J. Am. Chem. Soc. 1986, 108, 4652–4653

Stereospecific Alkylations of Molybdenum(II) Enolates from η^2-Acyl Complexes

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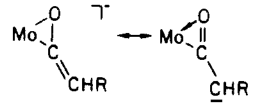
Received March 24, 1986

Deprotonation of η^1-acyl complexes forms transition metalloenolate reagents[1] from (π-C_5H_5)Fe(CO)L(C(O)R)[2] and cyclic organocobalt acyl reagents[3] which undergo diastereoselective alkylations. An anionic η^2-*C,O*-ketene ligand, also a metalloenolate, has been formed by deprotonation of the η^2-acyl ligand in (π-C_5H_5)$_2$ZrMe(C(O)R).[4] Hypothesizing that η^2-acyl precursors would yield more rigid enolate derivatives than related η^1-species, we have begun to study enolate reagents generated from pseudotetrahedral (Tp′)Mo(CO)L(C(O)CH_2R) complexes (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate). We report here spectroscopic characterization and alkylation and aldol reactions of these Mo(II) enolate complexes as well as the structure of one diastereomer of (Tp′)Mo(CO)[P(OPh)$_3$][C(O)CHMeBz].[5]

Photolysis of **1b**[6] in the presence of P(OPh)$_3$ yields **2**.[7] Both **1** and **2** can be deprotonated (*n*-BuLi or KH) to form the corresponding enolates (**3** and **4**, eq 1). Enolate derivatives **3a** and **4** have been characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies.[8] The absence of observable geminal coupling in the ^{1}H spectrum and the $^1J_{CH}$ values of 150 and 166 Hz for C_α, adjacent to the carbonyl moiety, suggest that I is the major contributing resonance form of enolate **3a** in solution. The ^{13}C chemical shifts of the enolate carbonyl carbons in both **3a** and **4** are similar to those of η^2-enolate zirconium derivatives[9] where the $[(\pi\text{-}C_5H_5)_2Zr(CH_3)(\eta^2\text{-}C(O)CH_2)]^-$ anion has been structurally characterized.[3] Of course the deprotonated η^2-acyl constitutes a ketene ligand, and both enolate and ketene nomenclatures appear in the literature. The vibrational frequencies of metal carbonyl ligands decrease roughly 100 cm^{-1} upon deprotonation as anticipated for formation of an electron-rich anionic metal complex. Although the ethyl acyl precursor **2** could form both *E* and *Z* enolate isomers, only a single isomer of **4** is detected by NMR.[10]

$$\underset{\substack{\mathbf{1a},\ L = CO,\ R = H\\ \mathbf{1b},\ L = CO,\ R = CH_3\\ \mathbf{2},\ L = P(OPh)_3,\ R = CH_3}}{Tp'(CO)LMo[C(O)CH_2R]} \xrightarrow{\text{base}} \underset{\substack{\mathbf{3a},\ L = CO,\ R = H\\ \mathbf{3b},\ L = CO,\ R = CH_3\\ \mathbf{4},\ L = P(OPh)_3,\ R = CH_3}}{[Tp'(CO)LMo[C(O)CHR]]^-} \quad (1)$$



I II

Alkylation at the α-carbon occurs when **3** or **4** is treated with alkyl halides. Reaction of **1a** with excess KH followed by MeI generates the *tert*-butyl complex **5**[11] (Scheme I). Although **3a** generates both mono- and dibenzylated η^2-acyl products when quenched with benzyl chloride, clean monobenzylation is observed when **3b** is treated with BzBr, and **6**[12] is isolated in 66% yield after purification.

