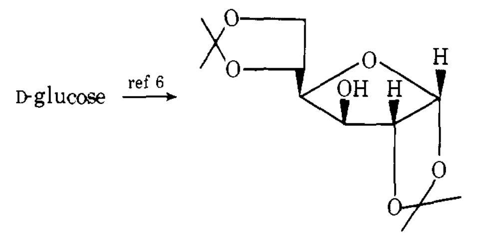
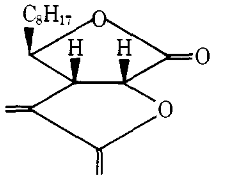


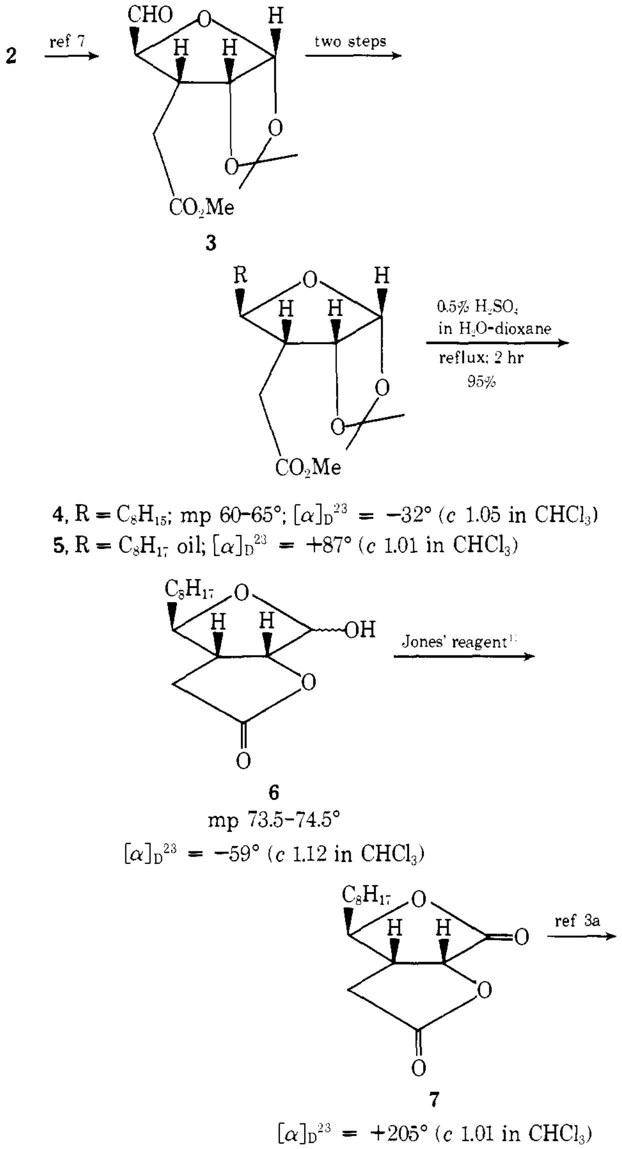
2

"diacetone glucose"



1

Scheme I



2 → 3

4, R = C_8H_{15}; mp 60-65°; $[\alpha]_D^{23} = -32°$ (c 1.05 in $CHCl_3$)
5, R = C_8H_{17} oil; $[\alpha]_D^{23} = +87°$ (c 1.01 in $CHCl_3$)

6
mp 73.5-74.5°
$[\alpha]_D^{23} = -59°$ (c 1.12 in $CHCl_3$)

7
$[\alpha]_D^{23} = +205°$ (c 1.01 in $CHCl_3$)

sequence in Scheme I would have yielded isoavenaciolide, contrary to the experimental results.

