Tetrahedron Letters, Vol. 34, No. 19, pp. 3075-3078, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Colloidal Palladium, Easily Formed in Organic Solvents, is a Highly Active and Stable Catalyst for Selective Hydrogenations and Dehydrohalogenations

Lissa A. Fowley, Demetrius Michos, Xiao-Liang Luo and Robert H. Crabtree*

Yale Chemistry Dept., 225 Prospect St., New Haven, CT 06511

Abstract: Collidal Pd formed in organic solvents from $Pd(hfacac)_2$ and silane or an Si-H-containing polymer is an active, stable and selective catalyst for hydrogenation and dehydrohalogenation.

Metallic Pd is a useful catalyst in organic chemistry, but it is almost always supported on a solid (e.g. Pd/C).[1] Colloidal metals could have usefully different properties, but they are usually aqueous and need to be stabilized with polymer additives, which seem to reduce their catalytic activities. Lewis [2a,b] has studied colloidal Pt catalysts and Schmid [2c] has reviewed the area.

$Pd(hfacac)_2$ (1) (hfacac = $CF_3COCHCOCF_3$)[3] is soluble in heptane, Et_2O, CH_2Cl_2, and Me_2CO, and can be reduced to a stable brown-yellow colloid (2) in these solvents upon addition of silanes $R_{(3-x)}SiH_x$. For example, the *n*-octylsilane/1/heptane colloid is stable for weeks, can withstand 150°C without precipitation and was found to consist of ca. 35Å particles by electron microscopy.[4] The excess silane limits the types of catalytic chemistry that can be studied, however, and so we have moved to the polymer polymethylhydrosiloxane (PMHS) $\{TMS(OSiHMe)_nOTMS\}$. This both reduces 1 and stabilizes the resulting colloid (3) even when present in very small amount (1 mol. PMHS / mol. Pd; PMHS calcd. as monomer) and allows us to generate 3 in a variety of solvents.

Under H_2, hydrogenation rates were exceptionally fast (Table I). Completion of the reaction, usually indicated by precipitation of Pd metal, normally takes only minutes at 25° C. Reduction of all double and triple bonds was complete but carbonyls, $-CO_2H$, $-CO_2R$, -CHO and arenes were untouched. In alkyne reduction, the intermediate olefin could be isolated by stopping the reaction after 1 mol. H_2 had been absorbed.

The hydrogenation of $PhNO_2$ to $PhNH_2$ and of PhCHO to $PhCH_3$ indicates a heterogeneous origin for the catalysis. In confirmation, metallic Hg, a selective poison for such catalysts,[5] gave rapid deactivation.

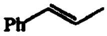
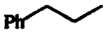
With a silane as the external reducing agent, both **2** and **3** gave only hydrogenation and not hydrosilation, but more selectively than with H_2. In polyunsaturated compounds, only the least hindered or the most activated double bond was reduced (Table 1). The rates of these reactions are highest in dry acetone at reflux, with completion usually within 4-8 hr., and depended strongly on the silane used. Me_2ClSiH, Ph_2MeSiH, and Et_3SiH were the most active. As in the Lewis system,[6] in the hydrogenations with H_2, the colloid was formed in air but run under H_2, and in silane hydrogenations, the reactions were run under dry air.

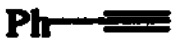
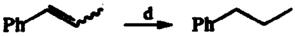
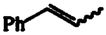
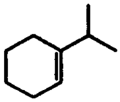
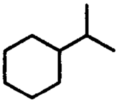
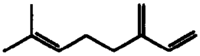
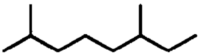
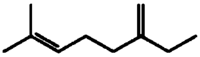
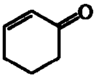
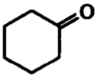
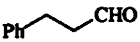
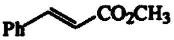
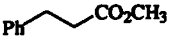
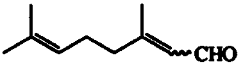
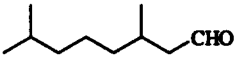
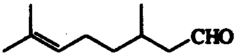
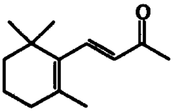
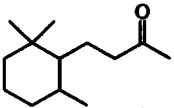
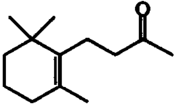
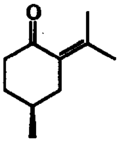
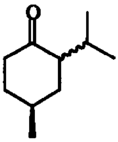
PhCOCl is reduced only to PhCHO with silane and **3** at room temperature.[7] No subsequent conversion to toluene was seen, even though starting with PhCHO leads to toluene under the same conditions. This is most likely due to partial poisoning of the catalyst by the Cl present in the substrate. Hydrogenolysis of aryl and benzyl halides and alcohols was also successful with both H_2 and silane (Table II).

