

Further studies are in progress.¹⁵

Supplementary Material Available: Fractional coordinates and stereoviews for I and II (4 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and C-C Bond-Forming Reactions of Carbon-Bound Molybdenum, Tungsten, and Rhenium Enolates. Detection of an η^3 -Oxaallyl Intermediate

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The generation and reactions of organotransition-metal enolates has recently led to several important contributions to organic synthesis. Enolates of type **1** (Scheme I) have been generated in situ by deprotonation of metal acyl complexes;¹ enolates of type **2** have been generated in situ by reactions involving complexes of early transition metals (e.g., Ti, Zr).² Both types have shown stereoselectivity in their aldol reactions with aldehydes.³

Several carbon-bound transition-metal enolates (type **3**) have also been generated and isolated. These have often been referred to in the literature as "substituted methyl", "acylmethyl", and "oxoalkyl" complexes, and surprisingly little is known about their chemistry.⁴ In particular, reactions with organic electrophiles such as aldehydes and nitriles have not been observed. We now wish to report (1) a general method for preparing carbon-bound transition-metal enolates, (2) the isolation and full characterization of several of these materials, (3) observation of photochemical aldol reactions for the tungsten and molybdenum complexes, (4) detection of an η^3 -enolate (i.e., an η^3 -oxaallyl complex) in one of the irradiations, and evidence that this is the critical intermediate

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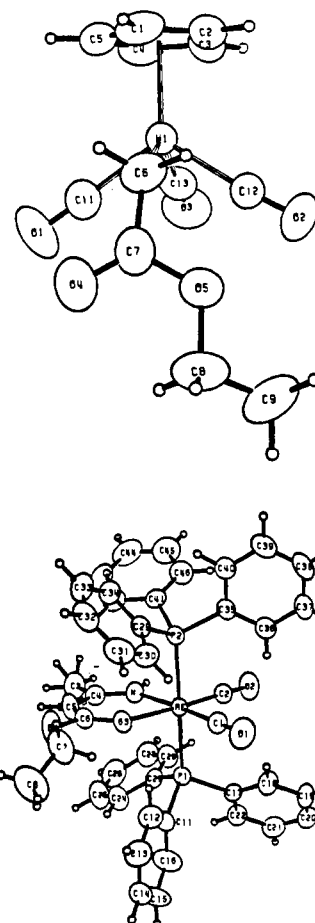


Figure 1. ORTEP structures of tungsten enolate **4a** and rhenium complex **11**.

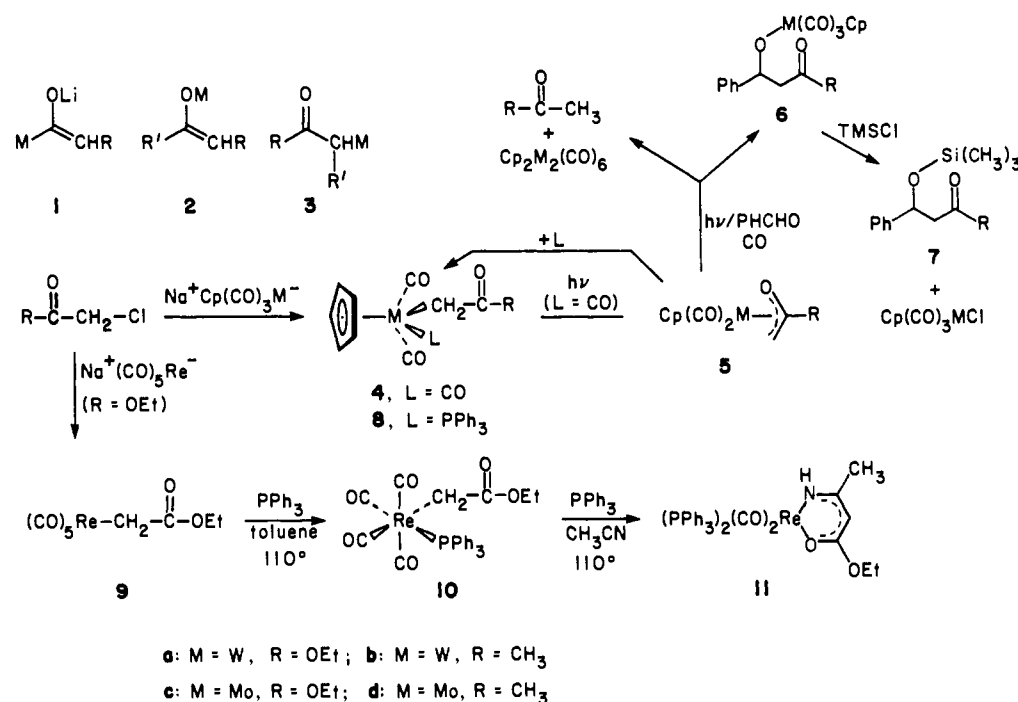
in the aldol reaction, and (5) observation of a striking condensation reaction with acetonitrile in the case of rhenium ester enolate **9**.

