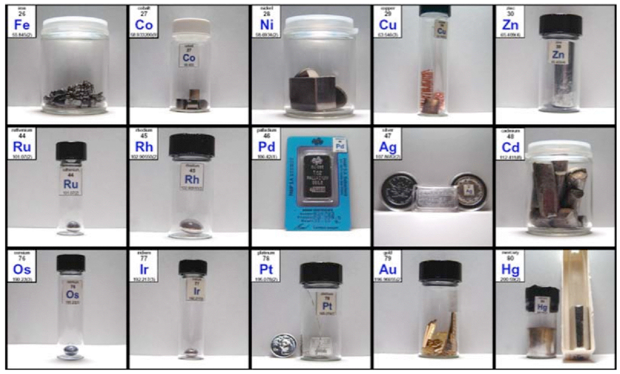
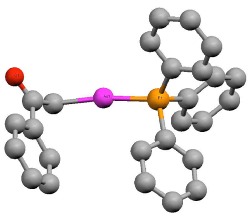
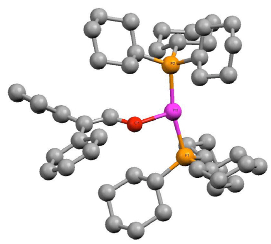
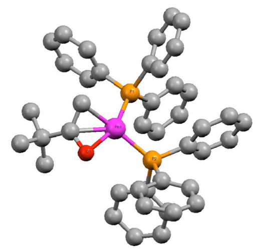
Late Transition Metal Enolates

Structure and Reactivity









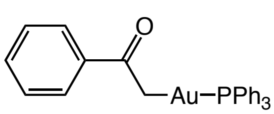
Stoltz Group Literature Group Meeting
9 May 2005
Presented by Justin Mohr

Outline

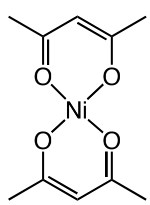
- Definitions
- General enolate structure
- Methods of enolate synthesis
- Survey of late transition metal enolates
- Enolates that have not been isolated: Cu, Ag, Cd, Os

Definitions

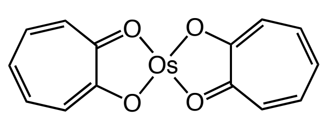
For the purposes of this talk, enolates will be restricted to unstabilized ketone or aldehyde enolates. Most multiply anionic ligand structures (e.g., metallocyclobutnanones), extended enolates, ketene complexes, metal pyruvates, and α-metallated enone structures will be omitted as well.



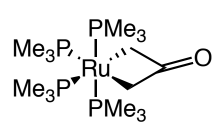
unstabilized acetophenone enolate
included



stabilized enolate
excluded

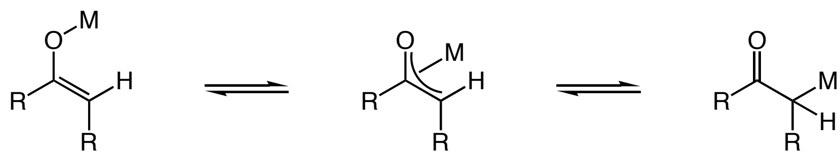


pseudoaromatic
excluded



multiply anionic
excluded

Enolate Structure - General



η^1-*O*-bound	η^3	η^1-*C*-bound

Typical bond lengths:

C-C 1.37 Å	C-C 1.39 Å	C-C 1.46 Å
C-O 1.34 Å	C-O 1.31 Å	C-O 1.22 Å

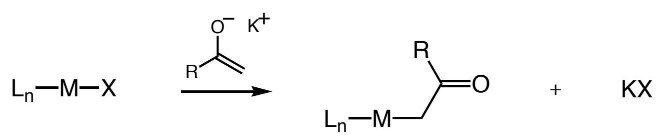
Other key structural evidence:

no carbonyl IR stretch	shifted carbonyl IR stretch	carbonyl IR stretch
vinylic C-H resonance in NMR	shifted carbonyl ^{13}C NMR resonance	carbonyl ^{13}C NMR resonance
no M-C coupling in NMR		M-C coupling in ^{13}C NMR

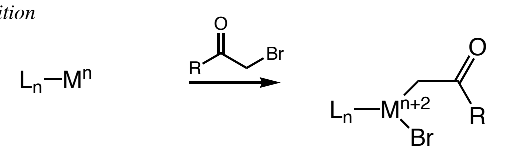
- In general, main group metals and early transition metals favor the *O*-bound form
- Late transition metals tend to favor the *C*-bound form
- η^3 form is generally rapid equilibrium between *O*- and *C*-bound forms
- Examples where the two extremes equilibrate on an observable time scale are rare

