Tetrahedron Letters Vol. 21, pp 2873 - 2876
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0040-4039/80/0722-2873$02.00/0

PREPARATION OF Pd(II) ENOLATE COMPLEXES AND THEIR REACTIONS

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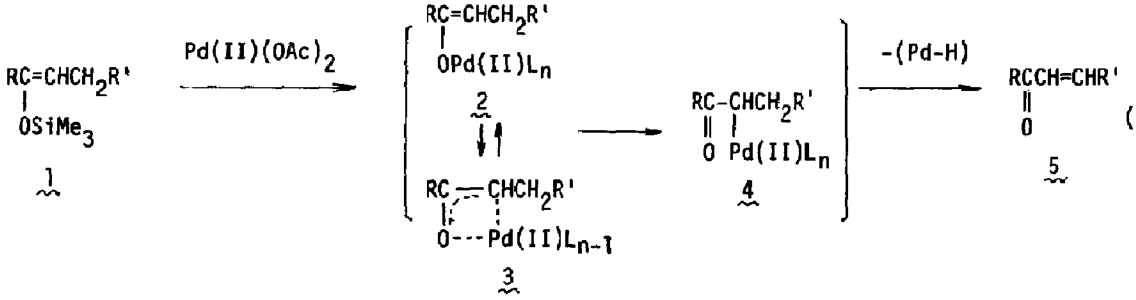
Summary: Palladium(II) enolate complexes have been prepared by the reaction of $Pd(II)Cl_2$-$(PhCN)_2$ with trimethylsilyl enol ethers and reacted with CO and ethylene.

We reported a series of reactions of silyl enol ethers with metal salts such as Ag_2O,[1] $CuCl_2$,[2] $FeCl_3$,[2] and $PdCl_2$,[2] in which we assumed the silicon-oxygen bond of silyl enol ethers is oxidatively cleaved with metal salts.

The reaction of silyl enol ethers with $Pd(II)(OAc)_2$ afforded α,β-unsaturated ketones and aldehydes[3a] according to the following equation.

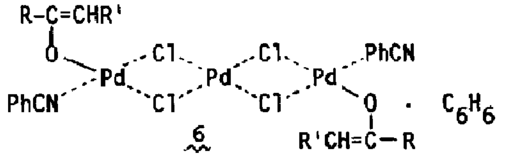


(1)

The Pd(II) induced dehydrosilylation of silyl enol ether (eq 1) was explained in terms of a β-elimination of palladium(II) hydride from σ-(α-acylalkyl)palladium(II) complex (4), which may be derived via palladium(II) enolate (2) or oxo-π-allylpalladium(II) intermediate (3).

Now we wish to describe (i) the formation of stable palladium(II) enolate complexes (6), which have no possibility of β-elimination of palladium(II) hydride, by the reaction of $Pd(II)$-$Cl_2(PhCN)_2$ with trimethylsilyl enol ethers of ketones such as tert-butyl neopentyl ketone,[4] camphor and pinacolone, and (ii) some reactions of the palladium(II) complexes (6) with CO, ethylene and butadiene.

To a solution of Pd(II)Cl_2(PhCN)$_2$ (2.5 mmol) in benzene (30 ml), trimethylsilyl enol ethe of tert-butyl neopentyl ketone (3.0 mmol) was added and stirred at room temperature overnight. After the solution was filtered, the filtrate was triturated with hexane to precipitate a yell palladium(II) complex (6a) in 81% yield. The structural assignment is based on elemental analysis [Calcd for $C_{40}H_{54}O_2N_2Cl_4Pd_3$ C, 45.50; H, 5.12; N, 2.65; Cl, 13.46. Found C, 45.48; H, 5.22; N, 2.60; Cl, 13.45] and, spectral data [NMR ($CDCl_3$ with TMS) δ 1.20 (s, 18H), 1.35 (s, 18H), 4.00 (broad s, 2H), 7.25 (s, 6H), 7.30-7.85 (m, 10H); IR (KBr disk) 2270, 1650, 1085, 762, 687, 335 cm^{-1}]. The intense IR band at 1650 cm^{-1} and NMR signal at δ 4.00, which are comparable with those of the starting silyl enol ether[5] are taken to indicate the Pd(II) enola structure (6a).