Treatment of the carbonylmetallate salts⁵ Na[Cp(CO)₃M] (M = Mo, W) or Na[(CO)₅Re] with α -bromo ketones or esters leads only to halogen transfer (giving Cp(CO)₃MBr and (CO)₅ReBr, perhaps by radical processes) rather than alkylation, and no metal enolates are formed. In sharp contrast, alkylation with α -chloro carbonyl compounds⁴ⁱ leads successfully in all the cases illustrated in Scheme I to the enolates **4a-d** and **9**. These materials were isolated by crystallization from hexane and characterized fully by IR, ¹H and ¹³C NMR spectroscopy and by elemental analysis. In addition, crystals of the [(ethoxycarbonyl)methyl]tungsten complex **4a** suitable for X-ray analysis, mp 37–38 °C, were obtained by slow evaporation of an ether solution at –40 °C. Solution of the structure⁶ confirmed the carbon-bound enolate formulation,

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(6) Following are selected data for the two X-ray structures reported in this paper. Both structures were solved by Patterson methods and refined by standard least-squares and Fourier techniques. Peaks corresponding to the expected positions of most of the hydrogen atoms were found by difference Fourier techniques; hydrogens were included in the structure factor calculations in their expected positions but were not refined in least squares. (a) For tungsten ester **4a**: space group *P1*; *a* = 8.8376 (10) Å, *b* = 10.9925 (15) Å, *c* = 13.9447 (21) Å, α = 88.482 (12)°, β = 79.956 (11)°, γ = 89.554 (10)°, *V* = 1333.7 (5) Å³; *D*_c = 2.092 g cm⁻³; μ_{calc} ($\mu\text{o K}\alpha$) = 88.56 cm⁻¹. A total of 3476 unique reflections were collected; the final residuals for which 326 variables refined against the 3154 data for which $F^2 > 3\sigma F^2$ were *R* = 1.85%; *R*_w = 3.19%, and GOF = 1.85. For rhenium addition product (PPh₃)₂(CO)₂(C₆H₅NO₂)Re (**11**): space group *P2₁/c*; *a* = 9.5049 (15) Å, *b* = 24.3527 (34) Å, *c* = 18.6400 (30) Å; β = 116.488 (13)°, *V* = 3861.7 (22) Å³; *D*_c = 1.54 g cm⁻³; μ_{calc} ($\mu\text{o K}\alpha$) = 33.12 cm⁻¹. A total of 5037 unique reflections were collected; the final residuals for which 469 variables refined against the 3570 data for which $F^2 > 3\sigma F^2$ were *R* = 1.69%; *R*_w = 2.00%; and GOF = 1.092. Full details of the structure determinations are being deposited with the Cambridge X-ray structure determination archives.

Scheme I



as illustrated in the ORTEP diagram shown in Figure 1.

The tungsten enolate **4a** is light sensitive but stable to air and thermally robust. Even in the presence of benzaldehyde, it remains unchanged after heating for 52 h at 110 °C in C₆D₆. However, as shown in Scheme I, irradiation with benzaldehyde leads to a metal salt of the aldol addition product **6a** (75–77% yield by ¹H NMR internal standard) along with 11% ethyl acetate. Aqueous workup provides the pure aldol in 38% isolated yield. If trimethylsilyl chloride is added after irradiation, or if the irradiation is carried out in the presence of trimethylsilyl chloride, and the reaction mixture is then heated at 60 °C or irradiated at room temperature for an additional 2 h, **6a** is quantitatively converted into the silylated aldol **7**.⁷ The course of this reaction was investigated more carefully by irradiating **4a** in an NMR tube in the absence of aldehyde. Under these conditions, irradiation ($\lambda_{\text{max}} > 340$ nm, medium-pressure Hg lamp, uranium glass filter) of **4a** results in loss of 1 equiv of CO (quantified by Toepler pumping the evolved gas) and generation of the η^3 -oxaallyl derivative **5a** (85% yield by ¹H NMR internal standard).

