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Oligomerization and isomerization of olefins by .eta.3-allyl complexes of palladium. The role of the allyl group

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corresponds to a normal C–O double bond whereas the endocyclic C(9)–O(2) distance (1.407 (9) Å) is close to that of a single bond. The P(3)–O(2) distance (1.632 (5) Å) is comparable to analogous distances in phosphite ligands.[12] Both Ir–C bonds are normal (Ir–C(1) = 2.093 (7) Å, Ir–C(8) = 2.046 (9) Å) and the Ir–Cl bond (2.475 (2) Å), which is almost identical with that in compound 1, reflects the high trans influence of C(8). The geometry about P(3) shows the strain imposed by the metallocycle. Thus, the Ir–P(3)–O(2) angle (100.6 (2) Å) is small, and the two Ir–P(3)–Ph angles (124.6 (2)° and 129.7 (2)°) are significantly larger than those involving the normal PPh_3 groups (average 116.0°). All other angles within the metallocycles are close to their expected values of 120°.

Both compounds **1** and **3** display the well-known tendency of Ir(I) compounds to undergo intramolecular C–H bond activation in the form of ortho-metalation reactions. In neither case, however, is the initial iridium hydride species observed; instead hydrogen transfer in **1** occurs, yielding the β-diketonate group, and in **3** metal activation of a P–Ph bond has resulted in reductive elimination of benzene and the formation of the P–O bond to give a diphenyl phosphinite group.

On the basis of similarities in spectral parameters between **1** and **2** and on the conversion of **1** to **2**, it is assumed at this stage that **2** is a geometrical isomer of **1**. Further studies are underway on these systems in attempts to obtain further information about these unusual dibenzoyldiazomethane activations.

Acknowledgment. We thank the University of Alberta and the National Sciences and Engineering Research Council of Canada for financial support.

Registry No. 1, 86272-05-1; 2, 86288-19-9; 3, 86272-06-2; $IrCl(PPh_3)_3$, 16070-58-9; $N_2C(C(O)Ph)_2$, 2085-31-6; *trans*-$[IrCl(N_2)(PPh_3)_2]$, 21414-18-6.

Supplementary Material Available: Tables summarizing the crystal data and intensity collection details, positional and thermal parameters and a listing of observed and calculated structure amplitudes (37 pages). Ordering information is given on any current masthead page.

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[12] (a) Nolte, M.; van der Stok, E. Singleton, E. *J. Organomet. Chem.* **1977**, *142*, 387. (b) Laing, M.; Nolte, M.; Singleton, E.; van der Stok, E. *Ibid.* **1978**, *146*, 77. (c) Guss, J. M.; Mason, R. *J. Chem. Soc., Dalton Trans.* **1972**, 2193.

Oligomerization and Isomerization of Olefins by η^3-Allyl Complexes of Palladium. The Role of the Allyl Group

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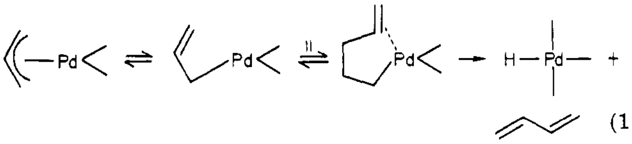
Summary: $[(\eta^3\text{-}C_3H_5)Pd(CD_3NO_2)_2](BF_4)$ is a catalyst for the dimerization and the isomerization of olefins. The allyl group is retained in the course of these catalytic reactions. A carbonium ion mechanism which does not involve the participation of the allyl group is proposed.