6

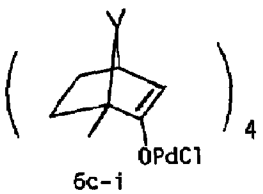
a : R=tert-Bu, R'=tert-Bu

b : R=Ph, R'=tert-Bu

Trimethylsilyl enol ether of phenyl neopentyl ketone was similarly reacted with Pd(II)Cl_2(PhCN)$_2$ to afford palladium(II) enolate complex (6b).

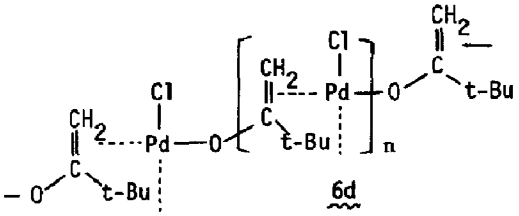
But, the similar treatment of trimethylsilyl enol ether of camphor with Pd(II)Cl_2(PhCN)$_2$ produc a reddish palladium(II) complex (6c-i) in 80-90% yield with a small amount of a yellowish palladium(II) complex (6c-ii).[6] The reddish palladium(II) complex 6c-i, of which elemental analysis showed a molecular formula $C_{10}H_{15}ClOPd$, existed in chloroform solution as tetramer [Molecular weight (Vapor Pressure Osmometry in $CHCl_3$): Calcd for tetramer 1172. Found 1140]. Spectral data [NMR ($CDCl_3$ with TMS) δ 0.5-2.4 (14H), 3.85 (s, 1H); IR (KBr disk) 1657, 1062 cm^{-} are consistent with palladium(II) enolate structure (6c-i).

Moreover, the reaction of trimethylsilyl enol ether of pinacolone with Pd(II)Cl_2(PhCN)$_2$ also afforded a yellow Pd(II) complex (6d), which has a molecular formula $C_6H_{11}ClOPd$, in 80% yield. The IR spectrum of 6d did not show any band at 1600-1700 cm^{-1} region, but did show an intense band at 1508 cm^{-1}. The NMR spectrum of 6d ($CDCl_3$) exhibited very broad signals at δ 1.0-2.0 and δ 2.7-4.1. Molecular weight determination indicated that palladium(I complex (6d) has a polymeric structure in chloroform [Mol. wt. 10600]. A number of alternati structures are possible for 6d, one of which would be a polymer as shown below.



6c-i

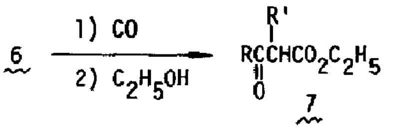
Palladium(II) complexes 6a, 6b, 6c-i and 6d are all stable even in air, and slowly decomp sed in solution. Attempts to prepare crystals of the palladium(II) complexes (6) have so far failed.



6d

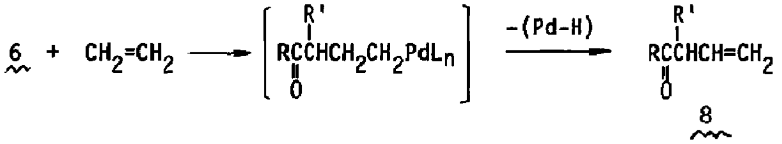
As expected, palladium(II) complexes 6a, 6b and 6c-i thus prepared reacted with CO, ethylene and butadiene to lead carbon-carbon bond formation at α-carbon of the starting ketones in high yields.

For the instance, palladium(II) complex (6a) (1 mmole equiv.) was reacted in benzene (10 ml) with 50 atm. of CO at 50°C for 5 hr and subsequently treated with ethanol (10 ml) under 50 atm. of CO at 50°C for 3 hr to produce ethyl t-butylpivaroylacetate (7a) in an almost quantitative yield [7a : IR (neat) 1740, 1712 cm^{-1}; NMR ($CDCl_3$ with TMS) δ 1.05 (s, 9H), 1.10 (s, 9H), 1.25 (t, 3H), 3.75 (s, 1H), 4.15 (q, 2H)]. Similarly, palladium(II) complexes (6b and 6c-i) were reacted with CO to give the corresponding β-keto esters 7b and 7c-i[7] in high yields.



a	R=tert-Bu, R'=tert-Bu	100%
b	R=Ph, R'=tert-Bu	86%
c	3-carboethoxycamphor	85% (exo : endo=1:4)

The reaction of palladium(II) complexes (6) with ethylene was carried out by heating a solution of 6 (1 mmole equiv.) in toluene (15 ml) with 50 atm. of ethylene at 50°C for 5 hr. The reaction of 6a and 6b with ethylene furnished 2,2-dimethyl-4-tert-butyl-5-hexen-3-one (8a) (87%) and phenyl (1-tert-butyl-2-propenyl) ketone (8b) (75%), respectively, as a single product.

