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CONFIGURATIONAL PRODUCT CONTROL IN REACTIONS OF TRANS- AND CIS-DIALKYLBIS(TERTIARY PHOSPHINE)PALLADIUM(II) WITH CARBON MONOXIDE. EVIDENCE SUPPORTING AN ALKYL MIGRATION MECHANISM IN CO INSERTION INTO Pd-C BOND

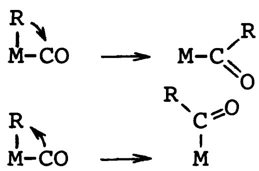
Fumiyuki OZAWA and Akio YAMAMOTO*
Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, Nagatsuta, Midori-ku,
Yokohama 227

Reactions of trans- and cis-PdR_2L_2 (R = Me, Et, Pr, and Bu; L = tertiary phosphine ligands) with carbon monoxide in solutions were found to give strikingly different products depending on the configurations of the dialkylpalladium complexes. The results can be explained reasonably by assuming reactions proceeding by alkyl migration mechanisms.

Insertion of carbon monoxide into a transition metal-carbon bond constitutes one of the most important elementary steps in transition metal-promoted reactions utilizing carbon monoxide.[1] Mechanistically the CO insertion process is believed to proceed by migration of an alkyl group to a coordinated CO ligand to give an acyl group (a) and not by a CO migration process (b):

(a) Alkyl migration

(b) CO migration



Unequivocal evidence for supporting the alkyl migration mechanism, however, has been reported in only one case regarding octahedral methyl(pentacarbonyl)manganese[2] and in the great majority of cases the reaction mechanism involving the alkyl migration has been implicated based on indirect experimental data.[3] We now report that the reactions of CO with square planar dialkylpalladium complexes PdR_2L_2[4-7] proceed under configurational constraint and the reaction products can be accounted for most consistently by assuming the alkyl migration mechanism.

The reactions of carbon monoxide with trans- and cis-PdR_2L_2 proceed readily at room temperature in toluene to give products which have been characterized by GLC analysis as summarized in the Table. Pd(0) complexes having carbonyl and tertiary phosphine ligands were recovered from the toluene solution after the completion of reactions as confirmed by IR spectra. A clear-cut dichotomy is observed in the reaction products of trans- and cis-$PdEt_2L_2$, the former providing 3-pentanone whereas the latter affording ethylene and propionaldehyde accompanied by only a minor

Table. The Reaction Products of PdR_2L_2 with CO[a)]

Compounds	Products (mol/mol of complex)			
	R(-H)	RCOR	RCOCOR	RCHO
trans-$PdMe_2(PEt_3)_2$	—	0.92	0.0	—
trans-$PdMe_2(PEt_2Ph)_2$	—	0.83	0.0	—
trans-$PdMe_2(PMePh_2)_2$	—	0.80	0.0	—
trans-$PdMe_2(PEtPh_2)_2$	—	0.89	0.0	—
trans-$PdEt_2(PMe_2Ph)_2$	0.0	1.0	—[b)]	trace
trans-$PdEt_2(PEt_2Ph)_2$	0.0	1.0	—[b)]	trace
trans-$PdPr_2(PMePh_2)_2$	0.0	0.98	0.0	0.0
trans-$PdBu_2(PMe_2Ph)_2$	0.0	1.1	0.0	0.0
cis-$PdMe_2(PEt_2Ph)_2$	—	0.79	0.03	—
cis-$PdMe_2(PMePh_2)_2$	—	0.73	0.08	—
cis-$PdMe_2(PEtPh_2)_2$	—	0.72	0.06	—
cis-$PdEt_2(PMe_2Ph)_2$	0.94	0.06	—[b)]	0.83
cis-$PdEt_2(PEt_2Ph)_2$	0.86	0.06	—[b)]	0.72

a) In toluene, at room temperature. b) Not measured.

amount of 3-pentanone.