Hydrogenation of **4** in ethanol over 10% Pd-C afforded **5** (87%) as a noncrystalline material (*m/e* 328 (M), 327 (M − 1). Treatment with acid caused simultaneous removal of the acetonide and lactonization to the hemiacetal **6** in 95% yield (Anal. ($C_{14}H_{24}O_4$) C, H). Oxidation[11] of **6** afforded the bislactone **7** (77%) which had been obtained previously in racemic form by Parker and Johnson, in the first synthesis of *dl* avenaciolide.[3a] Accordingly **7** was transformed to **1** in 50% yield as described by these workers.[3a] The resulting material had a ^{1}H NMR spectrum identical with a sample of the *dl* mixture kindly supplied by Dr. Johnson.[3a]

For this preparation of **1**, mp 50-51° and $[\alpha]^{29.5}_D = -41.08°$ (*c* 0.274 in EtOH).[9] (Anal. ($C_{15}H_{22}O_4$) C, H). For naturally occuring avenaciolide[4], mp 49-50°, 54-56° and $[\alpha]^{26.5}_D = -41.6°$ (*c* 1.27 in EtOH). For *dl*-avenaciolide,[3] mp 54-57°.

The foregoing therefore indicates that the chirality of naturally occuring avenaciolide is (3a*R*, 4*R*, 6a*R*) and not (3a*S*, 4*S*, 6a*S*) as previously suggested.[4,5] In addition configurational assignments of this entire series of fungicides are also probably incorrect, since these had been related to avenaciolide.[10] Syntheses of these analogs are underway and will be reported in due course.

Acknowledgments. We are indebted to the National Research Council of Canada and Bristol Laboratories (Syracuse) for financial assistance and to Professor Francis Johnson and our colleagues Drs. Mark Yunker and Steve Tam for helpful discussions.

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Robert Charles Anderson, Bert Fraser-Reid*
Department of Chemistry, University of Waterloo
Waterloo, Ontario, Canada

Received March 21, 1975

Molybdenum(0) and Tungsten(0) Interactions with Olefins. Direct Observation of Reversible Hydrogen Exchange Processes by Nuclear Magnetic Resonance

Sir:

Molybdenum and tungsten species are known to catalyze several olefin reactions (e.g., metathesis) but little mechanistic data are available. We present here some studies on the interaction of olefins with zerovalent complexes of these metals and the observation of hydrogen transfer processes central to several catalytic processes.

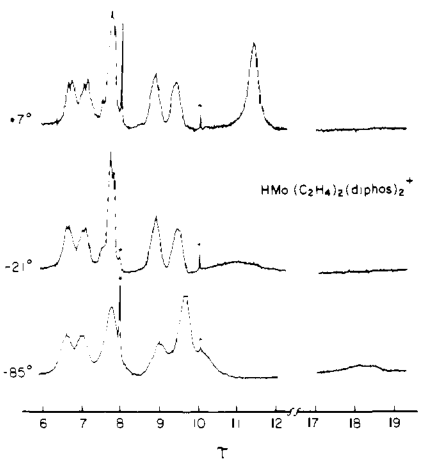
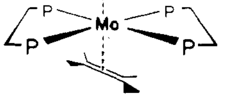


Figure 1. Variable temperature ^1H NMR spectrum at 100 MHz of HMo$(C_2H_4)_2$(diphos)$_2$ in CD_2Cl_2 (* is impurity).

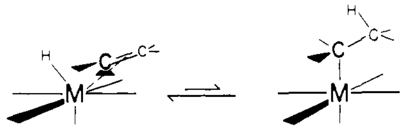
trans-Mo$(N_2)_2$(diphos)$_2$ (diphos = $Ph_2PCH_2CH_2PPh_2$)[1] when heated with C_2H_4 (1 atm) in benzene at 55° for 2 hours yields orange crystals of Mo$(C_2H_4)_2$(diphos)$_2$[2,3] (**1**). The tungsten analog W$(C_2H_4)_2$(diphos)$_2$ was best prepared by reduction (Na–Hg) in THF of WCl_4(diphos) in presence of diphos (1 mol) and excess C_2H_4.