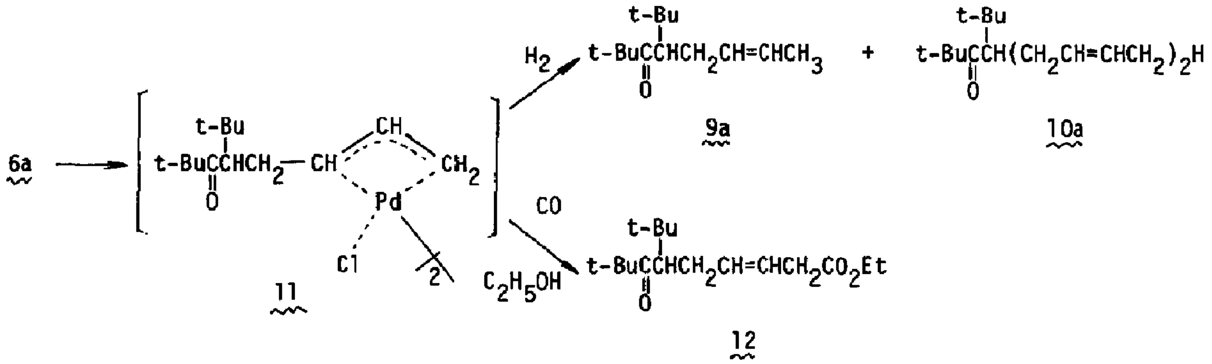


a : R=tert-Bu, R'=tert-Bu
b : R=Ph, R'=tert-Bu

But, in the reaction (50°C, 7 hr) of palladium(II) complex (6c-i) with ethylene, a mixture of 3-vinylcamphor, (Z)-3-ethylidenecamphor[8] and (E)-3-ethylidenecamphor[8] was produced in 5%, 27% and 46% yields, respectively.

Palladium(II)complex 6d was also reacted with CO and ethylene but in low yields (∼10%).

Finally, palladium(II) complex (6a) (1 mmol equiv.) was heated with butadiene (5 ml) in benzene (10 ml) at 80°C for 4 hr to afford a yellow solution of which hydrogenation (50 atm. H_2, 20°C, 10 hr) gave 2,2-dimethyl-4-tert-butyl-6-octen-3-one (9a) in 62% yield together with a small amount of 10a.



On the other hand, the yellow solution was treated with CO (50 atm) in the presence of ethanol (10 ml) at 50°C for 4 hr to give 12 in moderate yield. This finding suggests that π-allyl palladium(II) complex (11) may be formed as an intermediate.

References and Notes.

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5) Trimethylsilyl enol ether of tert-butyl neopentyl ketone : IR (neat) 1647 cm^{-1}; NMR (CDCl$_3$ with TMS) δ 0.19 (s, 9H), 0.95 (s, 9H), 0.98 (s, 9H), 4.32 (s, 1H).

6) Palladium(II) complex 6c-ii was separated from 6c-i by precipitating from chloroform solution with hexane. 6c-ii Molecular formula $C_6H_{15}ClOPd$; IR (KBr disk) 1630 cm^{-1} ; Osmometric molecular weight determination indicated 6c-ii is existing in chloroform as octamer.

7) endo-3-Carbethoxycamphor : NMR (CDCl$_3$ with TMS) δ 3.20 (d, 1H, J=5.3 Hz). exo-3-Carbethoxy camphor : NMR (CDCl$_3$ with TMS) δ 2.75 (s, 1H).

8) (Z)-3-Ethylidenecamphor : IR (neat) 1726, 1658; NMR (CDCl$_3$ with TMS) δ 0.80 (s, 3H), 0.90–0.95 (m, 6H), 1.2–2.0 (m, 4H), 2.05 (d, 3H), 2.35 (d, 1H), 5.75 (q, 1H).

(E)-3-Ethylidenecamphor : IR (neat) 1730, 1664; NMR (CDCl$_3$ with TMS) δ 0.75 (s, 3H), 1.00 (s, 6H), 1.2–2.0 (m, 4H), 1.75 (d, 3H), 2.65 (m, 1H), 6.35 (q, 1H).

(Received in Japan 26 April 1980)