$$\underline{cis}\text{-}PdEt_2L_2 + CO \longrightarrow EtCHO + C_2H_4 + Pd(CO)_nL_m$$

$$\underline{trans}\text{-}PdR_2L_2 + CO \longrightarrow RCOR + Pd(CO)_nL_m$$

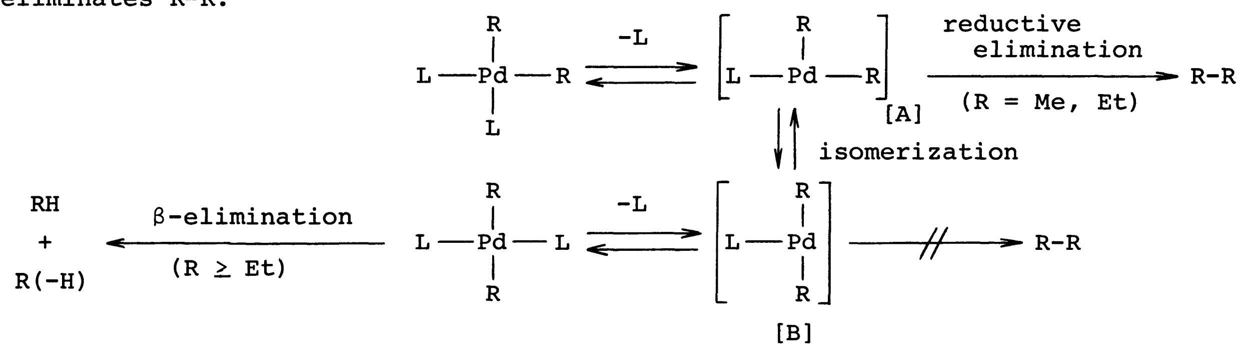
R = Me, Et, Pr, and Bu

The results with _trans_- and _cis_-dimethyl homologs are less dramatic giving acetone as the main product but formation of significant amounts of diketone only from the _cis_-dimethyl complexes was noticed, in contrast to the absence of the diketone formation in the reactions with the _trans_-isomers.

$$\underline{cis}\text{-}PdMe_2L_2 + CO \longrightarrow \underset{\text{(major)}}{MeCOMe} + \underset{\text{(minor)}}{MeCOCOMe} + Pd(CO)_nL_m$$

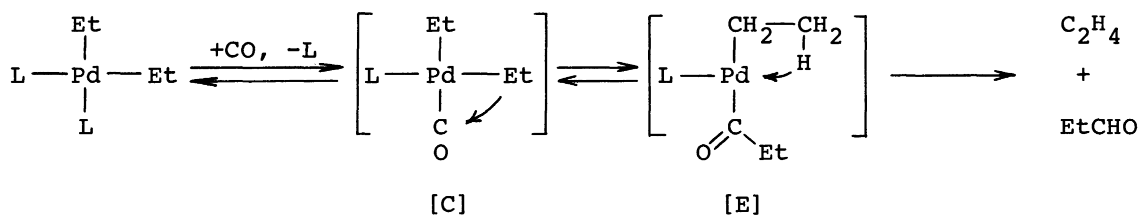
The reactions of the dialkyl complexes with CO are retarded by addition of tertiary phosphines. The rate of CO absorption of _cis_-$PdMe_2L_2$ was significantly slower than that of _trans_-$PdMe_2L_2$. The reaction of $PdMe_2L_2$ with CO was found out to be intramolecular since a reaction of a 1 : 1 mixture of _trans_-$Pd(CH_3)_2L_2$ and trans-$Pd(CD_3)_2L_2$ with CO liberated CH_3COCH_3 and CD_3COCD_3 with negligible amount of CH_3COCD_3.

These conspicuous differences in the reactions of PdR_2L_2 with CO depending on the configurations of the starting dialkylpalladium complexes are considered to be closely related with the previously reported thermolysis behavior of the dialkylpalladium complexes dictated by their configurations.[5-8)] _Trans_-$PdEt_2L_2$ on thermolysis liberated ethane and ethylene as β-elimination products, whereas cis-PdR_2L_2 (R = Me, Et) cleanly released the reductive elimination products. Kinetic studies revealed that the reductive elimination is preceded by dissociation of a tertiary phosphine ligand to give a three coordinated T-shaped intermediate PdR_2L [A] which reductively eliminates R-R.[6)]

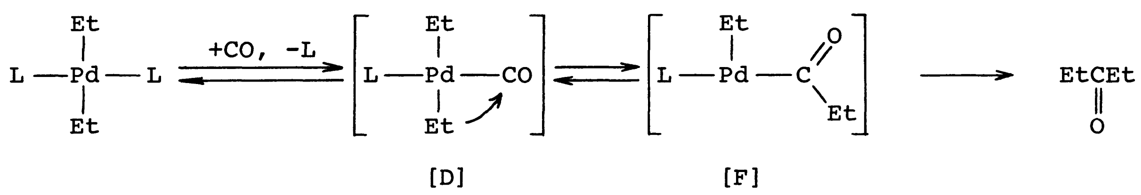


Trans-$PdMe_2L_2$ reductively eliminates ethane only after its isomerization to the T-shaped cis-dimethyl intermediate [A] and existence of an energy barrier between [A] and another T-shaped intermediate trans-$PdMe_2L$ [B] was revealed in agreement with theoretical treatment based on MO calculations.[8)]