General Methods of Metal Enolate Synthesis

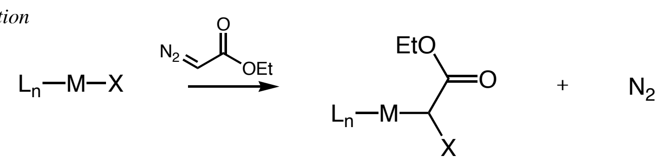
Ion exchange



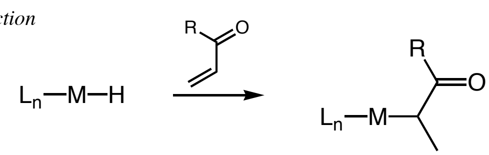
Oxidative addition



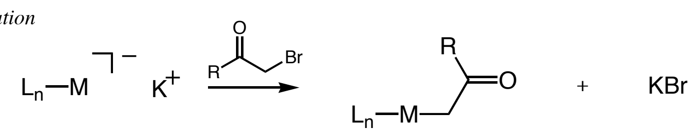
Carbene insertion



Conjugate reduction



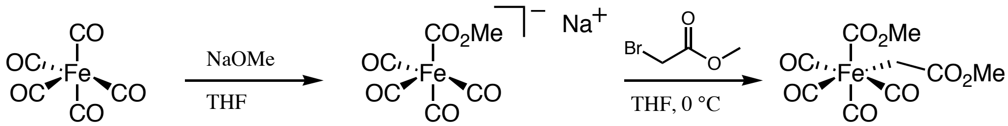
Metal alkylation



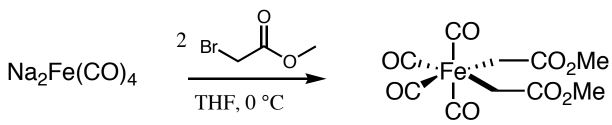
Survey of Late Transition Metal Enolates

First Row Metals: Iron

Fe



IR: ν(CH_2*CO_2*Me) 1712 cm^{-1}
^{1}H NMR: δ 2.29 (s, C*H_2*)
^{13}C NMR: δ 179.6 (CH_2*CO_2*Me)
δ 12.3 (*C*H_2CO_2Me)



IR: ν(CH_2*CO_2*Me) 1720 cm^{-1}
^{1}H NMR: δ 1.57 (s, C*H_2*)
^{13}C NMR: δ 179.9 (CH_2*CO_2*Me)
δ 11.5 (*C*H_2CO_2Me)

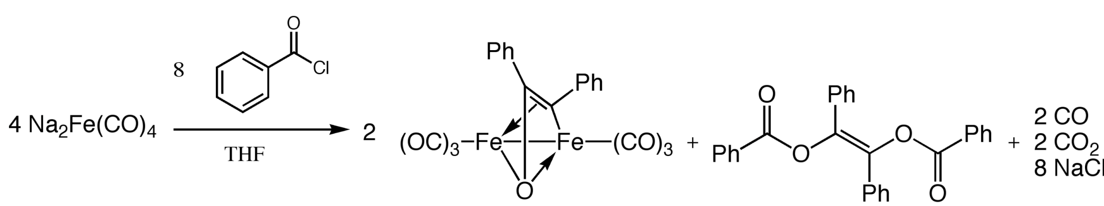
Complexes such as this have been postulated as intermediates in the carbonylation reaction of alkyl halides by $Na_2Fe(CO)_4$
(See, Collman, *JACS* 1972, **94**, 1788)

Abbayes, *JCSCC* 1988, 929

Survey of Late Transition Metal Enolates

First Row Metals: Iron

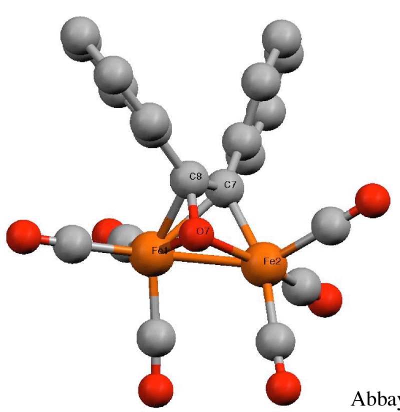
Fe



IR and NMR data are not conclusive

Bond lengths (Å):

C(7)-C(8)	1.399	like η^3
C(8)-O(7)	1.383	very long! indicative of 3-coordinate O
Fe(1)-C(7)	2.104	
Fe(1)-C(8)	2.028	
Fe(2)-C(7)	1.962	
Fe(2)-C(8)	2.472	beyond bonding distance
Fe(1)-O(7)	1.982	
Fe(2)-O(7)	1.994	
Fe(1)-Fe(2)	2.461	



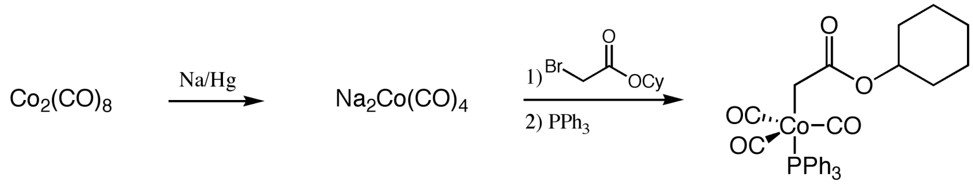
an electron transfer mechanism is proposed, but further studies have been inconclusive

Abbayes, *Organometallics*, **1987**, *6*, 2262

Survey of Late Transition Metal Enolates

First Row Metals: Cobalt

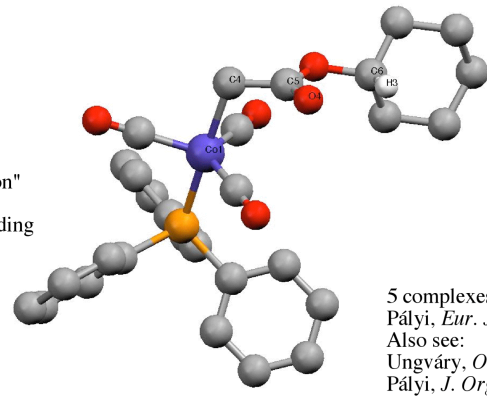
Co



IR: ν(CH_2CO_2Me) 1705 cm^{-1}
^{1}H NMR: δ 2.16 (CH_2, $^3J_{H\text{-}P}$ = 3.1)
^{13}C NMR: δ 5.78 (CH_2, $^3J_{C\text{-}P}$ = 16.1)
^{31}P NMR: δ 57.78