We report a series of dimerization and isomerization of olefins catalyzed by $[(\eta^3\text{-}C_3H_5)Pd(CD_3NO_2)_2](BF_4)$, **1a**, *where the allyl group is retained in the course of the reaction.* Cationic, η^3-allyl complexes of Pd(II) prepared either in situ,[1,2] or separately,[3] have been reported to catalyze the oligomerization and cooligomerization of monoolefins,[1] the cooligomerization of monoolefins with dienes,[2] and the telomerization of dienes with alcohols.[3] While the mechanism of these reactions is not well understood, it has been postulated[2d] that the active catalyst is a palladium(II) hydride formed initially by the insertion of an olefin into a σ-allyl–palladium followed by a β-hydrogen abstraction step, eq 1. However, to our knowledge,



(1)

such a mechanism involving an initial loss of the allyl ligand has never been verified experimentally. On the other hand, our observations clearly indicate that this mechanism is inoperative, at least for the systems that we have studied.

The cationic η^3-allyl complexes $[(\eta^3\text{-}C_3H_5)Pd(solvent)_2](BF_4)$ (solvents CD_3NO_2, **1a**,[4] and CH_3CN, **1b**[5]) were generated by the addition of 2 equiv of $AgBF_4$ to $[(\eta^3\text{-}C_3H_5)PdCl]_2$,[6] **2**, in an appropriate solvent system. The catalytic properties of **1a** are summarized in Table I. In every case, following the completion of the catalytic reaction, **1a** was recovered in near-quantitative yields,[9] thus ruling out eq 1, at least as the major mechanistic pathway. In order to further confirm this observation, the dimerization of $PhCH{=}CH_2$ was followed by ^1H NMR using a $PhCH{=}CH_2$/**1a** ratio of 1. Again, no species other than 1,3-diphenyl-1-butene[7] and **1a** was observed at the end of the reaction. It may be pointed out that our observations are fully consistent with that of Kurosowa and Asada,[10] who have observed the complete retention of the allyl fragment in the catalytic isomerization of olefins by $[(\eta^3\text{-}CH_2CMeCH_2)Pt(PPh_3)(CH_2{=}CHR)]ClO_4$(R = alkyl).

It is interesting to note that the corresponding neutral μ-chloro dimer **2** was ineffective for the dimerization of $PhCH{=}CH_2$ and $Ph_2C{=}CH_2$ under conditions identical with those employed in case of **1a**. The poor catalytic activity of **2** for the dimerization of C_2H_4 has also been demonstrated.[1a] We have also shown that a higher temperature (80 vs. 25 °C for **1a**) was required for the di-

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[1] (a) Barlow, M. G.; Bryant, M. J.; Haszeldine, R. N.; Mackie, A. G. *J. Organomet. Chem.* **1970**, *21*, 215. (b) Wilke, G. Ger. Offen. 1 520 964, 1974. (c) Hattori, S.; Munakata, H.; Tatsuoka, K.; Shimizu, T. Ger. Offen. 2 234 922, 1974; U.S. Patent 3 803 254, 1974.

[2] (a) Ito, T.; Kawai, T.; Takami, Y. *Chem. Lett.* **1972**, 1047. (b) Ito, T.; Kawai, T.; Takami, Y. *Tetrahedron Lett.* **1972**, 4775. (c) Ito, T.; Takahashi, K.; Takami, Y. *Tetrahedron Lett.* **1973**, 5049. (d) Ito, T.; Takahashi, K.; Takami, Y. Nippon *Kagaku Kaishi* **1974**, 1097. (e) Ito, T.; Takami, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1220.

[3] Grenouillet, P.; Neibecker, D.; Poirier, J.; Tkatchenko, I. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 767.

[4] ^1H NMR ($CDCl_3$–CD_3NO_2, ppm): 5.94 (1 H, m), 4.54 (2 H, d, *J* = 7 Hz), 3.44 (2 H, d, *J* = 12 Hz).

[5] ^1H NMR ($CDCl_3$–CD_3NO_2, ppm): 5.80 (1 H, m), 4.45 (2 H, d, *J* = 7 Hz), 3.30 (2 H, d, *J* = 12 Hz), 2.23 (6 H, s).

[6] Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220.

