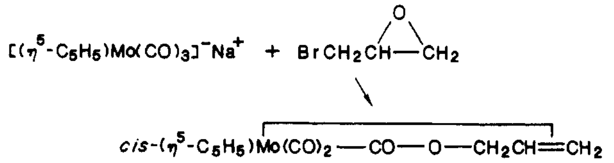
Scheme I



into tetrahydrofurans.[4] In this process an intramolecular attack by the C=O group of the acetate upon the epoxide ring is the key step, and the mechanism we suggest for the complex formation is outlined in Scheme Ia. This involves the initial formation of a σ-bonded epoxymethyl complex A, followed by migratory CO insertion to produce the 16e coordinatively unsaturated complex B. This may be trapped by the phosphine to form C which contains a very nucleophilic acyl group by virtue of the contributing resonance structure C_a. We suggest this group participates in an intramolecular attack to yield the ultimately isolated furan complex. A previous example of an intramolecular attack by a metal acyl group due to its nucleophilicity is provided by the isolation of a cyclic cationic carbene complex upon treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2)_3Br$ with PPh_3.[5]

Support for the proposed mechanism was obtained from the reaction of the molybdenum carbonylate and epibromohydrin in the absence of triphenylphosphine (eq 2). In this reaction no furan ring was formed and a different intramolecular rearrangement involving CO incorporation took place.

This result shows the importance of trapping the 16e complex B by PPh_3 (Scheme Ia). In the absence of this ligand, the O atom of the epoxide interacts with the electron-deficient Mo atom, probably to form a transient allyloxy complex which upon rapid migratory CO insertion



(2)

will form the isolated σ–π complex (Scheme Ib).[6] If triphenylphosphine is added to a reaction mixture of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-Na^+$ and epibromohydrin, only the σ–π complex is isolated. Furthermore, thermal (refluxing THF solution) or photochemical treatment of the σ–π complex with PPh_3 leads to the isolation of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(PPh_3)]$.[7] These reactions preclude the intermediacy of the σ–π complex in the formation of the furan complex.

Extension of this new chemistry to oxiranes, episulfides, and related ring systems along with formation of variously substituted furans is currently in progress.

Acknowledgment. Support of this research by the Robert A. Welch Foundation, Houston, TX, and by a Texas Advanced Technology Research Award is gratefully acknowledged. Financial support and leave of absence to R.C.-O. from the Instituto de Quimica, UNAM, are also acknowledged.

Supplementary Material Available: Tables of crystal data, atom coordinates, bond lengths and angles, anisotropic temperature factors, and hydrogen coordinates (6 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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(6) The reaction was performed on the same scale, in the same manner, as that in the presence of triphenylphosphine to yield 0.85g (2.8 mmol, 74%) of the σ–π complex. Elution of the column with a 40:60 hexane/CH_2Cl_2 solvent mixture removed any $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ formed, and the product was eluted with CH_2Cl_2: orange solid; mp 95 °C darkens, 112–113 °C dec. Anal. Found (Calcd): C, 44.1 (43.7); H, 3.45 (3.31). IR: ν(CO) (CH_2Cl_2), 2012 (s), 1949 (s, bd), 1646 (m) cm^{-1}. NMR (ppm, C_6D_6): ^{13}C, 235.2 (CO), 228.4 (CO), 215.3 (Mo-CO-O), 93.1 (C_5H_5), 79.3 (CH_2=CH), 65.7 (CH_2=CH), 31.8 (CH_2); ^1H, 2.14 (d, J = 3.8 Hz, Mo-CO-O-CH_aH_b), 2.36 (d, J = 6.5 Hz, Mo-CO-O-CH_aH_b), 3.89 (m, CH=CH_aH_b), 4.41 (d, J = 5.9 Hz, CH=CH_aH_b), 4.84 (C_5H_5).

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Reaction of the (Trimethylsilyl)diazomethane Anion with Metal Complexes: Synthesis and X-ray Study of Iodomethyltris(trimethylphosphine)rhodium(III) (Trimethylsilyl)diazomethane, $RhICH_3(PMe_3)_3\{C(N_2)SiMe_3\}$

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Received March 3, 1987

Summary: $LiC(N_2)SiMe_3$ reacts with $Rh(PMe_3)_4Cl$ at low temperature to give $Rh\{C(N_2)SiMe_3\}(PMe_3)_4$ (**1**) in high yield. This complex adds MeI oxidatively in benzene to give orange $Rh\{C(N_2)SiMe_3\}MeI(PMe_3)_3\cdot C_6H_6$ (**2**). **2** crystallizes in the space group *Pnma*, with a = 9.352 (1) Å, b = 10.916 (2) Å, c = 29.358 (5) Å, Z = 4, and V = 2997 Å^3. Controlled thermolysis generates several rhodium species, of which $RhI(Me)_2(PMe_3)_3$ has been isolated as the final product.

0276-7333/87/2306-1822$01.50/0