Compound **5a** is air and thermally sensitive, and efforts to isolate it in pure form have so far been unsuccessful. However, solutions of **5a** were generated quantitatively in a photochemical reactor by flushing the reaction mixture with N₂ during the irradiation. These solutions are stable for hours at room temperature or days at –40 °C. The oxaallyl structure is fully consistent with the proton and carbon NMR spectra of this species, including the shift of the metal carbonyl absorptions in the IR spectrum to lower frequency (e.g., 2011 and 1930 cm⁻¹ for **4a**; 1942 and 1847 cm⁻¹ for **5a**), the observation of diastereotopic methylene protons in the ester groups of **5a** and **5c**, and the immediate and highly stereoselective conversion of **5a** to the new cis-phosphine-substituted η^1 -enolate **8** on treatment with PPh₃ (89% isolated yield). Reaction of 2 equiv of benzaldehyde with **5a** in benzene-*d*₆ over a period of 4 days in the absence of light yields a 2:1 mixture of

the aldol addition product **6a** and ethyl acetate. Intermediate **5a** reacts with benzaldehyde more rapidly if a benzene-*d*₆ solution of the two reactants is irradiated in a sealed tube under the foregoing conditions; complete reaction is observed in 6 h (0.01 M **5a**, 0.01 M benzaldehyde, Hanovia 450-W medium-pressure lamp, uranium glass filter). These observations suggest that in the photochemical reaction with benzaldehyde irradiation produces the oxaallyl complex and that this species reacts thermally to give aldol addition product and ketone or ester. Similar observations have been made with each of the four tungsten and molybdenum enolates illustrated in Scheme I.

The rhenium enolate **9** undergoes aldol reactions thermally, although with less efficiency than the photochemical processes observed with the tungsten and molybdenum systems. In addition, we have fortuitously uncovered an unusual reaction of this system with acetonitrile. Reaction of **9** with phosphines leads stereospecifically to the cis-substituted complex **10**. When either compound **9** or **10** is heated at 110 °C for 2 days with excess PPh₃ in acetonitrile, a sharp-melting, crystalline material precipitates and has been isolated in 44% yield. Determination of the structure of this material by X-ray diffraction (see Scheme I and the ORTEP diagram in Figure 1) showed it to be **11**, a rhenium complex of the condensation product of the enolate moiety with acetonitrile.⁶

In summary, carbon-bound transition-metal enolates can be prepared in a straightforward and general way; they may be isolated and characterized by conventional techniques and are capable of undergoing aldol addition reactions with benzaldehyde. Our experiments in the rhenium series demonstrate that carbon-carbon bond-forming reactions with much less reactive electrophiles, such as nitriles, are also possible. Preliminary investigations have provided a strong indication that oxaallyl complexes are intermediates in the tungsten and molybdenum aldol reactions, but many additional mechanistic questions remain to be answered about these processes. Research in our laboratories continues to be aimed at answering these questions, as well as extending the condensation reactions to additional aldehydes and other electrophiles and application of these reactions in asymmetric synthesis.

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(7) Although the yield of silylated aldol **7** at this point is about 75%, as indicated by ¹H NMR internal standard, we have not yet worked out an efficient isolation procedure. When the photochemical aldol reaction is carried out on a 4-mmol scale, we are able to isolate the crystalline cyclopentadienyltricarbonyltungsten(I) chloride in 85% yield, silyl ether **7a** in 40% yield, and the unsilylated aldol in 17% yield. The low isolated yield of aldol product seems to be simply a technical problem that reflects the instability of **7a** and the corresponding aldol to the isolation and purification procedures we have investigated so far.

Supplementary Material Available: Experimental procedures for preparation of the tungsten and rhenium enolates, including ^1H NMR, ^{13}C NMR, IR, and analytical data for **4a-d**, **5-7**, **8a**, and **9-11** (6 pages). Ordering information is given on any current masthead page.

Selective Catalytic Oxidation of Organic Compounds by Nitrogen Dioxide

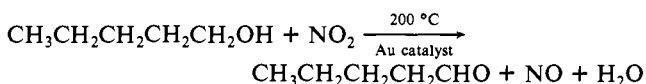
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New, catalyzed, gas-phase reduction/oxidation reactions that are highly selective and efficient are described in this paper. The reactions are based upon the surface-catalyzed reduction of nitrogen dioxide (NO_2) by organic compounds that can readily be dehydrogenated or oxidized. These reactions between certain organic compounds and NO_2 , which are catalyzed by metals—most effectively by gold—constitute the basis not only for new selective approaches to synthesis but also for selective and sensitive chromatography detectors.¹ Oxidation of organic compounds by nitric acid and nitrogen oxides has been reviewed.² In one report³ gold was used to catalyze the reaction of oxygen with alkenes, but gold catalysis of the oxidation of specific organic compounds by NO_2 is novel. The uncatalyzed gas-phase reaction of NO_2 with alcohols has been reported to give the corresponding nitrite,⁴ in contrast to the aldehydes obtained in the present gold-catalyzed reactions. Copper oxide catalysts facilitate the conversion of alcohols to aldehydes by quite different processes in which hydrogen is a byproduct.^{5,6}

At temperatures ranging from ambient to 400 °C, NO_2 can dehydrogenate or oxidize certain classes of organic compounds on the gold catalyst surface, while more inert classes of organic compounds are unreactive. We have examined several reactions to identify the oxidation products. Experiments have been performed using microgram quantities of starting materials which elute from a gas chromatograph and then transmit the catalyst bed within 1 s (calculated residence time is 0.16 s). For example, gas chromatography/mass spectrometry (GC/MS) analysis of the products resulting from reaction of 1-pentanol indicates complete oxidation at 200 °C; no unreacted starting material was detected and no reaction products other than pentanal, nitric oxide (NO), and water were observed under these conditions.