Bond lengths (Å):

Co(1)-C(4) 2.090
C(4)-C(5) 1.477 ← *C*-bound
C(5)-O(4) 1.213 ←
Co(1)-C(5) 2.933 ← "auto-solvation"
C(6)-H(3) 1.086
O(4)-H(3) 2.304 ← within H-bonding distance



Sum of van der Waals radii

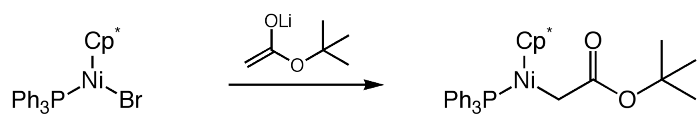
Co + C = 3.85 Å

5 complexes
Pályi, *Eur. J. Inorg. Chem.* **2001**, 2297
Also see:
Ungváry, *Organometallics* **1993**, *12*, 2849
Pályi, *J. Organomet. Chem.* **1981**, *209*, 183

Survey of Late Transition Metal Enolates

First Row Metals: Nickel

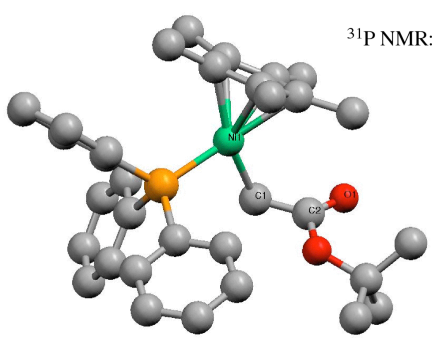
Ni



IR: ν(CH_2CO_2-*t*-Bu) 1673 cm^{-1}
^{1}H NMR: δ 0.75 (CH_2, $^3J_{H\text{-}P}$ = 8.3)
^{13}C NMR: δ −0.9 (CH_2, $^3J_{C\text{-}P}$ = 15.2)
δ 181.8 (CH_2CO_2-*t*-Bu)
^{31}P NMR: δ 50.44

Bond lengths (Å):

Ni(1)-C(1) 2.027
C(1)-C(2) 1.414 ← *C*-bound
C(2)-O(1) 1.221 ←

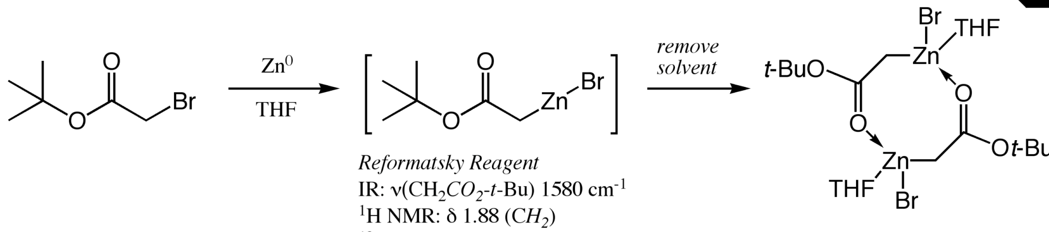


Bergman & Heathcock, *Organometallics* **1990**, *9*, 30
Also see:
Poveda & Carmona, *JCSDT* **1992**, 1491
Otsuka, *JACS* **1973**, *95*, 3180
Meisters, *J. Organomet. Chem.* **1974**, *82*, 315
Cámpora *JACS* **2003**, *125*, 1482

Survey of Late Transition Metal Enolates

First Row Metals: Zinc

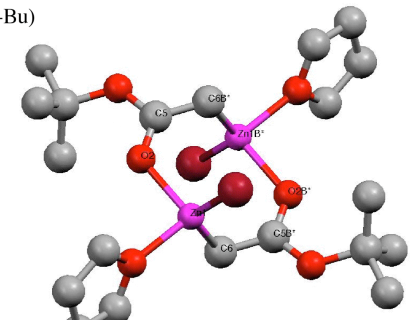
Zn



Reformatsky Reagent
IR: $\nu(CH_2CO_2\text{-}t\text{-Bu})$ 1580 cm^{-1}
^{1}H NMR: δ 1.88 (CH_2)
^{13}C NMR: δ 22.7 (CH_2)
δ 186.2 ($CH_2CO_2\text{-}t\text{-Bu}$)

Bond lengths (Å):

Zn(1)-O(2)	2.02	
Zn(1)-C(6)	1.98	
C(5)-C(6B*)	1.41	← *C*-bound
C(5)-O(2)	1.31	← coordinated carbonyl long C=O bond