Taking these previous informations into account we now consider that the reaction patterns of PdR_2L_2 with CO can be explained most satisfactorily by assuming three-coordinated acyl-alkylpalladium intermediates formed by alkyl migration. In the reactions of cis- and trans-$PdEt_2L_2$ one of the tertiary phosphine ligands will be displaced first by CO most probably with retention of the configuration giving [C] or [D]. The ensuing migration of an ethyl group to the coordinated CO ligand affords the ethyl-propionyl intermediate [E] or [F]:



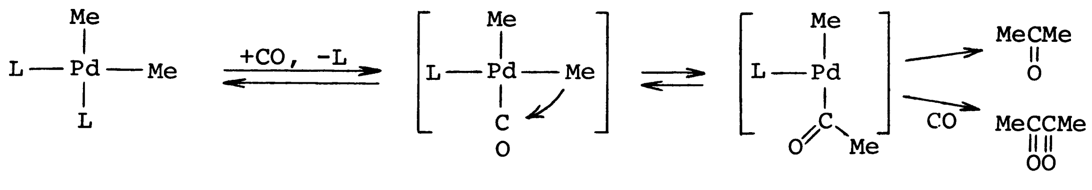
(1)



(2)

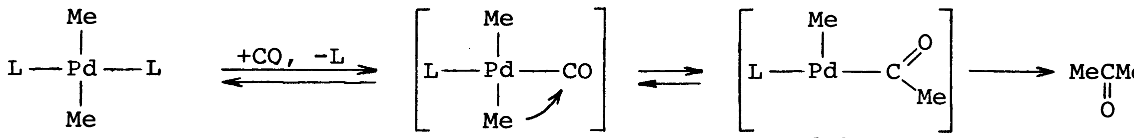
In the intermediate T-shaped complexes [E] and [F], the cis-isomer [F] has a favorable configuration for the immediate reductive elimination of 3-pentanone, whereas the trans-isomer [E] has a vacant site suitable for β-hydrogen elimination to liberate ethylene and EtCHO by reductive elimination of the propionyl and the hydrido ligands. The alternative CO migration to the ethyl group in [C] and [D] would give 3-pentanone from cis-$PdEt_2L_2$ and ethylene and EtCHO from trans-$PdEt_2L_2$ in disagreement with the experimental results.

The formation of some diketone from cis-$PdMe_2L_2$ and none from trans-$PdMe_2L_2$ can be also accounted for consistently by assuming configurational stabilities of the acyl-alkyl intermediates formed by the alkyl migration. The intermediate trans-Pd(OCMe)MeL [G] produced from cis-$PdMe_2L_2$ by methyl migration is considered less prone to reductive elimination than the cis-acetyl-methyl isomer [H] and may undergo further CO insertion to give MeCOCOMe.



(3)

[G]



(4)

[H]

In fact the reaction of CO with cis-$PdMe_2L_2$ proceeded more slowly than that with trans-$PdMe_2L_2$. Furthermore addition of $HNEt_2$ to the reaction system of cis-$PdMe_2L_2$ with CO gave 20 % of $MeCONEt_2$ per palladium in addition to acetone, indicating that the acetyl group in [G] was trapped by the nucleophile, whereas similar trapping experiment using trans-$PdMe_2L_2$ gave no amide. Whether the further CO insertion takes place into Pd-Me to give bis-acetyl or into Pd-COMe to give pyruvoyl-methyl complex is presently unknown.

The mechanism presented here seems reasonable if the behavior of dialkylpalladium complexes thermolyzed under constraint of planar configurations[6,7] is taking into consideration. The other mechanistic possibilities, however, such as those involving penta-coordinated intermediates can not be excluded. In the reactions of alkylnickel complexes with CO, formation of acetone and 2,3-butanedione from $NiMe_2$(bipyridine) and of ethylene and propionaldehyde from $NiEt_2(Ph_2PCH_2CH_2PPh_2)$ was observed in contrast to the present results regarding the palladium analogs.[9] In the reactions of nickel complexes different mechanisms from those of palladium alkyls involving the penta-coordinated intermediates may be operative.

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