The limit of detection of volatile byproducts and unreacted starting material was estimated to be $\leq 1\%$ of the pentanal formed. Identification of compounds was accomplished by comparison of mass spectral data and of chromatographic retention times with those of authentic standards.

Other primary alcohols have been catalytically converted to the corresponding aldehydes in a similar manner using NO_2 . With the gold catalyst at 350–400 °C, 4-methyl-2-pentanol was rapidly oxidized to 4-methyl-2-pentanone. Again the conversion was virtually quantitative and proceeded without significant formation

of byproducts; no detectable starting alcohol remained in the product. Under similar reaction conditions, aliphatic ketones can undergo catalytic dehydrogenation to form α,β -unsaturated ketones, but in lower yield than obtained with alcohols. Olefins can also be dehydrogenated; for example, cyclohexene is oxidized by NO_2 on gold surfaces at 350–400 °C to benzene.

When uncoated borosilicate glass beads were substituted for the gold-coated catalyst beads none of these reactions occurred to a detectable extent under the same conditions used for the catalyzed experiments. However, a small amount of *n*-amyl nitrite was observed when no catalyst was present in the reaction of NO_2 with 1-pentanol, which is in agreement with previously reported work.⁴ Likewise, with the catalyst present but with air instead of NO_2 substituted as a possible oxidizing agent, oxidation was not observed for any of these compounds.

Gold-catalyzed gas-phase oxidation with NO_2 offers an attractive new synthesis approach because it is selective, occurs rapidly, can be performed on small as well as large scales, and generates an easily removed gaseous byproduct, NO. The NO can be removed and easily oxidized back to NO_2 by air to allow for recycle processes with net consumption of only oxygen and the compound being oxidized.

Several catalysts were prepared and investigated, including copper, silver, and gold supported on silica, different forms of silica support, and different forms of solid gold and gold alloys. Under the conditions tested the highest NO production, oxidation efficiency, and stability was achieved with pure gold supported on borosilicate glass beads. Less specificity was observed with gold alloys. The supported catalyst was prepared by precipitating auric chloride onto glass beads (0.5-mm diameter).⁷⁻⁹ After air drying, the gold was reduced by flowing hydrogen over the beads at 400 °C for 2 h, then washing the beads well with water, and finally treating them again under hydrogen at 400 °C for 6 h.

The apparatus consisted of a heated catalyst bed, a means of introducing sufficient NO_2 into the catalyst bed, a means of introducing the organic reducing agent, and a sorbent for collecting and analyzing the reaction products. The catalyst bed, a gas-phase, single-pass, packed bed reactor, consisted of a 4-mm i.d. by 8-cm length of quartz tubing, filled with 1 g of gold-coated beads, maintaining at the desired temperature (200–400 °C). A thermostated Teflon permeation tube produced a constant 11 $\mu\text{g}/\text{min}$ emission of NO_2 in a helium carrier gas stream flowing at 30 mL/min. A gas chromatograph was used to introduce selected reducing agents into this NO_2 doped carrier gas as it passed over the catalyst. The effluent of the catalyst bed was directed to a NO chemiluminescence detector through a polymeric sorbent trap of Tenax GC. In this manner any NO produced was detected¹⁰ immediately upon reaction of the reducing agent with NO_2 . Subsequently, the sorbent cartridge was removed, and the reaction products were thermally desorbed and cryogenically focused^{11,12} for analysis using GC/MS.

The following classes of compounds, when allowed to react with NO_2 in a catalyst bed at 350–400 °C, produced NO and corresponding oxidation products: alcohols, aldehydes, phenols, ketones, olefins, carboxylic acids and amines. Hundreds of compounds that produce nitric oxide have been studied.¹³ The following are representatives of the different compound classes: 2-octanol, benzyl alcohol, benzaldehyde, nonanal, 5-nonanone, 2,6-dimethylaniline, 2,6-dimethylphenol, 2-hexene, 1-nitropropane, *tert*-butyl disulfide, 1-octanethiol, naphthalene, indole, diethylethyl phosphonate, triethyl phosphite, and triethyl phosphate. Yields of NO vary from compound to compound according to ease of oxidation and reaction conditions but are reproducible under fixed

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