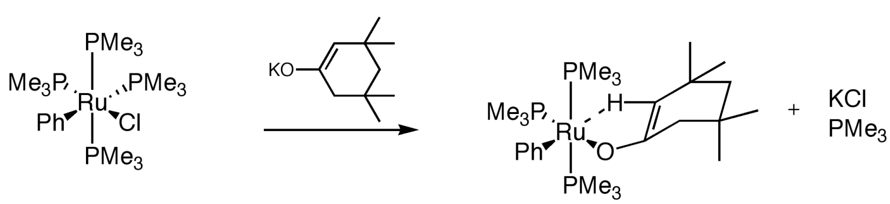
Computations suggest that the *C*-bound form is 7.8 kcal/mol lower in energy than the *O*-bound form with an interconversion by 1,3-shift (E_a = 26.5 kcal/mol). Bond formation was calculated to occur with an E_a = 55 kcal/mol from the monomeric *C*-bound form or 15.45 kcal/mol from the monomeric *O*-bound form. Dimerization is calculated to be exothermic (~5 kcal/mol). Reaction from the dimer to product is high in energy (31.8 kcal/mol), suggesting reaction occurs from the monomer. (Dewar, *JACS* **1987**, *109*, 6553)

Boersma, *Organometallics*, **1984**, *3*, 1403
Orsini, *TL* **1982**, *23*, 3945
Reformatsky, *Ber. Dtsch. Chem. Ges.* **1887**, *20*, 1210
Also see:
Heathcock, *Organometallics* **1987**, *6*, 2069
Boersma, *Recueil* **1973**, *92*, 229

Survey of Late Transition Metal Enolates

Second Row Metals: Ruthenium

Ru

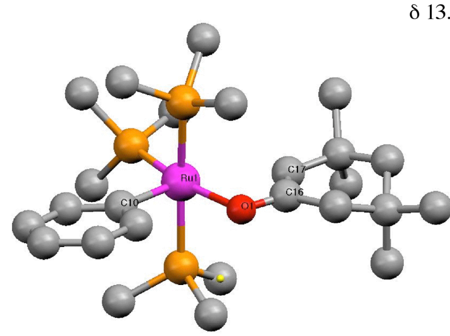


^{1}H NMR: δ -1.25 (O-C=C*H*)
^{13}C NMR: δ 76.97 (O-C=*C*H)
δ 164.98 (O-*C*=CH)
^{31}P NMR: δ 0.82
δ 13.54 ($J_{P\text{-}P}$ = 32.6)

Bond lengths (Å):

Ru(1)-C(10)	2.030	
Ru(1)-O(1)	2.127	
O(1)-C(16)	1.314	← *O*-bound
C(5)-O(2)	1.352	← *O*-bound

H atom involved in agostic interaction was not located or refined. Estimated Ru(1)-H(18) length is 2.14 ångstroms.

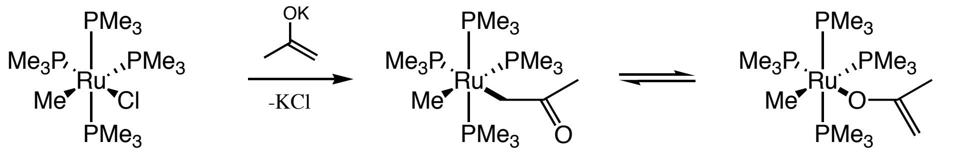


Bergman & Anderson, *Organometallics* **1991**, *10*, 3326

Survey of Late Transition Metal Enolates

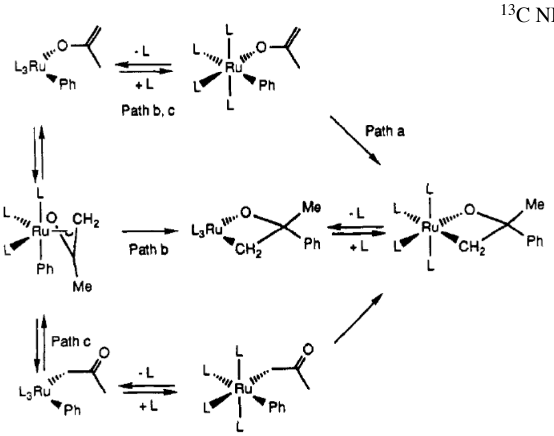
Second Row Metals: Ruthenium

Ru



IR: ν(CH_2COCH_3) 1620 cm^{-1}
^{1}H NMR: δ 1.90 (m, CH_2)
^{13}C NMR: δ 22.83 (m, CH_2)

^{1}H NMR: δ 3.50, δ 3.96 (O-C=CH_2)
^{13}C NMR: δ 75.68 (O-C=CH_2)



Temperature (°C)	Ratio (*C* : *O*)
5	1 : 2.8 ± 0.2
60	1 : 4.4 ± 0.3

ΔH = 1.5 ± 0.3 kcal/mol ⟵ favors *C*-bound form

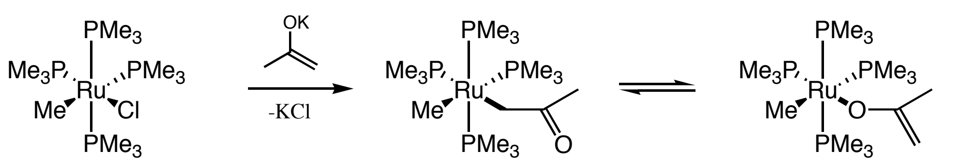
ΔS = 7.6 ± 1.5 eu ⟵ favors *O*-bound form

Bergman & Anderson, *JACS* **1990**, *112*, 5670
Bergman & Anderson, *Organometallics* **1991**, *10*, 3326

