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CATALYSIS OF CYCLOPROPENYLIDENE PALLADIUM(II) COMPLEXES FOR THE ISOMERIZATION OF QUADRICYCLANE TO NORBORNADIENE

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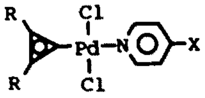
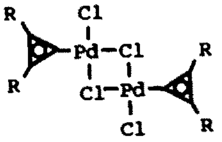
Abstract: New palladium complexes of cyclopropenylidenes of the type of trans-$Cl_2Pd(CP)(Py-X)$ have been synthesized, where CP is di-t-butylcyclopropenylidene or bis(diisopropylamino)cyclopropenylidene, and Py-X is 4-substituted pyridines (X = H, CH_3, CN). The complexes revealed high catalytic activity toward the cycloreversion of quadricyclane (Q) to norbornadiene (NBD). Based on a detailed kinetic study, it is concluded that liberation of Py-X is prerequisite for the metal to interact with Q. The rate of the reaction obeys a rate expression $d[NBD]/dt = k^{cat}[cat]^{1/2}[Q]$. The apparent catalytic activity (k^{cat}) can be related to the catalytic activity (k^*) of the coordinatively unsaturated species $Cl_2Pd(CP)$ and the dissociation constant (K) for pyridine liberation by $k^{cat} = k^*K^{1/2}$. The values k^* and K are discussed in relation to the nature of ligands.

Molecular rearrangements of highly strained compounds catalyzed by transition-metal complexes have attracted considerable attention during last two decades.[1] Recently, in connection with the importance of light energy storage system based on photochemical formation of strained molecules special cautions have been focused on the catalysis of transition-metal complexes for exothermic valence isomerizations of the kind of molecules, especially for quadricyclane (Q) to norbornadiene (NBD).[2] In the course of our study on molecular energy storage,[3] we have screened diverse transition metal complexes for the isomerization of Q to NBD, and found cyclopropenylidene palladium complexes (1, 2 and 4) exhibited high catalytic activity.[4]



1 a; R=t-Bu, X=H
b; R=t-Bu, X=CH_3
c; R=t-Bu, X=CN

2 a; R=i-Pr_2N, X=H
b; R=i-Pr_2N, X=CH_3
c; R=i-Pr_2N, X=CN



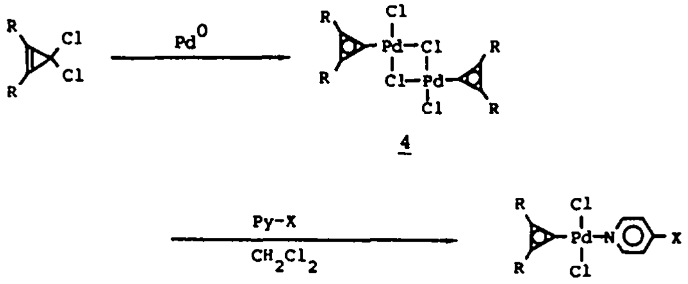
4 a; R=t-Bu
b; R=i-Pr_2N

Besides the interest in their use as the catalyst, these new type of complexes would benefit studies of the mechanisms of the catalysis of d^8 square planar complexes as following. Information concerning the actual catalytic species is significant both to mechanistic consideration of the electronic structure of metal-carbocycle interaction and design of efficient catalysts. The possible key intermediate is thought to involve a coordination of Q to the metal either via an exchange with the originally coordinated ligand or by extension of the coordination around the metal. These two reaction features can be related to the widely studied two mechanisms for substitution reaction of square planar complexes, $MA_3X + Y \rightarrow MA_3Y + X$. One is a dissociative path via coordinatively unsaturated species and the other an associative one via trigonal bipyramidal transition state.[5] Using a species such as $MLL'X_2$, the ability to change systematically just one ligand L' would open a unique method to perform a study of such sort. However, for these species, the tendency toward disproportionation to more symmetric one ($ML_2X_2 + ML'_2X_2$) has obviously deterred investigations.[6]

Cyclopropenylidene metal complexes might offer us such an opportunity, because the cyclopropenylidene ligand is inert to dissociation despite of its electroneutrality. This paper deals with the syntheses of cyclopropenylidene Pd(II) complexes and examination of the mechanisms of the cycloreversion of Q to NBD catalyzed by them.