[7] ^1H NMR ($CDCl_3$, ppm): 7.4–7.2 (10 H, m), 6.38 (2 H, d, *J* = 5 Hz), 3.63 (1 H, m, *J* = 5 Hz, 6.9 Hz), 1.45 (3 H, d, *J* = 6.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 145.5, 137.5, 135.1, 128.6–126.1, 42.5, 21.2. Mol wt ($CHCl_3$): found 212; calcd, 208. Hydrogenation product: 1,3-diphenylbutane. ^1H NMR ($CDCl_3$, ppm): 7.3–7.1 (10 H, m); 2.65 (1 H, m, *J* = 7 Hz, 7 Hz); 2.50 (2 H, t, *J* = 7.6 Hz); 1.90 (2 H, m, *J* = 7 Hz, 7.6 Hz); 1.24 (3 H, d, *J* = 7 Hz).

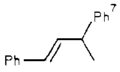
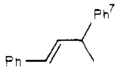
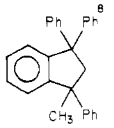
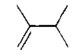
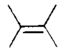
[8] ^1H NMR ($CDCl_3$, ppm): 7.4–7.0 (19 H, m), 3.45, 3.10 (2 H, ABq, *J* = 12 Hz), 1.6 (3 H, s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 150.5–147.5, 128.8–125.0, 61.4, 60.9, 51.2, 28.9. Mass spectrum: *m/e* 360 (M^+).

[9] In the experiment where 1 equiv of PPh_3 was added to **1a** prior to the addition of $PhCH{=}CH_2$ (Table I), an $(\eta^3\text{-}C_3H_5)Pd^{II}$ compound with ^1H NMR shifts slightly different from those of **1a** was observed, presumably due to the coordination of PPh_3. This species was recovered following the catalytic dimerization of $PhCH{=}CH_2$ (Table I).

[10] Kurosowa, H.; Asada, N. *Organometallics* **1983**, *2*, 251.

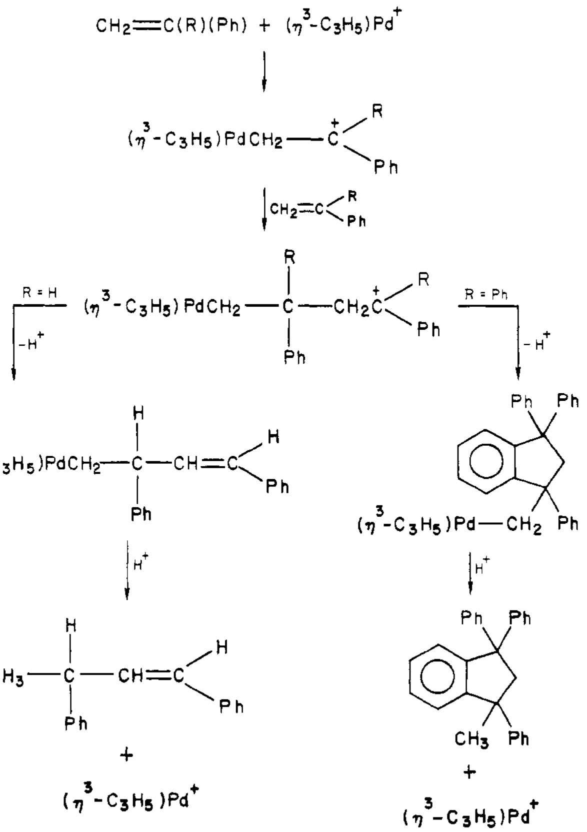
0276-7333/83/2302-1059$01.50/0

Table I

cat.[a]	olefin	olefin/ cat.	temp, °C	time	product	yield, %	cat. recovered,[b] %
1a	$CH_2{=}CH_2$	c	25	1 day	butenes[d]	e	f
1a	$PhCH{=}CH_2$	100	25	1 day		94	91
1a + PPh_3[g]	$PhCH{=}CH_2$	100	80	1 h		93	88[9]
1a	$Ph_2C{=}CH_2$	50	100	6 h		61	92
1a		10	25	1 h		90[h]	83