Survey of Late Transition Metal Enolates

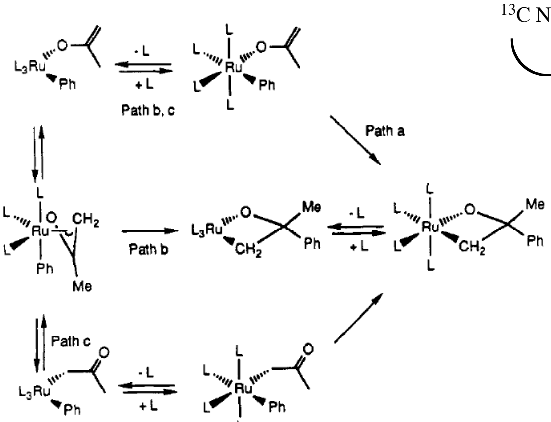
Second Row Metals: Ruthenium

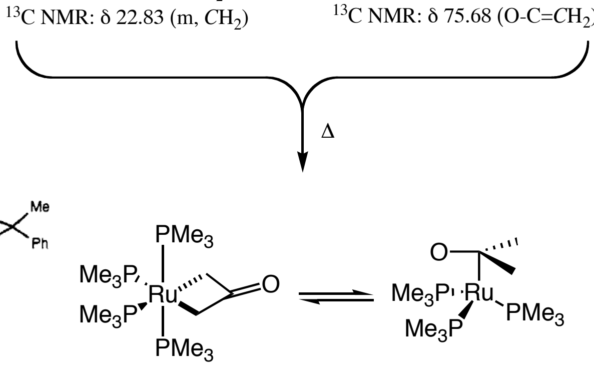
Ru



IR: ν(CH_2COCH_3) 1620 cm^{-1}
^{1}H NMR: δ 1.90 (m, CH_2)
^{13}C NMR: δ 22.83 (m, CH_2)

^{1}H NMR: δ 3.50, δ 3.96 (O-C=CH_2)
^{13}C NMR: δ 75.68 (O-C=CH_2)



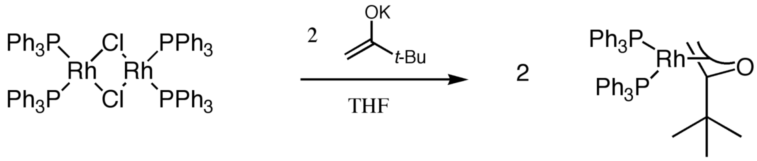


Bergman & Anderson, *JACS* **1990**, *112*, 5670
Bergman & Anderson, *Organometallics* **1991**, *10*, 3326

Survey of Late Transition Metal Enolates

Second Row Metals: Rhodium

Rh



IR: ν(*O*-*C*-CH_2) 1440, 1099 cm^{-1}

^1H NMR: δ 2.82, 3.57 (C*H*$_2$, $J_{C\text{-}H}$ = 153)

^{13}C NMR: δ 54.3 (O-C-*C*H_2, $J_{Rh\text{-}C}$ = 23.5)

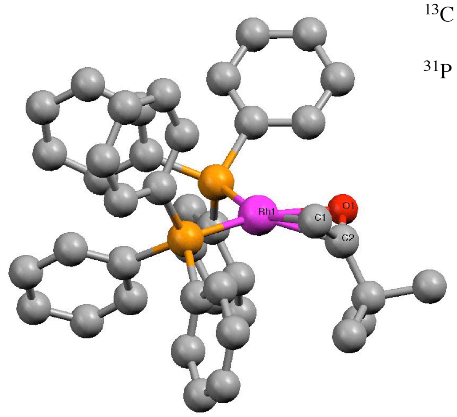
δ 175.0 (O-*C*-CH_2, $J_{Rh\text{-}C}$ = 4.6)

^{31}P NMR: δ 38.1 ($J_{P\text{-}P}$ = 36.9, $J_{Rh\text{-}C}$ = 193.0)

δ 55.7 ($J_{P\text{-}P}$ = 36.9, $J_{Rh\text{-}C}$ = 222.8)

Bond lengths (Å):

Rh(1)-C(1)	2.163	
Rh(1)-C(2)	2.208	
Rh(1)-O(1)	2.131	
O(1)-C(2)	1.305	η^3
C(1)-C(2)	1.391	η^3



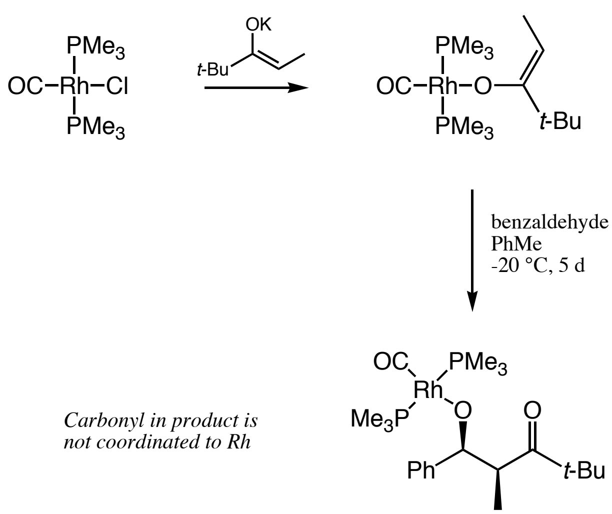
At higher T the ^1H signals coalesce, indicating isomerization. The ^{31}P signals do not, however. Therefore a four-coordinate intermediate is likely. Observed Δ*G* = 14.4 kcal/mol.