Cyclopropenylidene palladium complexes, **1**, **2** and **4** were prepared according to Scheme 1, as partly reported in our previous report.[7] The structural proof with respect to the cis- and trans-configurations of **1** and **2** was obtained from their FIR spectra. If the complexes have cis-configuration, one of the Pd-Cl bond should receive the large trans-influence of the carbene ligand to give the Pd-Cl stretching band at around 280 cm^{-1}. As given in experimenatal part, **1** and **2** gave one or two Pd-Cl stretching bands in the region 325 cm^{-1} ∿ 350 cm^{-1}, and no bands were observed at lower frequency region 320 cm^{-1} ∿ 260 cm^{-1}. Thus, the FIR spectra of the complexes **1** and **2** are compatible with their trans configurations.

Scheme 1



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For all complexes, quantitative cycloreversion of Q to NBD was observed based on glc analysis and NMR measurement. Kinetic measurement was carried out at 27 °C in $CHCl_3$ (or $CDCl_3$) and CH_2Cl_2. The kinetic order with respect to the catalysts was determined by measuring pseudo-first order kinetic constant (k) of the formation of NBD using various concentrations of catalyst (Table I). Results shown in Table I give a one half kinetic order of the reaction in the catalyst as demonstrated in Figure 1 for **1a** and **2a** for examples. Thus, the cycloreversion catalyzed by **1** and **2** is considered to be essentially first order in Q and one-half order in the catalyst, and the experimental rate expression can be written as

$$d[NBD]/dt = k[Q] = k^{cat}[cat]^{1/2}[Q] \quad \text{----- eq. 1}$$

This kinetic feature excludes the mechanism in which an axial site of the square planar complex is an active site (Mechanism B), since the rate of the reaction should be first order in the catalyst in this case. As shown in Table I, in each series of complex, catalytic activity k^{cat} increases with the electron-withdrawing nature of the substituent on the 4-position of the pyridine ligand. These results can be explained in terms of the mechanism A, in which the dissociation of pyridine is assumed as a prerequisite for Q to interact with "catalyst". The mechanism affords a theoretical rate expression[9]

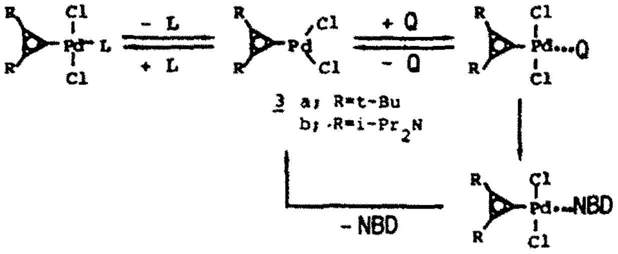
$$d[NBD]/dt = k^{*}K^{1/2}[cat]^{1/2}[Q] \quad \text{------ eq. 2}$$

Inspection of eq. 1 and eq. 2 gives a relationship, $k^{cat} = k^{*}K^{1/2}$. Thus, catalyst activity k^{cat} can be divided into two factors, k^{*} and K, where k^{*} represents a catalytic activity of coordinatively unsaturated species (3), and its equilibrium concentration is determined by K (Scheme 2, see References and Notes.).[9] In this mechanism, when L is added externally we may set up an equation[9]

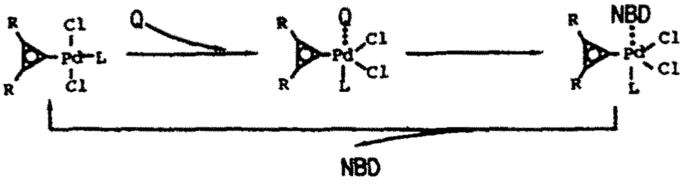
$$\frac{k^2 - k_\ell^2}{k_\ell} = k^{*}[L]_{add} \qquad \text{----- eq. 3}$$

where k and k_ℓ are the pseudo first order kinetic constants in the absence and in the presence of externally added pyridine of its concentration of $[L]_{add}$, respectively. As shown in Figure 2 for the cases of **1a**, **c**, $(k^2 - k_\ell^2)/k_\ell$ varies linearly with $[L]_{add}$, and the slope of the plots gives k^{*} according to eq. 3. Thus, it is reasonable to consider that predominant catalytic species is the coordinatively unsaturated species (3).