The ^1H NMR of **1** in C_6D_6 at 25° shows resonances of coordinated ethylene at τ 9.10 and 9.35 (broad, 4 H:4 H). At 98°, these two resonances coalesce and form a quintet (J_{P-H} = 5 Hz). The corresponding ^{31}P decoupled spectrum at 25° (although poorly resolved) is consistent with an AA′BB′ pattern which at 98° yields a sharp singlet. The ^{31}P spectrum (^1H decoupled) is a singlet at −62.1 ppm (relative to 85% H_3PO_4 external reference) in toluene from 25 to −85°. On this basis and chemical observations,[4] a trans octahedral structure is assigned as shown below. Presumably



the trans stereochemical arrangement prevents metallocycle formation as found for Ir(I)[5] and Ti(II).[6] Interestingly, the ethylene molecules are staggered with respect to one another and eclipse the trans P–Mo–P vectors. Rapid rotation about the metal–olefin bond occurs at 98° with an estimated barrier of 15.3 kcal mol^{-1}.

Protonation of **1** with CF_3COOH (1 mol) in C_6H_6 at 5° yields HMo$(C_2H_4)_2$(diphos)$_2^+CF_3COO^-$ as orange-brown crystals. The ^1H NMR in CD_2Cl_2 at 7° (Figure 1) shows inter alia vinylic resonances at τ 8.78 and 9.32 (relative intensities 2 H:2 H) and broad singlet at τ 11.33 (5 H). On cooling the solution, the resonance at τ 11.33 broadens and at −85°, new resonances grow in at ca. τ 9.62 and 10.04 (total integrated intensity of vinylic resonances now 8 H), and a broad unresolved resonance[7] appears at τ 18.23 (1 H). Clearly this latter resonance results from a Mo–H interaction, which at +7° exchanges rapidly and reversibly with *half* of the bound ethylene protons. This is the first case[8] where the *insertion–deinsertion process, fundamental to many catalytic mechanisms, can be observed directly.* The ethyl derivative is presumably the intermediate, viz.



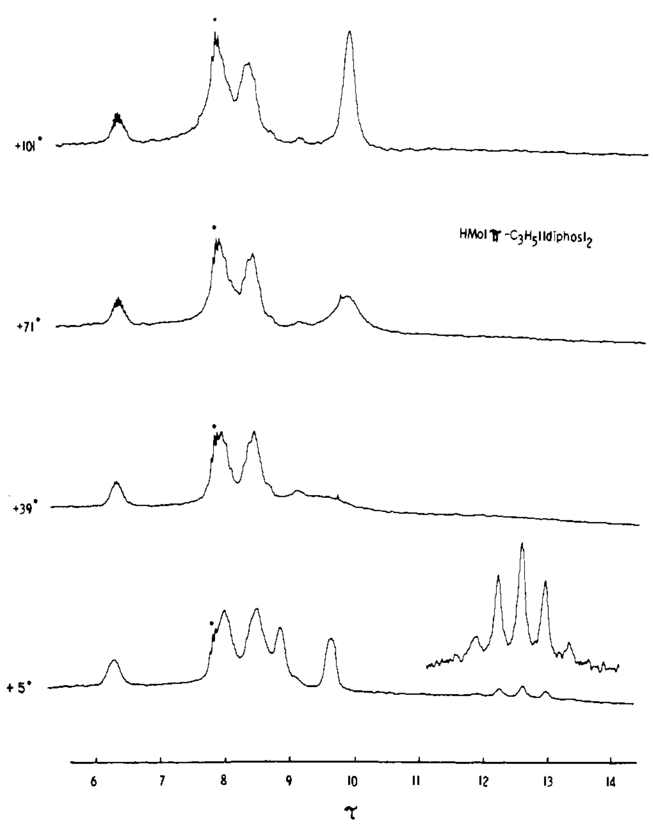
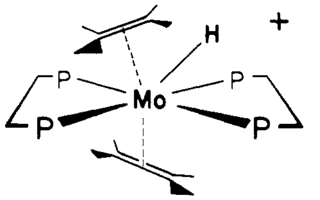
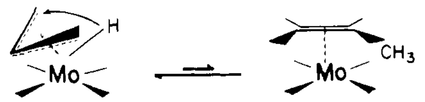


Figure 2. Variable temperature ^1H NMR spectrum at 100 MHz of HMo(π-C_3H_5)(diphos)$_2$ (* is impurity).