Slough, *Organometallics* **1994**, *13*, 890
Also see:
Milstein, *JACS* **1982**, *104*, 5227
Werner, *Organometallics* **1995**, *14*, 619

Survey of Late Transition Metal Enolates

Second Row Metals: Rhodium

Rh



IR: no organic C=O stretch

^1H NMR: δ 4.14 (q, O-C=C*H*)

^{13}C NMR: δ 137.23 (O-C=*C*H)

δ 169.78 (O-*C*=CH)

Carbonyl in product is not coordinated to Rh

Catalytic aldol also achieved using enol-silanes.

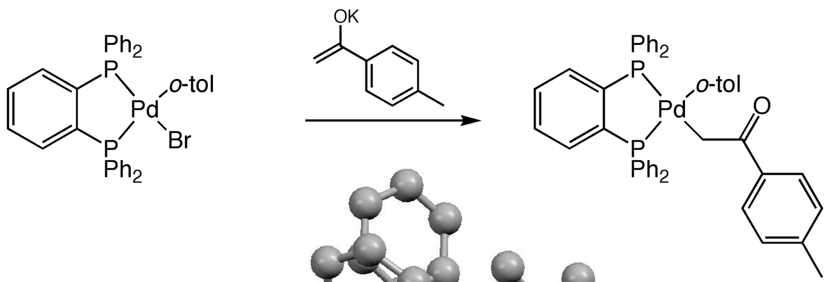
79% yield
all *syn*

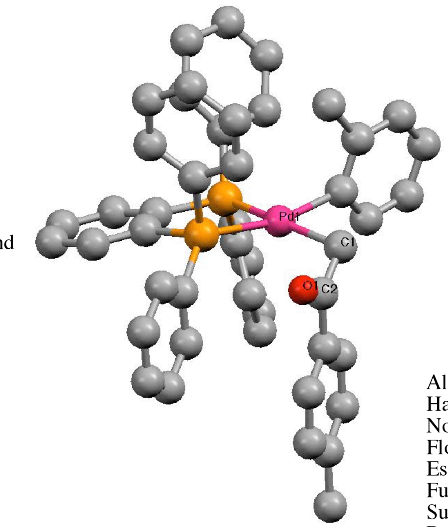
Bergman & Heathcock, *JACS* **1989**, *111*, 938

Survey of Late Transition Metal Enolates

Second Row Metals: Palladium

Pd





Bond lengths (Å):

Pd(1)-C(1) 2.145
C(1)-C(2) 1.454 ←
C(2)-O(1) 1.225 ← *C*-bound

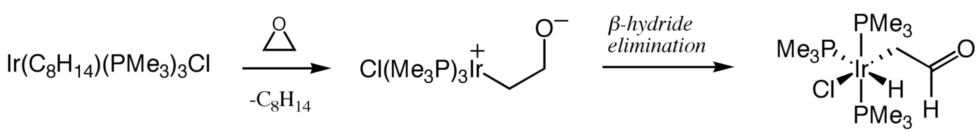
Hartwig, *Organometallics* **2004**, *23*, 3398

Also see:
Hartwig, *JACS* **2001**, *123*, 5816
Novak, *Organometallics* **2002**, *21*, 1462
Floriani, *Organometallics* **1993**, *12*, 4899
Espinet, *Organometallics* **1999**, *18*, 5571
Fuchita, *Inorg. Chim. Acta* **1993**, *208*, 43
Suzuki, *Inorg. Chim. Acta* **1993**, *208*, 225
Brown, *ACIEE* **1996**, *35*, 657

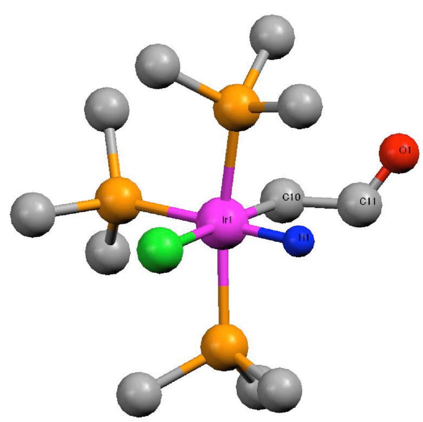
Survey of Late Transition Metal Enolates

Second Row Metals: Iridium

Ir



IR: ν(CH_2COH) 1663 cm^{-1}
^1H NMR: δ 1.92 (app. q, CH_2)
δ 8.76 (t, C*HO*)
^{31}P NMR: δ -52.4 (1P)
δ -45.2 (2P, $J_{P\text{-}P} = 21$)



Bond lengths (Å):

Ir(1)-C(10) 2.127
Ir(1)-H(1) 1.64
C(10)-C(11) 1.478 ←
C(11)-O(1) 1.210 ← *C*-bound

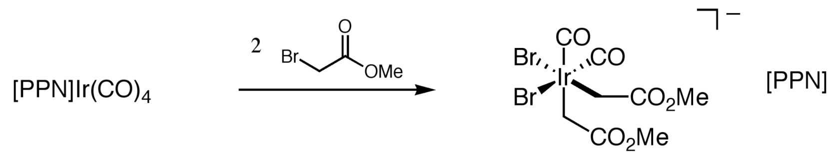
Complexes such as this have been implicated in TM catalyzed isomerization of epoxides.