Mechanism A



Mechanism B



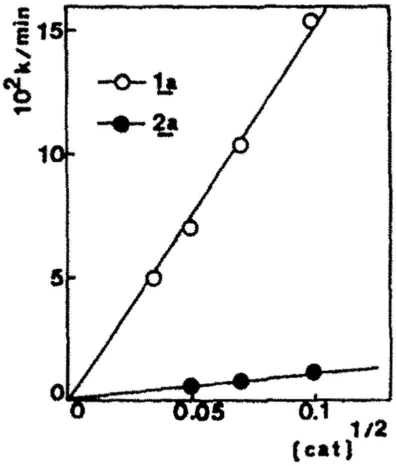


Figure 1. Plots of k vs. $[cat]^{1/2}$ used.

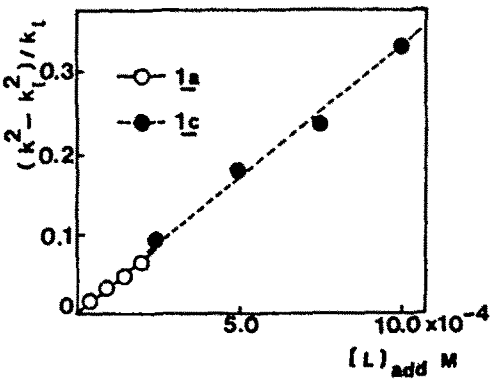
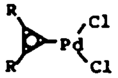


Figure 2. Plots of $(k^2 - k_\ell^2)/k_\ell$ vs. $[L]_{add}$.

The values, k^{cat}, k^* and K, thus obtained are given in Table I. It is noteworthy that complexes possessing common cyclopropenylidene revealed essentially the same value of k^*, strongly suggesting a common active species in each series. The variation of catalytic activity k^{cat} with respect to the change of the substituent on pyridine can be reasonably explained in terms of K, which increases by changing the substituent nature from electron-donating to electron-withdrawing . The k^* value was found to depend markedly on the electronic nature of the cyclopropenylidene ligand. The catalytic activity of **3a** possessing di-t-butylcyclopropenylidene was estimated to be 45 times stronger than that of bis(di-isopropylamino)cyclopropenylidene counterpart **3b**. The trend might be explained in terms of the electron affinity of the metal in **3**, which increases with the electronegative nature of the ligand. The carbene carbon of bis(di-isopropylamino)-cyclopropenylidene is considered to be less positive than that of di-t-butylcyclopropenylidene due to the strong π-electron donating nature of the amino groups,[8] and correspondingly, palladium metal in **3a** should have higher electron affinity than in **3b**. The value K is affected conversely by the nature of the cyclopropenylidene ligand. In the total activity $k^{cat} = k^*K^{1/2}$, the effect of the electronic property of the ligand is stronger on k^* than on K.

Di-μ-chlorospecies **4** revealed high catalytic activity in comparison with the corresponding pyridine complex. For example, as shown in Table I, **4b** exhibited much higher catalytic activity than **2a**. The dissociation constant K for **4b** defined as eq. 4 was determined to be 6.4×10^{-5} in CH_2Cl_2 at 27 °C by the measurement of the electronic spectra of **4b** ranging in concentration from 10^{-5} M to 10^{-3} M (Experimental). The $k^* = 4.3\ sec^{-1}M^{-1}$ evaluated from $k^{cat} = 3.3 \times 10^{-2}\ sec^{-1}M^{-1/2}$ and $K = 6.4 \times 10^{-5}$ is in good agreement with the k^* value ($4.0\ sec^{-1}M^{-1}$) for **2a** in CH_2Cl_2, indicating the same catalytic species for **2a** and **4b**. This result also supports the proposed predissociation of **4b** into coordinatively unsaturated species **3b** prior to rate limiting step. The high catalytic activity of the di-μ-chlorospecies is attributed to the large dissociation constant.