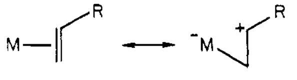
[a] ~1 × 10^{-2} M solution of the catalyst in a 2:1 mixture of CH_3NO_2 and $CHCl_3$ was used. [b] Analyzed by ^1H NMR by using an olefin/catalyst ratio of 5; no other Pd-containing species was observed. [c] 500 psi pressure of C_2H_4 was used [d] Ratio of 1-butene/*cis*-2-butene/*trans*-2-butene = 37:36:27. [e] The yield of butenes could not be quantified due to their high volatility. [f] Although 1a was observed, no quantitative analysis was possible due to technical problems. [g] One equivalent of PPh_3 was added to a solution of 1a prior to the addition of $PhCH{=}CH_2$. [h] At equilibrium, ratio of 2,3-dimethyl-1-butene/2,3-dimethyl-2-butene = 10:90.

Scheme I



merization of $PhCH{=}CH_2$ when 1 equiv of PPh_3 was added to **1a** (see Table I). These observations indicate that the catalytic activity is decreased significantly when the electrophilicity of the Pd(II) center and its accessibility to organic substrates is decreased. The latter effect was also demonstrated through the following experiment. The addition of 5 equiv (relative to **1a**) of CH_3CN to a CD_3NO_2–$CDCl_3$ solution of **1a** caused its complete conversion to **1b**. This solution was then found to be totally inactive (for olefin/catalyst ratio of 5) for either the dimerization of $PhCH{=}CH_2$ or the isomerization of 2,3-dimethyl-1-butene under conditions identical with those employed for **1a** (Table I). This was consistent with our previous observation[11] that the catalytic activity of CH_3CN-coordinated transition-metal cations vis-à-vis olefins were invariably decreased on changing the solvent from CH_3NO_2 to CH_3CN, due to the better coordinating ability of CH_3CN.[12]

We had earlier observed[13] a dramatic increase in catalytic activity when Pd(II) compounds of the type PdX_2 (X = coordinating anion, e.g., OAc or Cl) were converted to the corresponding dication, e.g., $Pd(CH_3CN)_4^{2+}$. Since the principal interaction of the Pd(II) center with olefins involves the formation of incipient carbonium ions (I),[13a] we



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ascribed this increased activity to an increase in electrophilicity on going from the neutral to the corresponding cationic compound. The head-to-tail arrangement in the dimers of $Ph(R)C{=}CH_2$ (R = H, Ph) (Table I) is consistent with a cationic mechanism and also supports the formation of incipient carbonium ions when **1a** interacts with olefins. Thus the formation of the dimers may be rationalized through the following mechanism, which does not involve the participation of the allyl group, Scheme I. The catalytic isomerization of olefins may also be rationalized through a mechanism involving incipient carbonium ions.[13b]

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Registry No. 1a, 86324-64-3; C_2H_4, 74-85-1; $PhCH{=}CH_2$, 100-42-5; $Ph_2C{=}CH_2$, 530-48-3; $[(\eta^3\text{-}C_3H_5)PdCl]_2$, 12012-95-2; $[(\eta^3\text{-}C_3H_5)Pd(CH_3CN)_2]BF_4$, 86324-65-4; 2,3-dimethyl-1-butene, 563-78-0; 1,1,3-triphenyl-3-methylindan, 19303-32-3; 1,3-diphenyl-1-butene, 7614-93-9.

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(11) Sen, A.; Thomas, R. R. *Organometallics* **1982**, *1*, 1251.

(12) A similar solvent effect has been reported for the Pd(II)-catalyzed codimerization of $PhCH{=}CH_2$ and C_2H_4. See: Kawamoto, K.; Imanaka, T.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2512.

(13) (a) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627. (b) Sen, A.; Lai, T.-W. *Inorg. Chem.* **1981**, *20*, 4036. (c) Sen, A.; Lai, T.-W. *Organometallics* **1982**, *1*, 415.