A Novel Intramolecular Insertion of a Metal Acyl Group into an Organic Ketone

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Synthesis of metal-butyrolactones *via* insertion of a metal acyl bond into an organic ketone is demonstrated, and the crystal structure of one example is reported; labelling experiments exclude the possibility that this insertion is initiated by intramolecular attack of the enol on the acyl group.

Transition-metal acyl species are of great value in synthetic organometallic chemistry and homogeneous catalysis.[1] The acyl group has been reported to undergo insertion into small molecules such as alkene, alkyne, allene and carbon monoxide,[2] and no instance of insertion into the carbonyl groups of organic molecules has been reported either inter- or intramolecularly. In this paper, we report synthesis of γ-lactone related derivatives *via* an intramolecular insertion of a metal acyl bond into an organic ketone group.

Outlined in Scheme 1, the reaction between 3-chloromethylpent-3-en-2-one in cold tetrahydrofuran (THF) (1 equiv. −78 °C, 3 h) gave **1** as a yellow oil† (65%). Stirring **1** alone in ether (23 °C, 36 h) led to gradual deposition of a yellow precipitate **2** (*ca.* 65% yield) of which the molecular structure has been determined by X-ray diffraction.‡ The ORTEP drawing is provided in Fig. 1 which reveals that the organic moiety has undergone cyclization to generate a butyrolactone ring; the $Mocp(CO)_2$ fragment is linked to the C(13), C(10) and C(9) atoms with reasonable Mo–C distances of 2.313(3)–2.360(3) Å.

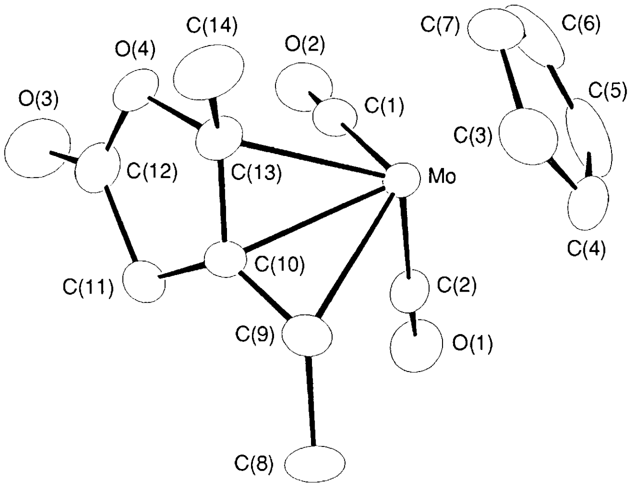
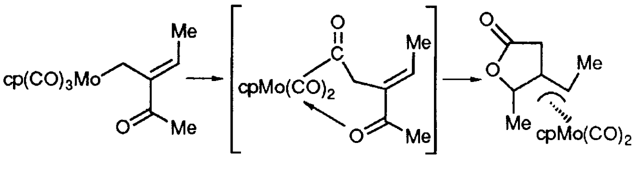


Fig. 1 ORTEP drawing of complex **2**. Pertinent bond distances: Mo–C(13) 2.315(3), Mo–C(10) 2.313(3), Mo–C(9) 2.360(3), C(12)–O(4) 1.315(5), C(12)–O(3) 1.189 Å.

The rearrangement of **1** to **2** has provided a novel example of intramolecular insertion of a metal acyl group into an organic ketone. In order to test the possibility that this insertion is initiated by an intramolecular enol attack on the acyl group,[3] we have performed a labelling experiment using a 10-fold excess of D_2O during cyclization. Spectral analysis§ of **2** thus formed (12% yield) showed no sign of deuterium incorporation. In the case of cyclization using Et_3N (1.5 equiv.) and D_2O (5–10 fold excess), the yield of **2** decreased to 3–5% with negligible incorporation of deuterium. These results indicate a simple insertion mode in which a π-ketone is prerequisite.

Formation of the enolate of **2** was achieved through deprotonation by lithium diisopropylamide (LDA) in cold THF (−78 °C). This enolate reacted with MeI (1.0 equiv.) to give **3** (62% yield) as a single diastereoisomer. Treatment of this enolate with *N*,*N*-dimethylmethyleneammonium iodide, followed by MeI alkylation then deammination with aqueous $NaHCO_3$, produced the mixtures **4** (46%) and **5** (16%), which are separable on a silica column. Likewise, only one diastereoisomer was detected for **5** in the ^1H NMR limit. Complex **4** is an α-methylene-γ-lactone, a class of compound which is of continuing interest.[5]



1 **2**

Scheme 1

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† Satisfactory analytic and/or spectroscopic data were obtained for all new compounds.