4 $\rightleftharpoons$ 2 x  ----- eq. 4

3

Table I. Values (k, k^{cat}, k^* and K) Characterizing Catalytic Activity of **1**, **2** and **4** toward the Isomerization of Q to NBD

cat.	solv.	10^3 [cat] mol/l	10^3 k a) sec^{-1}	10^2 k^{cat} a) $sec^{-1}M^{-1/2}$	k^* b) $sec^{-1}M^{-1}$	10^9 K c)
1a	$CDCl_3$	0.5	0.53	2.4	330	5.3
		1.25	0.83	2.3		
1b	$CDCl_3$	5.0	1.6	2.2	(325)d)	4.6
1c	$CDCl_3$	0.05	0.7	9.9	320	97
		0.5	2.25	10		
2a	$CDCl_3$	1.0	0.037	0.12	7.0	29
		5.0	0.08	0.11		
		10.0	0.12	0.12		
2b	$CDCl_3$	5.0	0.08	0.11	(6.8)d)	26
2c	$CDCl_3$	5.0	0.22	0.31	6.5	230
2a	CH_2Cl_2	5.0	0.08	0.11	4.0	76
4b	CH_2Cl_2	5.0	0.17	3.3	4.3f)	64000e)

a) Values determined at 27 ± 1 °C. [Q] = 0.1 M. b) Determined by the plots of eq. 3 as shown in Fig. 2. c) Evaluated from k^{cat} and k^* based on $k^{cat} = k^*K^{1/2}$. d) Mean value of k^* for pyridine and p-cyanopyridine complexes. e) Determined by measurement of electronic spectra (See Experimental). f) See text.

In summary, cyclopropenylidene Pd(II) complexes have been found to be an efficient and stable catalyst for the isomerization of Q to NBD. The following conclusions have been emerged from this study. The isomerization reaction involves a coordination of Q via an exchange with the originally coordinated ligand. The displacement proceeds via dissociative path, $Cl_2PdLL' \longrightarrow Cl_2PdL' + L$, and the bimolecular substitution path is not involved. Therefore, the apparent catalytic activity k^{cat} can be written as $k^{cat} = k^*K^{1/2}$. The less σ-donative the leaving ligand (L) is, the larger the value K is. The electronic nature of the remaining ligand (L') affects on k^* and K conversely. The electronegative nature of L' increases k^*, whereas decreases K value. The effect of L' on k^{cat} via k^* is larger than via $K^{1/2}$, and therefore, electronegative nature of the ligand enhances the total catalytic activity.

This is the first systematic kinetic study which correlate the catalytic activity of d^8 square planar complexes toward the isomerization of Q to NBD to their structure including ligand nature.

EXPERIMENTAL

All melting points were determined on a Yanagimoto micro melting point apparatus and uncorrected. Infrared spectra were measured with a JASCO A-102 spectrophotometer. ^1H-NMR spectra were obtained on a JEOL JNM FX-90Q system. Electronic spectra were taken with a HITACHI spectrophotometer 340. Elemental analyses were performed at Microanalytical Center of Kyoto University. Benzene was distilled over Na. Spectroscopic grade chloroform and methylene chloride were distilled over $CaCl_2$.

General Procedure of Syntheses of 1 and 2. 4-Substituted pyridine (1.68 mmol) was added to a solution of di-μ-chlorospecies **4** (0.76 mmol) in 15 ml of CH_2Cl_2 at room temperature. After 0.5 h stirring, the solvent was removed in vacuo, and the residue was recrystallized from ether/CH_2Cl_2 to give pale yellow crystals.

Compounds		mp (°C)	Anal. (calcd.)				IR (KBr) FIR (nujol) cm^{-1}	^1H-NMR ($CDCl_3$) δ ppm
			C	H	Cl	N		
1a	$C_{16}H_{23}Cl_2NPd$	150	47.50 (47.23)	5.84 (5.70)	17.36 (17.45)	3.62 (3.45)	1604, 1345 346, 328	9.33-8.90, 7.70-7.20 (m, 5H), 1.56 (s, 18H)
1b	$C_{17}H_{25}Cl_2NPd$	147-148	48.56 (48.54)	5.86 (5.99)	16.64 (16.85)	3.08 (3.33)	1618, 1350	8.79-7.14 (AA'BB', 4H), 2.37 (s, 3H), 1.51 (s, 18H).
1c	$C_{17}H_{22}Cl_2N_2Pd$	128-129	47.07 (47.30)	5.16 (5.14)	16.56 (16.43)	6.74 (6.49)	2230, 1612, 1344, 348, 330	9.27-7.61 (AA'BB', 4H), 1.51 (s, 18H)
2a	$C_{20}H_{33}Cl_2N_3Pd$	276(dec)	48.15 (48.75)	6.79 (6.75)	14.80 (14.39)	8.53 (8.53)	1851, 1500, 1332, 337	8.99 (m, 1H), 7.71 (m, 2H), 7.28 (m, 2H) 3.85 (sept, 4H), 1.50 (d, 24H).
2b	$C_{21}H_{35}Cl_2N_3Pd$	276(dec)	49.55 (49.77)	6.79 (6.96)	14.25 (13.99)	8.29 (8.29)	1853, 1498, 1328	8.82-7.09 (AA'BB', 4H), 3.84 (sept, 4H) 2.23 (s, 3H), 1.50 (d, 24H).
2c	$C_{21}H_{32}Cl_2N_4Pd$	274(dec)	48.68 (48.71)	6.29 (6.23)	13.98 (13.69)	10.76 (10.82)	2225, 1848, 1498, 1322, 330	9.30-7.54 (AA'BB', 4H), 3.85 (sept, 4H) 1.49 (d, 24H).