Milstein, *JACS* **1982**, *104*, 3773
Also see:
Crisp, *Aust. J. Chem.* **1986**, *39*, 1363

Survey of Late Transition Metal Enolates

Second Row Metals: Iridium

Ir



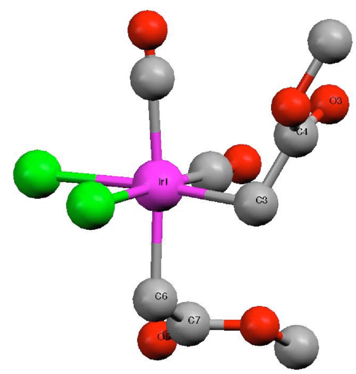
$[PPN] = N(PPh_3)_2^+$

IR: $\nu(CH_2CO_2\text{-}t\text{-Bu})$ 1712 cm^{-1}
^1H NMR: δ 2.70 (d, $J_{H\text{-}H}$ = 9), δ 3.15 (d, $J_{H\text{-}H}$ = 9) (CH_2)
δ 2.73 (d, $J_{H\text{-}H}$ = 8.8), δ 3.34 (d, $J_{H\text{-}H}$ = 8.8) (CH_2)
^{13}C NMR: δ 14.5, δ 16.1 (CH_2)
δ 181.3 (CO_2CH_3)

Bond lengths (Å):

trans to CO
Ir(1)-C(6) 2.038
C(6)-C(7) 1.489 ← *C*-bound
O(5)-C(7) 1.201 ←

trans to Br
Ir(1)-C(3) 2.158
C(3)-C(4) 1.498 ← *C*-bound
C(4)-O(3) 1.217 ←

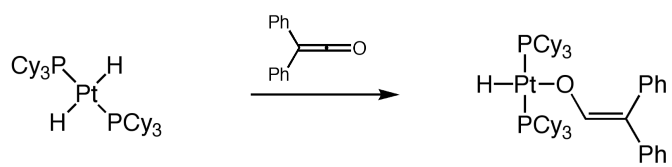


Cenini, *Organometallics* **1990**, *9*, 929

Platinum Enolates

An O-bound enolate

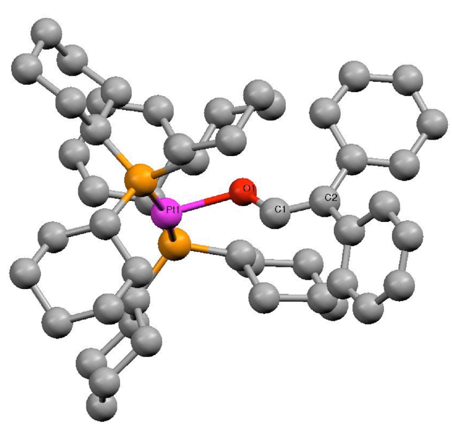
Pt



^1H NMR: δ 7.0 (O-C*H*=C)

Bond lengths (Å):

Pt(1)-O(1) 2.124
C(1)-C(2) 1.37 ← *O*-bound
C(1)-O(1) 1.33 ←

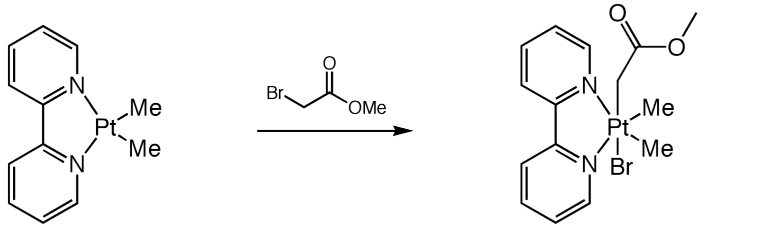


Musco, *J. Organomet. Chem.* **1986**, *301*, 237

Platinum Enolates

Oxidative Addition Caught in the Act

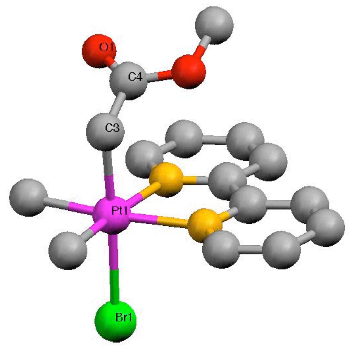
Pt



IR: ν(CH_2*CO_2*-*t*-Bu) 1714 cm^{-1}
^{1}H NMR: δ 2.01 (C*H_2*, $J_{\text{Pt-H}} = 96$)

Bond lengths (Å):

Pt(1)-C(3)	2.077	
C(3)-C(4)	1.482 ←	*C*-bound
C(4)-O(1)	1.207 ←	



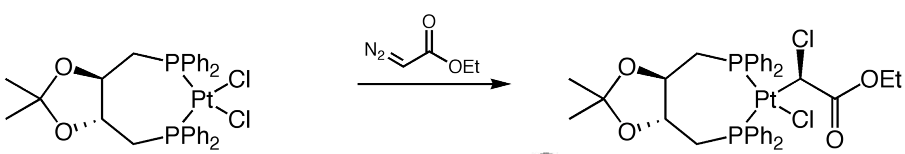
Crystal structure of related acid enolate shows intermolecular hydrogen bonds. See: Puddephatt, *Organometallics* **2000**, *19*, 1635.