Scheme I

$$\underset{\mathbf{1a}}{[Mo]C(O)CH_3} \xrightarrow[\text{2. MeI}]{\text{1. KH}} \underset{\mathbf{5}}{[Mo]C(O)CMe_3}$$

$$\underset{\mathbf{1b}}{[Mo]C(O)CH_2Me} \xrightarrow[\text{1. BzBr}]{\text{1. }n\text{-BuLi}} \underset{\mathbf{6}}{[Mo]C(O)CHMeBz} \xrightarrow{L,\ h\nu} \underset{\mathbf{7a} + \mathbf{7b}\ (80:20)}{[Mo']C(O)CHMeBz}$$

$$\underset{\mathbf{2}}{[Mo']C(O)CH_2Me} \xrightarrow[\text{1. BzBr}]{\text{1. }n\text{-BuLi}} \underset{\mathbf{7a}\ (\geq 98:2)}{[Mo']C(O)CHMeBz}$$

$$\underset{\mathbf{8}}{[Mo']C(O)CH_2Bz} \xrightarrow[\text{1. MeI}]{\text{1. }n\text{-BuLi}} \underset{\mathbf{7b}}{[Mo']C(O)CHMeBz}$$

$$[Mo] = (Tp')Mo(CO)_2;\ [Mo'] = (Tp')Mo(CO)[P(OPh)_3]$$

The possibility of stereoselective elaboration of the acyl ligand was explored with a racemic mixture of the chiral-at-metal phosphite complex **4**. This enolate reacts with benzyl bromide to form the monobenzylated product **7**. NMR data for both diastereomers of **7** were obtained for an 80:20 mixture of **7a** and **7b** prepared by photolysis of the dicarbonyl η^2-acyl complex **6**, chiral only at carbon, in the presence of P(OPh)$_3$.[13] Treatment of **2** with *n*-BuLi and BzBr followed by chromatography on alumina yields only **7a** as monitored by ^{1}H, ^{13}C, and ^{31}P NMR. The selectivity of the alkylation was assayed more directly by recording a ^{31}P spectrum of the crude reaction product. A solution of enolate reagent **4** was added to excess benzyl bromide at 0 °C. Only **7a**

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(1) For a thorough discussion of enolate chemistry, see: *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: Orlando, FL, 1984; Vol. 3.

(2) (a) Davies, S. G.; Walker, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, 209–210. (b) Davies, S. G.; Easton, R. J. C.; Walker, J. C.; Warner, P. *J. Organomet. Chem.* **1985**, *296*, C40–C42. (c) Ambler, P. W.; Davies, S. G. *Tetrahedron Lett.* **1985**, *26*, 2129–2130. (d) Liebeskind, L. S.; Welker, M. E. *Tetrahedron Lett.* **1985**, *26*, 3079–3082. (e) Liebeskind, L. S.; Welker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441–443. (f) Liebeskind, L. S.; Welker, M. E. *Tetrahedron Lett.* **1984**, *25*, 4341–4344. (g) For related Re chemistry, see: Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1185.

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(5) Abbreviations used in this paper are defined as follows: Me = CH_3; Bu = *n*-C_4H_9; Ph = C_6H_5; Bz = $CH_2C_6H_5$; THF = tetrahydrofuran.

(6) Compound **1** was prepared by a route similar to that reported for the analogous complexes containing unsubstituted pyrazole: (a) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588–595. (b) Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *Organometallics* **1983**, *2*, 1475–1477.

(7) **2**: IR(KBr) 1796 cm^{-1} (ν(CO)); ^{1}H NMR (CD_2Cl_2) δ 1.62 (t, $^3J_{HH}$ = 8 Hz, CH_2CH_3), 1.86–2.50 (Tp′ CH_3), 4.04 (m, $CH_aH_bCH_3$), 4.31 (m, $CH_aH_bCH_3$), 5.23–5.92 (Tp′ H), 6.75–7.42 (m, P(OC_6H_5)$_3$); ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 10.7–15.9 (Tp′ CH_3 and CH_2CH_3) 36.9 (t, $^1J_{CH}$ = 133 Hz, CH_2CH_3), 106.5–107.8 (d, $^1J_{CH}$ = 173 Hz, Tp′ CH), 120.8–129.2, 151.9 (P(OC_6H_5)$_3$), 144.4–154.1 (Tp′ CCH_3), 233.8 (d, $^2J_{PC}$ = 14 Hz, MoCO), 263.9 (d, $^2J_{PC}$ = 51 Hz, C(O)CH_2); ^{31}P{^{1}H} NMR (THF/10% C_6D_6) δ 167.5.