Kinetic Measurement. The catalyzed isomerization of Q to NBD was followed kinetically by integration of the olefinic proton signals in the NMR spectrum of the NBD formed. The samples were prepared by mixing a solution (0.5 ml) of Q in $CDCl_3$ with a solution of catalyst of the same volume so that desired concentrations of Q and cat. were obtained. The sample preparation was performed at 27 °C and the sample was transferred to the NMR cavity setting at the same temperature. The spectra were taken as a function of suitable time intervals. In addition to the NMR kinetic measurements, glc analysis were performed also. In this case, large excess pyridine was added to an aliquot of the reaction mixture before glc analysis, since large excess pyridine inhibits the reaction completely. The two kinetic analyses were compatible with each other.

Determination of the dissociation constant K of 4b. Electronic spectra of the solution of **4b** in methylene chloride were measured at 27 °C for various apparent concentrations of [**4b**] = C_n ranging from 10^{-5} M to 10^{-3} M. UV cells of light-path ℓ = 0.3, 1.0 and 5.0 cm were used so that absorbances (A) appropriate for the measurement were obtained. The shape of absorption ($\varepsilon_n^{obsd} = A/\ell C_n$ vs. λ) changes as a function of C_n as shown in Figure 3 by solid lines. The change should be attributed to the dissociation of **4b** into **3b** (eq. 4).
Thus,

$$[\mathbf{3b}]^2/(C_n - [\mathbf{3b}]/2) = K \quad \text{--- eq. 5}$$

$$[\mathbf{3b}] = \frac{\sqrt{K^2 - 16C_nK} - K}{4} = \alpha$$

$$[\mathbf{4b}] = C_n - \alpha/2 .$$

Thus, we may set up an equation for an apparent molar extinction

$$\varepsilon^{obsd}_{n,m} = A^{obsd}_{n,m} / C_n \cdot \ell$$

$$= \varepsilon^d_m + \alpha/C_n(\varepsilon^m_m - \varepsilon^d_m/2) \text{ --- eq. 6}$$

where $\varepsilon^{obsd}_{n,m}$ is an apparent extinction at wave length λ_m for the solution of **4b** of the concentration of C_n, ε^d_m and ε^m_m are molecular extinction of **4b** and **3b** at λ_m, respectively. Based on the experimental spectra at various concentration, C_n, the best value of K was determined to be 6.4×10^{-5} by an iterating computer calculation according to eq. 6. The dashed lines (d) and (e) in Figure 3 correspond to ε^d_m and ε^m_m, respectively. The dots are reproduced spectrum for $C_n = 1 \times 10^{-4}$ M according to eq. 6 using $K = 6.4 \times 10^{-5}$, ε^d_m and ε^m_m .

