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A Warning on the Use of Radical Traps as a Test for Radical Mechanisms: They React with Palladium Hydrido Complexes

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Studies of reaction mechanisms often need to rule out alternative pathways. A usual test of participation of radical mechanisms is the addition of radical traps, in the assumption that they will slow or stop radical reactions.[1,2] The stable radicals galvinoxyl, TEMPO, and DPPH (Chart 1) are among the most frequently used. The reliability of other reagents such as di-*tert*-butyl phenol (TBP) and other phenols, which can also react with radical species, has been questioned.[2] The mechanistic value of positive tests with a radical trap is based on the hypothesis that it reacts only with radical species in the medium and does not interfere in any other process. If this were not the case, the positive result of the test can be misleading. Palladium(II) hydrides are involved in many reactions that follow an insertion mechanism of unsaturated substrates into the Pd−H bond, such as Pd-migration (chain walking), alkene isomerization, and alkene hydrogenation, hydrosilylation, hydroboration, etc.[3] We show here that radical traps can react with some palladium hydrides and interfere in processes where they are involved.

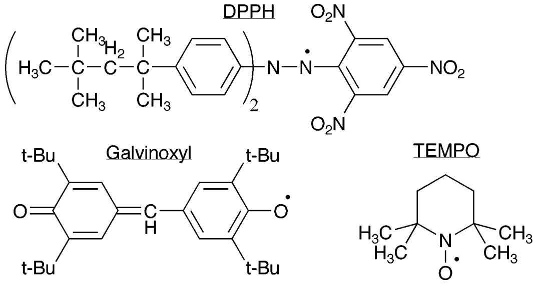
The addition of galvinoxyl to $[PdHCl(PPh_3)_2]$[4] (in $CDCl_3$, Pd:galvinoxyl = 1:1) produces 50% decomposition after 20 min at room temperature (complete decomposition after 50 min), whereas it is stable under the same conditions in the absence of the radical trap. $[PdHCl(PPh_3)_2]$ decomposes faster in the presence of DPPH (75% decomposition after 20 min) or TEMPO (complete decomposition after 10 min). In contrast, the cationic complex $[PdH(PEt_3)_3]BPh_4$[5] is apparently unaffected by galvinoxyl, DPPH, or TEMPO, and its solutions remain unchanged for at least 40 min at room temperature, whether in the absence or presence of the radical traps.[6]

The previous hydrides contain two or three phosphines. To check the reactivity of hydrides on less protected palladium centers (as they may be formed in the course of catalytic processes), we have also studied the effect of radical traps on the intramolecular hydride transfer in a dimer generated by β-H elimination from a palladium benzylic derivative (Scheme 1).[7]

The H-transfer and subsequent reductive elimination produces the alkane **3**, and the efficiency of the transfer is measured by the ratio **3**/**2**. This ratio should be 1 if all of the Pd−H formed (the same molar amount as **2**) leads to **3**, and should drop to 0 if, on the contrary, all of the hydride formed was trapped by the radical trap. The results obtained in the presence of different radical traps are collected in Table 1.

In the absence of additives, the efficiency of the transfer is 0.74 (entry 1, Table 1), and it is not affected by the presence of air (entry 2, Table 1). TBP also has no effect on the process. However, the addition of galvinoxyl, DPPH, or TEMPO do decrease the amount of **3** formed very noticeably, each with different effectiveness.

Chart 1. Some Common Radical Traps



Scheme 1. Decomposition of Complex **1**

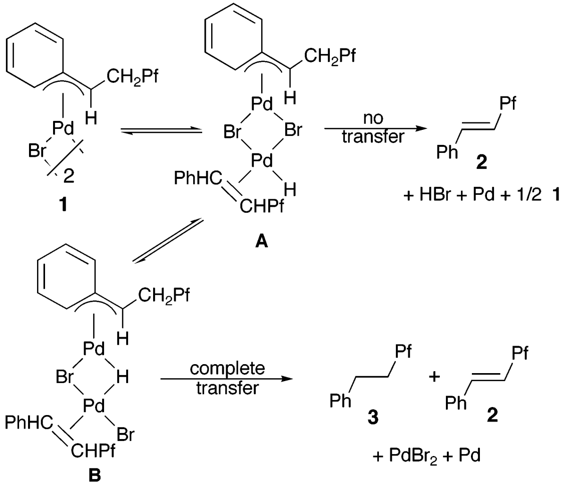


Table 1. Decomposition of Complex **1** in the Presence of Radical Traps[a]

entry	additive[b]	3/2
1	none	0.74
2	none, in air[c]	0.76
3	TBP	0.73
4	galvinoxyl	0.33
5	DPPH	0.18
6	TEMPO	0.11

[a] Samples of **1** in $CDCl_3$ in a N_2 atmosphere were left to decompose for 10 days. [b] Molar ratio **1**:additive = 1:2. [c] Oxygen can affect radical reactions.