(8) **3a**: IR(THF) 1913, 1716 cm^{-1} (ν(CO)); ^{1}H NMR (THF-d_8) δ 3.91 (s, C(O)CH_aH_b), 4.21 (s, C(O)CH_aH_b); ^{13}C{^{1}H} NMR (THF-d_8) δ 56.7 (dd, $^1J_{CH}$ = 150, 166 Hz, C(O)CH_2), 188.3 (s, C(O)CH_2). **4**: ^{1}H NMR (THF-d_8) δ 2.03 (d, $^3J_{HH}$ = 6.3 Hz, $CHCH_3$), 4.67 (dq, $^4J_{PH}$ = 1.7, $^3J_{HH}$ = 6.3 Hz, $CHCH_3$); ^{13}C{^{1}H} NMR (THF-d_8) 73.6 ($CHCH_3$), 185.2 (d, $^2J_{PC}$ = 51 Hz, C(O)CH); ^{31}P{^{1}H} NMR (THF-d_8) δ 169.8.

(9) (a) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068–2070. (b) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499–5500.

(10) If one assumes attack by the electrophile occurs over the CO then the geometry of the observed benzylation product (vide infra) would indicate that the reaction proceeds through the *E* enolate (the *Z*(O) enolate relative to the oxygen).

(11) **5**: IR(KBr) 1846, 1947 cm^{-1} (ν(CO)); ^{1}H NMR (C_6D_6) δ 1.61 (s, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ 27.6 (q, $^1J_{CH}$ = 127 Hz, C(CH_3)$_3$), 47.5 (m, $^2J_{CH}$ = 5 Hz, C(CH_3)$_3$), 250.8 (C(O)C).

(12) **6**: IR(KBr) 1828, 1958 cm^{-1} (ν(CO)); ^{1}H NMR (C_6D_6) δ 1.54 (d, $^3J_{HH}$ = 7.0 Hz, $CHCH_3$), 2.89 (dd, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 10.7 Hz, $CHCH_aH_bPh$), 3.77 (dd, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 4.5 Hz, $CHCH_aH_bPh$), 4.38 (m, C(O)CH), 7.10–7.29 (m, $CH_2C_6H_5$); ^{13}C{^{1}H} NMR (C_6D_6) δ 38.9 (t, $^1J_{CH}$ = 129 Hz, $CHCH_2Ph$), 50.5 (d, $^1J_{CH}$ = 135 Hz, C(O)CH), 126.7–131.8, 139.3 ($CH_2C_6H_5$), 251.7 (C(O)CH).

(13) **7a**: IR (KBr) 1816 cm^{-1} (ν(CO)); ^{1}H NMR (CD_2Cl_2) δ 1.48 (d, $^3J_{HH}$ = 6.9 Hz, $CHCH_3$), 2.75 (dd, $^2J_{HH}$ = 13.3, $^3J_{HH}$ = 10.8 Hz, $CHCH_aH_bPh$), 4.19 (dd, $^2J_{HH}$ = 13.3, $^3J_{HH}$ = 2.4 Hz, $CHCH_aH_bPh$), 5.3 (m, C(O)CH); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 39.2 (t, $^1J_{CH}$ = 136 Hz, $CHCH_2Ph$), 49.1 (d, $^1J_{CH}$ = 137 Hz, C(O)CH), 262.9 (d, $^2J_{PC}$ = 51 Hz, C(O)CH); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 166.2. **7b**: IR (KBr) 1816 cm^{-1} (ν(CO)); ^{1}H NMR (CD_2Cl_2) δ 1.72 (d, $^3J_{HH}$ = 7.3 Hz, $CHCH_3$), 3.08 (dd, $^2J_{HH}$ = 13.7, $^3J_{HH}$ = 9.6 Hz, $CHCH_aH_bPh$), 3.50 (dd, $^2J_{HH}$ = 13.7, $^3J_{HH}$ = 3.1 Hz, $CHCH_aH_bPh$), 5.2 (m, C(O)CH); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 40.0 (t, $^1J_{CH}$ = 129 Hz, $CHCH_2$), 49.4 (d, $^1J_{CH}$ = 134 Hz, C(O)CH), 263.9 (d, $^2J_{PC}$ = 53 Hz, C(O)CH); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 166.8.