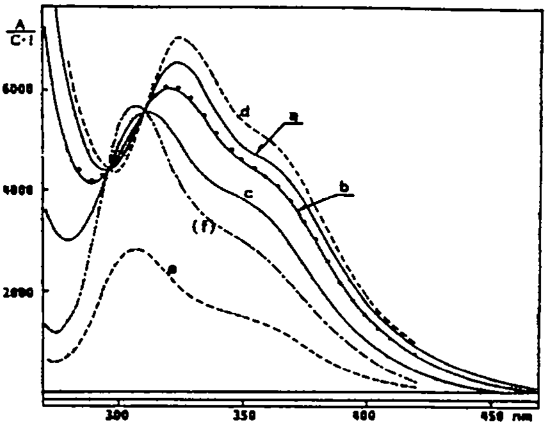


Figure 3. Absorption profile of the solution of **4b** in CH_2Cl_2 at 27 °C. Solid lines are the spectra of the solution of concentrations, 4×10^{-4} M (a), 1×10^{-4} M (b), and 1×10^{-5} M (c). The dashed lines are the calculated absorption of **4b** (---- d) and **3b** (---- e). The line (f) corresponds to 2 x (e). The dots (• • • •) is a reproduced spectrum for $C_n = 1 \times 10^{-4}$ M.

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(4) The catalytic activities of **1** and **4** were comparable with that of di-μ-chloro-bis(norbornadiene)-dirhodium (I) **5**. In addition to this, **1**, **2** and **4** are immune to oxidation in contrast to **5**. The complex **4** revealed high catalytic activity toward the isomerization of heavily substituted quadricyclanes in comparison with **5**.[3]

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(9) The rate expression eq. 2 is derived based on Scheme 2.

Scheme 2

$$\text{cat} \xrightleftharpoons{K} \text{cat}^* + L \quad \text{(eq. 7)} \qquad Q + \text{cat}^* \xrightleftharpoons{K_2} \text{cat}^*Q \quad \text{(eq. 8)}$$

$$\text{cat}^*Q \xrightarrow{k_r} \text{cat}^*\text{NBD} \quad \text{(eq. 9)} \qquad \text{cat}^*\text{NBD} \xrightleftharpoons{K_3} \text{cat}^* + \text{NBD} \quad \text{(eq. 10)}$$

where cat^* is a coordinatively unsaturated species (3).

Then, $[L] = [\text{cat}^*] + [\text{cat}^*Q] + [\text{cat}^*\text{NBD}]$ ---(eq. 11), $K[\text{cat}] = [\text{cat}^*][L]$ ---(eq. 12) $K_2[Q][\text{cat}^*] = [\text{cat}^*Q]$ ---(eq. 13) and $K_3[\text{cat}^*\text{NBD}] = [\text{cat}^*][\text{NBD}]$ ---(eq.14).

Assuming that eq. 9 is rate determining and that $[\text{cat}^*]$, $[\text{cat}^*\text{NBD}]$ and $[\text{cat}^*Q] \ll C_0$

$$r = k_r[\text{cat}^*Q] = k_rK_2K^{1/2}C_0^{1/2}[Q]/\sqrt{1 + [\text{NBD}]/K_3 + K_2[Q]} \text{ ---(eq. 15)}$$

where C_0 is initial concentration of catalyst. The experimental results, i. e., no detectable effects on the initial concentration of Q and NBD on the rate could be observed, indicate that $[\text{NBD}]/K_3 \ll 1$ and $K_2[Q] \ll 1$ in the experimental conditions.

Then eq. 15 becomes

$r = k_rK_2K^{1/2}C_0^{1/2}[Q]$ which is equivalent to eq. 2 when $k_rK_2 = k^*$.

In the mechanisms, eq. 8 - eq. 10, when L is added externally eq. 11 becomes

$$[L] = [\text{cat}^*] + [\text{cat}^*Q] + [\text{cat}^*\text{NBD}] + [L]_{add} \text{ ---(eq. 16)}.$$

Taking the same limiting conditions described above,

$C_0K = [\text{cat}^*]([\text{cat}^*] + [L]_{add})$ which turns to $C_0K - [\text{cat}^*]^2 = [\text{cat}^*][L]_{add}$.

Substitution for $[\text{cat}^*]$ in the equation in terms of $[\text{cat}^*] = [\text{cat}^*Q]/K_2[Q]$

$$C_0K - [\text{cat}^*Q]^2/K_2^2[Q]^2 = [\text{cat}^*Q][L]_{add}/K_2[Q] \text{ ---(eq. 17)}.$$

Since $k_\ell[Q] = k_r[\text{cat}^*Q]$ and $k = k_rK_2K^{1/2}C_0^{1/2}$, eq. 17 finally becomes eq. 3 using relation $k_rK_2 = k^*$.