Protonation occurs by capping an octahedral face (cf. HTa(CO)$(Me_2PCH_2CH_2PMe_2)_2$)[9] and exchange occurs only with the proximate ethylene. In agreement with this, both the protonation–deprotonation process and intramolecular rearrangement[7,9] are found to be slower than the hydrogen exchange process.



A different interaction occurs when propylene is used. Treatment of $MoCl_3(THF)_3$[1a] with Na–Hg in THF under propylene (1 atm) and in the presence of diphos (2 mol) yields an orange complex. Analytical, chemical, and spectroscopic (vide supra) data show this to be the π-allyl-hydride complex, HMo(π-C_3H_5)(diphos)$_2$. This is very stable,[10] decomposing only at >110° to yield propylene. The ^1H NMR (Figure 2) at +5° in benzene-d_6 shows the metal-hydride resonance as a quintet (J_{P-H} = 37 Hz) at τ 12.60 and π-C_3H_5 signals are at τ 9.62, 8.84, and 6.28 (2 H:2 H:1 H). On raising the temperature, the resonances at τ 12.60, 9.62, and 8.84 collapse (but *not* that at τ 6.28), and a signal at the average position (τ 10.12; 5 H) appears at +101°. Here we are observing exchange of the metal hydride with the terminal hydrogens of the π-allyl group—with the propylene complex presumed as intermediate. No exchange of the unique proton of the allyl group would occur, as is observed.



Hence this provides *the direct observation of the π-allyl-hydride exchange mechanism* proposed for 1,3 hydride shifts found in many metal catalyzed olefin reactions.

Acknowledgments. This work has been supported by the U.S. Army Research Office and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(4) Pyrolysis (>100°) or reaction of **1** with CO, N_2, or TCNE yielded only C_2H_4; with Br_2, C_2H_4 and $C_2H_4Br_2$ were produced. In reactions at 25° with excess HCl or CF_3COOH both C_2H_6 and C_2H_4 are evolved.

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(7) The tungsten analog behaves similarly but the hydride resonance is clearly resolved as a triplet of triplets ($J_{P_1\text{-}H}$ = 92 Hz, $J_{P_2\text{-}H}$ = 17 Hz) at −30°. Rapid rearrangement is thus not occurring (see also ref 9).

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J. W. Byrne, H. U. Blaser, J. A. Osborn*

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received April 2, 1975

Electron-Transfer Reactions in Metalloporphyrins

Sir:

This report describes some experiments concerning electron-transfer reactions with metalloporphyrins that demonstrate that the path of electron transfer to the metal ion center can be via the porphyrin π-cloud and not via the fifth and sixth metalloporphyrin ligand positions.[1-4]

The reduction of the water-soluble tetra[*p*-sulfonatophenyl]porphinatocobalt(III), Co(III)-TPPS,[5-7] by chromous ion leads to the below rate law which is similar to the previously observed rate laws for the reduction of metalloporphyrins.[1,2,8]

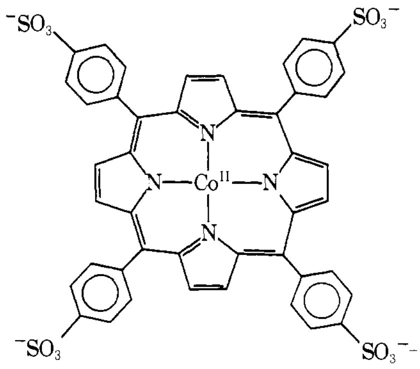
$$\text{rate of reduction} = \{k_1/[H^+] + k_2[Cl^-] + k_3[SCN^-]\}\,[Cr^{2+}][Co^{III}TPPS]$$