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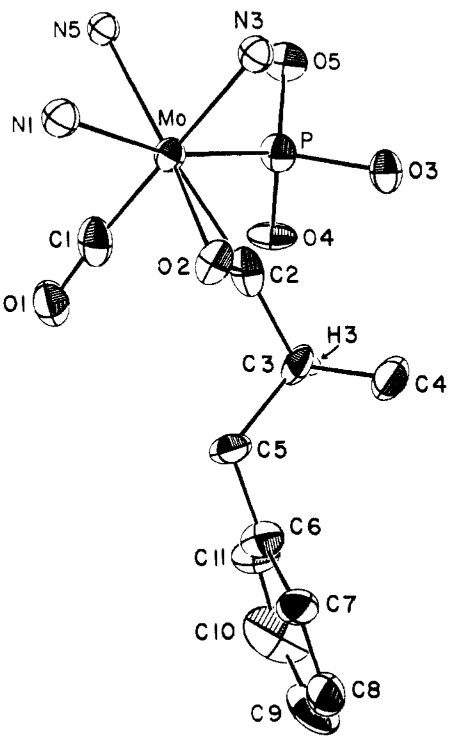

Figure 1. ORTEP diagram of the molybdenum coordination sphere in (Tp′)Mo(CO)[P(OPh)$_3$][η^2-C(O)CHMeBz] (**7a**) illustrating the atomic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level.

was detected in the ^{31}P spectrum, suggesting greater than 98% diastereoselectivity. Confirmation that the alkylation reaction is kinetically controlled was obtained by generating the η^2-benzylated methyl acyl, η^2-C(O)CH$_2$CH$_2$Ph (**8**),[14] which was then deprotonated and allowed to react with MeI. Only **7b** was detected by ^{1}H NMR following chromatography. A crystal structure of **7a** has been undertaken;[15] the geometry shown in Figure 1 is very similar to previous η^2-acyl TpM(CO)L[C(O)R] structural reports.[6b,16]

Aldol condensation reactions of transition-metal enolates have not been reported as frequently as alkylation reactions.[17] We find that metal enolate **3b** reacts with benzaldehyde to yield a deep indigo η^2-enone derivative resulting from dehydration of the initial β-hydroxy η^2-acyl product. (Note that the molybdenum η^2-benzoyl complex which has been structurally characterized is also highly colored.[16a]) The formation of (Tp′)CO)$_2$Mo(η^2-C(O)CMe=CHPh) (**9**)[18] suggests that a range of electrophiles will react with these molybdenum(II) enolate reagents.

Acknowledgment. Generous support of this research by the National Science Foundation (CHE-8310121) is gratefully acknowledged.

Supplementary Material Available: Tables of ^{1}H and ^{13}C NMR data for **2**–**9**, analytical data for **5**, **6**, and **7a**, X-ray data collection parameters for **7a**, and positional and thermal parameters and bond distances and angles for **7a** (21 pages). Ordering information is given on any current masthead page.