‡ *Crystal data* for **2**: $C_{14}H_{14}MoO_4$, monoclinic, space group $P2_1/n$, a = 11.541(6), b = 8.9977(16), c = 13.084(5) Å, β = 96.02(4)°, V = 1351.2(9) Å^3, Z = 4, M_r = 342.2021, D_c = 1.682 g cm^{-3}, $F(000)$ = 691.77, λ(Mo-Kα) = 0.7093 Å, R = 0.026, R_w = 0.026 for 2088 reflections with $I > 2\sigma(I)$ out of 2374 unique reflections and 173 parameters. Data were collected on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by the Patterson method. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were added at the idealized positions and included in the structure factor calculations. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Complex **1**: ^1H NMR (300 MHz, $CDCl_3$) δ 1.23 (d, *J* 7.3 Hz, 1H), 1.67 (d, *J* 7.3 Hz, 1H), 2.26 (s, 3H), 2.29 (d, *J* 6.9 Hz, 3H), 5.39 (s, 5H), 6.35 (q, *J* 6.9 Hz, 1H); ^{13}C NMR (75.5 MHz) δ 240.7, 228.9, 200.0, 150.2, 133.5, 93.0, 25.4, −11.3; IR (Nujol) 2012, 1924, 1662, cm^{-1}.

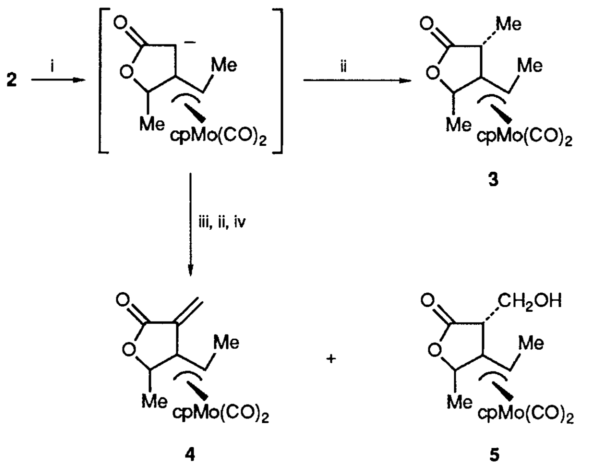
Complex **2**: ^1H NMR (400 MHz, 228 K, [$^2H_8$]toluene): (*endo* form) δ 1.49 (d, *J* 6.2 Hz, 3H), 1.56 (s, 3H), 1.71 (q, *J* 6.2 Hz, 1H), 2.56 (d, *J* 20.8 Hz, 1H), 2.95 (d, *J* 20.8 Hz, 1H), 4.68 (s, 5H), (*exo* form) δ 1.45 (s, 3H), 1.52 (q, *J* 6.0 Hz, 3H), 1.82 (d, *J* 6.0 Hz, 3H), 2.80 (d, *J* 21.4 Hz, 1H), 3.00 (d, *J* 21.4 Hz, 1H), 4.50 (s, 5H); ^{13}C NMR (100 MHz, 228 K, [$^2H_8$]toluene): (*endo* form) δ 239.0, 236.0, 173.3, 104.3, 94.6, 78.6, 48.6, 38.8, 23.4, 18.2; (*exo* form) δ 241.5, 239.5, 172.9, 108.1, 95.5, 92.3, 45.5, 36.9, 25.3, 17.7; IR (Nujol) 1946, 1866, 1776 cm^{-1}.

Complex **3**: ^1H NMR (400 MHz, [$^2H_8$]toluene, 223 K) δ 1.13 (d, *J* 7.3 Hz, 3H), 1.30 (s, 3H), 1.44 (q, *J* 6.4 Hz, 1H), 2.65 (q, *J* 7.4 Hz, 1H), 4.38 (s, 5H); IR (Nujol) 1947, 1864, 1772 cm^{-1}.

Complex **4**: ^1H NMR (300 MHz, C_6D_6) δ 1.29 (s, 3H), 1.39 (q, *J* 8.8 Hz, 1H), 1.50 (d, *J* 8.8 Hz, 3H), 4.48 (s, 5H), 4.78 (s, 1H), 5.09 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.9, 48.3, 48.6, 48.8, 93.1, 93.3, 94.2, 105.7, 116.6, 141.9, 220.9, 222.8; IR (Nujol) 1950, 1875, 1765, 1633 cm^{-1}.

Complex **5**: ^1H NMR (400 MHz, $CDCl_3$, 223 K) δ 1.43 (s, 3H), 1.47 (q, *J* 6.3 Hz, 1H), 1.85 (d, *J* 6.3 Hz, 3H), 1.94 (dd, *J* 6.1, 6.1 Hz, 1H), 2.47 (dd, *J* 10.0, 6.1 Hz, 1H), 4.17 (dd, *J* 10.0, 6.1 Hz, 1H), 5.37 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, 223 K) δ 15.0, 21.1, 46.6, 48.4, 77.3, 77.4, 95.1, 104.8, 177.6, 238.0; IR (Nujol) 1950, 1874, 1764 cm^{-1}.

Satisfactory elemental analyses (C, H) were obtained.



Scheme 2 *Reagents and conditions*: i, LDA, −78 °C; ii, MeI; iii, $CH_2{=}N^+Me_2I^-$; iv, $NaHCO_3$

Molybdenum-allyl complexes have been widely used in organic reactions.[6] In principle, these allyl complexes can be decomplexed in a more versatile manner.[7,8] Further application of this novel cyclization to organic synthesis through Pd–Ni-catalysed reactions is under current study.

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