The rate constants in the above equation evaluated at 30° and an ionic strength of 0.25 ($NaClO_4$) are $k_1 = 4.9$ sec^{-1}, $k_2 = 2.9 \times 10^4$ M^{-2} sec^{-1}, and $k_3 = 1.3 \times 10^6$ M^{-2} sec^{-1}. The results are valid between pH 1.0 and 5.0.[9]

Since the rate of Co^{III}TPPS-SCN formation is slower than the electron transfer[10,11] a bridged Co(III)-N-C-S-Cr(II) reaction pathway can be ruled out. This is in agreement with the studies of Pasternack and Sutin.[2]

To further probe the mechanism of this reaction a product study was carried out which demonstrates that the reaction products have the Cr(III) bound to the Co(II)-TPPS moiety. This was verified by carrying out the reaction under stoichiometric conditions employing ^{51}Cr as a tracer[12] and using cation exchange columns to separate the products.[14]

We infer that the Cr(III) is attached to the sulfonate group as shown in structure I. These experiments imply that the electron-transfer goes via the porphyrin π-cloud and not via the fifth and sixth position[15] and also clearly demonstrate that the anion effects in these metalloporphyrin reductions are due to nonbridging ligand effects.



I

Acknowledgment. This work was supported by a Grant from the National Science Foundation.

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(8) Our rate does differ in one respect from that of Sutin and Pasternack in that we have a zero intercept in the plot of $k_{obsd}/[Cr^{2+}]$ vs. $1/[H^+]$.

(9) The reactions were run under pseudo-first-order conditions in a Durrum-Gibson stopped-flow machine with Co(III)-TPPS concentration about 1×10^{-5} *M* and $[Cr^{2+}]$ at $(3\text{-}6) \times 10^{-3}$ *M*. The wavelengths at both 427 and 411 nms were employed to follow the course of the reaction.

(10) E. B. Fleischer and M. Krishnamurthy, *Ann. N.Y. Acad. Sci.*, **206**, 32 (1973).

(11) The rate constant k_3 is the same whether the SCN^- is placed with the Co(III)-TPPS solution or the Cr^{2+} solution.

(12) The chromium was also analyzed spectrally with the diphenylcarbohydrazide method.[13]

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(14) A stock solution of $^{51}Cr^{III}(H_2O)_6^{3+}$ (1949 (counts/min)/10 ml of 9×10^{-5} *M* solution) was employed in these experiments. If 10.0 ml of the above solution was passed through an ion exchange column of Dowex 50W-X8 (9 × 1 in.) the eluent collected had an activity of 249 counts/min. A blank water solution had a counting rate of 236 counts/min. Thus the ion exchange resin caught 99% of the $Cr(H_2O)_6^{3+}$. If an equimolar mixture of $^{51}Cr(H_2O)_6^{3+}$ and Co(III)-TPPS was passed through the column the porphyrin containing eluent had a counting rate of 267 counts/min. On the other hand, when an equimolar mixture of $^{51}Cr(H_2O)_6^{2+}$ (produced by Zn(Hg) reduction of the radioactive chromic solution) and Co(III)-TPPS was passed through the column the porphyrin containing eluent now had a counting rate of 1951 counts/min. Thus the products of the reaction of chromous ion with the cobaltic porphyrin (chromic and cobaltous porphyrin) were completely eluted off the column. This demonstrates that the chromic ion is bound to the metalloporphyrin via the electron-transfer reaction. Interestingly, one can reoxidize the Cr(III)-Co(II)-TPPS with ferricyanide to the Cr(III)-Co(III)-TPPS and rereduce (with a different rate) the Co(III) center with $Cr(H_2O)_6^{2+}$ and isolate a $[Cr(III)]_2$-Co(II)-TPPS product.

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E. B. Fleischer,* M. Krishnamurthy, S. K. Cheung

Department of Chemistry, University of California
Irvine, California 92664

Received November 20, 1974

Nickel-Promoted Synthesis of Cyclic Biphenyls. Total Synthesis of Alnusone Dimethyl Ether

Sir:

Organotransition metal complexes are appearing with increasing frequency in synthetic methodology and in com-