Alkene isomerization is a common process catalyzed by metal hydrides. The accepted mechanism involves, for each 1,2-shift, insertion of the double bond into the M−H bond and subsequent β-H elimination. $[PdHCl(PPh_3)_2]$ and $[PdH(PEt_3)_3](BPh_4)$ were not good catalysts for alkene isomerization, probably because the coordination of the olefin to palladium was difficult. Complex **1**, with a more electrophilic and accessible palladium center (the olefin can coordinate producing bridge splitting), turns out to be a very

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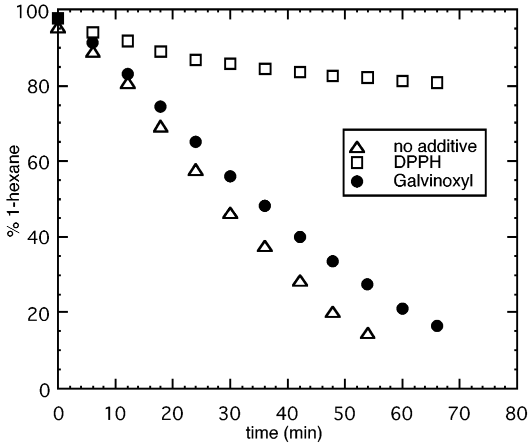
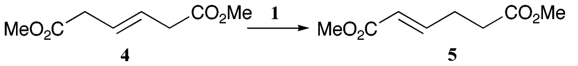
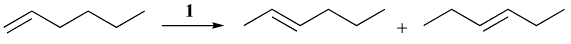


Figure 1. Disappearance of 1-hexene (to give a mixture of 2- and 3-hexene), catalyzed by **1**, in the absence and presence of radical traps.

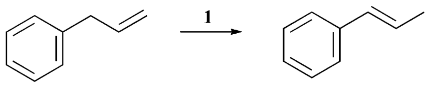
efficient catalyst for olefin isomerization. The transformations collected in eqs 1−3 were studied.



(1)



(2)



(3)

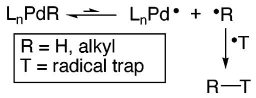
The isomerization of the internal olefin **4** to the conjugated alkene **5** in $CDCl_3$ proceeds with 61% conversion after 1 h at room temperature in the presence of 0.1 mol % of catalyst **1** (eq 1). This is close to completion, because the equilibrium mixture was found to be **4**:**5** = 33:67. The presence of galvinoxyl in a similar reaction mixture (Pd:galvinoxyl = 1:1) slowed the isomerization down, and only 34% conversion to **5** was observed after 1 h. When DPPH was used as additive (Pd:DPPH = 1:1), only 2% conversion was observed after 1 h, and no further isomerization occurred in 5 h.

In another test, the isomerization of terminal to internal alkenes (eqs 2 and 3) catalyzed by **1** turned out to be instantaneous at room temperature. The isomerization of 1-hexene in $CDCl_3$ to give an equilibrium mixture of 2-hexene and 3-hexene was followed at 263 K using 0.1 mol % of catalyst. The observed rate constant is $k_{\mathrm{isom}} = 0.0266 \pm 0.0003\ \mathrm{s}^{-1}$. The same isomerization was carried out in the presence of radical traps (Pd:trap = 1:1), and the disappearance of 1-hexene versus time is represented in Figure 1. Galvinoxyl produces a modest but perceptible decrease of the reaction rate ($k_{\mathrm{isom}} = 0.0225 \pm 0.0004\ \mathrm{s}^{-1}$). With DPPH the initial isomerization rate drops dramatically ($k_{\mathrm{isom}} = 0.0076 \pm 0.0004\ \mathrm{s}^{-1}$), and the reaction is almost halted after 20−30 min; after 1 h only 19% conversion is observed, versus 90% without additive, or 79% with galvinoxyl.