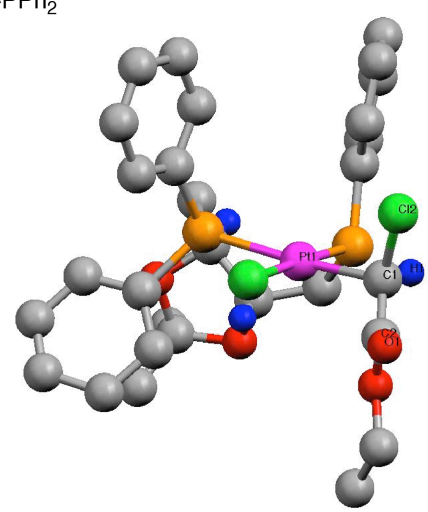
Puddephatt, *Organometallics* **1993**, *12*, 4592

Platinum Enolates

Chiral Enolates

Pt





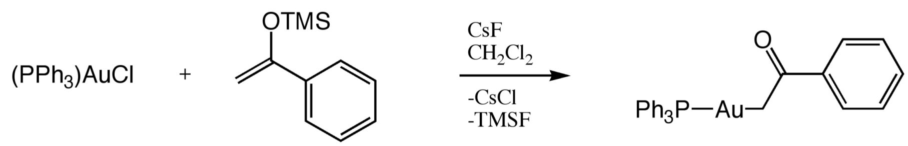
(one Ph omitted for clarity)

Bergamini, *Organometallics* **1991**, *10*, 2989

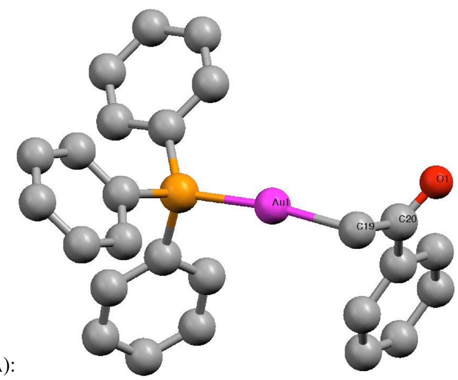
Survey of Late Transition Metal Enolates

Second Row Metals: Gold

Au



IR: ν(*C*=*O*) 1632 cm^{-1}
^{1}H NMR: δ 3.16 (C*H*$_2$, $J_{\text{P-H}}$ = 11.0)
^{13}C NMR: δ 43.1 (*C*H$_2$, $J_{\text{C-P}}$ = 66.0)
δ 202.3 (*C*=O, $J_{\text{C-P}}$ = 4.4)



Bond lengths (Å):

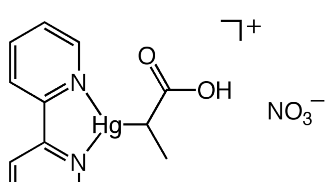
Au(1)-C(19)	2.101
C(19)-C(20)	1.459 ← *C*-bound
O(1)-C(20)	1.225 ← *C*-bound

Ito, *J. Organomet. Chem.* **1988**, *342*, C41
Also see:
Jones, *J. Organomet. Chem.* **1993**, *456*, 305
Bolesov, *J. Organomet. Chem.* **1989**, *369*, 267
Bolesov, *J. Organomet. Chem.* **1985**, *286*, 129
Floriana, *JACS* **1986**, *108*, 8298

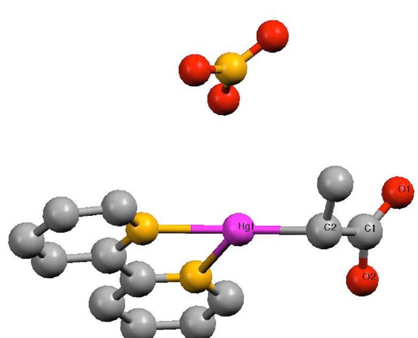
Survey of Late Transition Metal Enolates

Second Row Metals: Mercury

Hg



IR: ν(*CO*$_2$H) 1682 cm^{-1}



These complexes are stable as the *C*-bound enolate even in the presence of acidic protons. In many cases, intermolecular hydrogen bonds can be observed in the solid state.

Mercurial enolates can be isolated and undergo free radical reactions. See: Russel, *JACS* **1979**, *101*, 1312; *JOC* **1990**, *55*, 1080.

Enolates with chiral Hg can be prepared and do not invert! See: Sokolov, *J. Organomet. Chem.* **1980**, *201*, 29.

Trasmetallation with palladium, followed by intramolecular Heck reaction has also been achieved. See: Larock, *TL* **1990**, *31*, 17; *TL* **1989**, *30*, 2767.

Bond lengths (Å):

Hg(1)-C(2)	2.11
C(1)-C(2)	1.505 ← *C*-bound
O(1)-C(1)	1.205 ← *C*-bound
O(2)-C(1)	1.333

Colig, *Organometallics* **1993**, *12*, 4708

Also see:
Popovic, *J. Organomet. Chem.* **1991**, *411*, 19
Small, *Acta Cryst.* **1981**, *B37*, 2223
Korpar-Colig, *Acta Cryst.* **1992**, *C48*, 1116
Kazitsyna, *J. Struct. Chem. (Engl. Trans.)* **1967**, *8*, 911
Strelenko, *J. Organomet. Chem.* **1980**, *192*, 297
Barluenga, *Synthesis*, **1979**, 893