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[14] **8**: IR(THF) 1816 cm^{-1} (ν(CO)); ^{1}H NMR (CD$_2$Cl$_2$) 3.2–4.7 (m, C(O)(C*H*$_2$)$_2$Ph).

[15] The crystal selected was triclinic of space group $P\bar{1}$ with unit cell dimensions a = 14.142 (4) Å, b = 15.625 (4) Å, c = 11.147 (2) Å, α = 99.88 (2)°, β = 92.23 (2)°, γ = 90.50 (2)°, and z = 2. Data were collected with an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation). Of the 4139 reflections monitored, 3017 reflections with $I > 3\sigma(I)$ were used in the structure solution. Final agreement indices of R = 7.7% and R_w = 6.8% resulted with hydrogens placed in calculated positions, the phenyl carbons of the triphenylphosphite and all of the hydridotris(3,5-dimethylpyrazolyl)borate atoms refined isotropically, and the remaining atoms refined anisotropically.

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[18] 9: IR (KBr) 1943, 1846 cm^{-1} (ν(CO)); ^{1}H NMR (CD$_2$Cl$_2$) δ 2.62 (d, $^3J_{HH}$ = 1.3 Hz, C(CH$_3$)=, 7.46–7.73 (m, CHC$_6$*H*$_5$), 7.99 (q, $^3J_{HH}$ = 1.3 Hz, =C*H*Ph); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 130.0 (q, $^2J_{CH}$ = 8 Hz, *C*(CH$_3$)=), 148.9 (dq, $^1J_{CH}$ = 159, $^3J_{CH}$ = 4 Hz, =*C*HPh), 238.5 (*C*(O)C(CH$_3$)).

Hydrogenolysis of *n*-Butane over the (111) and (110)-(1×2) Surfaces of Iridium: A Direct Correlation between Catalytic Selectivity and Surface Structure[†]

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Received March 24, 1986

The importance of surface structure in determining the activity and selectivity of various classes of heterogeneously catalyzed reactions is well-known. Boudart[1] has applied Taylor's concept of "active centers"[2] to catalysis by supported metals, stressing the need to examine the sensitivity of the *specific activity* (per site basis) to the average metallic particle size ("dispersion"). Although many reactions over supported catalysts, including the hydrogenolysis of alkanes, have been found to be "structure-sensitive",[1] a microscopic understanding of this variation in catalytic properties with particle size has remained elusive. Except in the limit of nearly atomic dispersion, changes in the surface of the catalyst particle with size will be geometric,[3] involving variations in the relative number of atoms in high-symmetry microfacets and at low-coordination-number edge and corner positions where these high-symmetry planes intersect.[5]

Foger and Anderson[6] have reported that the selectivity for the hydrogenolysis of n-C$_4$H$_{10}$ by supported Ir catalysts is extremely sensitive to the average metal particle size.[7] The structure sensitivity is most apparent for clusters of diameter ≲40 Å, where there is a rapid change in the average coordination number of the metal surface atoms.[11] Since the use of oriented single crystals as catalysts allows an *unambiguous* assessment of the effects of

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[†] Work performed at Sandia National Laboratories and supported by the U.S. Department of Energy under Contract DE-AC04-76DP00789. We acknowledge the partial support of the Office of Basic Energy Sciences, Division of Chemical Science.

[‡] Visiting from the Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.

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[3] Any perturbation in the electronic properties will result from the differing *surface* geometries. Strong metal–support interactions are negligible for nonreducible oxides such as Al$_2$O$_3$ and SiO$_2$, whereas they may be significant for reducible oxides such as TiO$_2$.[4]

[4] See, e.g.: Foger, K. In *Catalysis—Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: Berlin, 1984; Vol. 6, p 227 and references therein.

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[7] Similar results have been reported for the hydrogenolysis of n-C$_4$H$_{10}$ by supported Pt[8] and the hydrogenolysis of n-C$_5$H$_{12}$ by supported Pt[9] and Rh.[10]

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