The experiments reported here demonstrate that radical traps can react with some palladium hydrides, halting reactions that follow an insertion mechanism involving Pd−H bonds. In other words, some of these additives can be efficient palladium hydride traps as well. The question arises whether they will react also with Pd−alkyl or Pd−aryl bonds. To check this point, we tested the compounds $[PdMeCl(PPh_3)_2]$[8] and $[PdPhCl(PPh_3)_2]$[9] with the radical traps TEMPO and galvinoxyl under the same conditions that had produced decomposition for $[PdHCl(PPh_3)_2]$. After 7 h, the solutions of the methyl and phenyl compounds remained unaltered.

The features observed can be summarized as follows: (1) The reaction rate seems to decrease in the order TEMPO > DPPH > galvinoxyl (Table 1, and reactions with $[PdHCl(PPh_3)_2]$). This order is clearly unrelated to the strength of the T−H bond that is formed,[10] but consistent with a kinetic control associated mainly with the different steric protection of these radical traps. (2) The reaction rate increases with the electron density on the metal ($[PdHCl(PPh_3)_2] > [PdH(PEt_3)_3]^+$). (3) Alkyl and aryl complexes are unaffected. If the reaction with hydrides was associated with H• being formed by reversible bond homolysis (Scheme 2), the radical traps should react as well with the methyl or phenyl derivatives. Because this is not the case, it seems unlikely that radicals are formed in these complexes, either for the Me, for the Ph, or for the hydrido complexes.

Scheme 2



A mechanism that can explain the observations is the direct attack of the radical on the coordinated H, leading to polarization of the electron density and eventual homolysis of the Pd−H bond (eq 4), as proposed for H-abstraction in organic systems,[11] and for H• transfer from metal hydrides to the substituted trityl radical ($(p\text{-tBuC}_6H_4)_3C\bullet$).[12] The success of this interaction depends on sufficient orbital overlap and Pd−H bond polarization. The more polarizable and diffuse hydride orbitals of neutral complexes should interact better than the more compact and less polarizable orbitals of a cationic complex. For the same reason, a less hindered hydride and a less sterically protected radical trap should react faster. Finally, the reaction with more hindered alkyls and aryls, needing orbital reorganization, should be disfavored.

$$L_nPd{-}H \; + \; \bullet T \xrightarrow{[L_nPd\text{- -}H\text{- - -}T]^{\ddagger}_{\bullet}} L_nPd\bullet \; + \; H{-}T \qquad (4)$$

In summary, classical transition metal hydride catalyzed reactions can be perturbed and arrested by radical traps, and positive test results can be misleading.

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References

(1) Sawamoto, M.; Kamigaito, M. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 1803−1814.
(2) Matyjaszewski, K. *Macromolecules* **1998**, *31*, 4710−4717.
(3) Tsuji, J. *Palladium Reagents and Catalysts. Innovations in Organic Synthesis*; Wiley: Chichester, 1995.
(4) Tanase, T.; Ohizumi, T.; Kobayashi, K.; Yamamoto, Y. *Organometallics* **1996**, *15*, 3404−3411.
(5) Schunn, R. A. *Inorg. Chem.* **1976**, *15*, 208−212.
(6) NMR tubes were charged with the palladium hydride, radical trap (molar ratio Pd:radical trap = 1:1), and $CDCl_3$ (0.6 mL). The freshly prepared samples were monitored every 10 min by ^{31}P and ^{1}H NMR.
(7) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1997**, *16*, 4030−4032.
(8) $[PdMeCl(PPh_3)_2]$ was prepared by addition of 2 equiv of PPh_3 to [PdMeCl(COD)] (Rulke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769−5778).
(9) Coulson, D. R. *Chem. Commun.* **1968**, 1530.
(10) (a) Mahoney, L. R.; Mendenhall, G. D.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 8610−8614. (b) Lucarini, M.; Pedulli, G. F.; Cipollone, M. *J. Org. Chem.* **1994**, *59*, 5063−5070.
(11) Ingold, K. U. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 2, p 67.
(12) (a) Eisenberg, D. C.; Norton, J. R. *Isr. J. Chem.* **1991**, *31*, 55−65 and references therein. (b) Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4888−4895.

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