The system is highly selective. Other known palladium(0) catalyzed reactions ,[8] such as reductive amination of olefins, hydroboration of olefins, the Heck reaction of PhI and styrene, and 1,4-reduction of pyridine did not occur. The colloid demonstrated little promise as a directing reagent for hydrogenation of terpinen-4-ol. Rhodium analogs of **2** and **3** were also synthesized from $[Rh(COD)Cl]_2$,[9] but while equally stable, were less active.

In summary, colloids stabilized by reducing polymers such as PMHS are active, selective and stable catalysts and may therefore be useful in synthetic chemistry.

Table 1. Hydrogenation results.[a]

Substrate	Reagents	Yield[b]	Product(s)[c]
	3, H_2	>99%	
	3, Me_2ClSiH	>99%	
	3, Et_3SiH	39%	

	3, Et_3SiH	54%	
	3, H_2	>99%	
	3, Ph_2MeSiH	10%	
	3, H_2	>99%	
	3, Ph_2MeSiH	<5%	
	3, H_2 3, Ph_2MeSiH	>99% 24%	
	3, H_2	>99%	
	3, Me_2ClSiH	e	
	3, H_2 3, Me_2ClSiH	>99% 94%	
	3, H_2 3, Et_3SiH	~80% 73%	
	3, H_2 3, Et_3SiH	>99% >99%	
	3, H_2	>99%	
	3, Et_3SiH	>99%	
	3, H_2	>99%	
	3, Me_2ClSiH	e	
	3, H_2	>99%	
	3, Et_3SiH	>98%	
	3, H_2 3, Et_3SiH	>99%[f] 65%	
$PhNO_2$	3, H_2	>99%	$PhNH_2$

PhCHO	3, H_2	>99%	$PhCH_3$
	3, Et_3SiH	<5%	$PhCH_3$
PhCOCl	3, H_2	>99%	PhCHO

[a] Hydrogenation with H_2: PMHS (0.1 µL) was added to $Pd(hfacac)_2$ (0.5 mL, 1 mM in ether) at 25° C to form 3 under air. The substrate(1.31 x 10^{-4} mol) was then added, followed by substitution by an H_2 atmosphere. Silane reductions: PMHS (0.2 µL) was added to $Pd(hfacac)_2$ (1.0 mL,1 mM in acetone) at 25° C to form 3 under air. Silane (2.82 x 10^{-4} mol) was then added, followed by substrate (2.62 x 10^{-4} mol). The solution was then heated to reflux under dry air. R_6Si_2 presumably formed. [b] Yields from GC data. [c] Products were identified by GC/MS and ^{1}H NMR. [d] Alkene formed (>95%) if reaction halted after 1 mol H_2 absorbed. [e] Other isomers present in product. [f] ca. 1:1 ratio of isomers

Table II. Dehydrogalogenation Results.[a]

Substrate	Silane	X	T.O./hr.[b]
PhX	Et_3SiH	I	11.6
	Et_3SiH	Br	7.6
	Et_3SiH	Cl	5.0
	Et_3SiH	F	0
$PhCH_2X$	Et_3SiH	Cl	13.4
	H_2	Cl	175
	Et_3SiH	OH	0.04
	H_2	OH	90

[a] Conditions similar to above. [b] Turnover = mole product per mole substrate per hour

Acknowledgement: We thank Dr. J. Bradley (Exxon C. R&D.) for TEM data.

References and Notes

1. Rylander, P.N. *Catalytic Hydrogenation Over Platinum Metals* Academic Press:, New York, 1967, and references cited therein.
2. (a) Lewis, L.N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228. (b) Lewis, L.N.; Lewis, N. *Chem. Mater*. **1989**, *1*, 106. (c) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709.
3. Siedle, A.R. *Inorg. Synthesis* **1990**, *112*, 5998.
4. Bradley, J., unpublished data, 1992.
5. (a) Crabtree, R.H.; Anton, D.R. *Organometallics* **1983**, *2*, 855. (b) Whitesides, G.M.; Hackett, M.; Brainard, R.L.; Lavalleye, J.-P.P.M.; Sowinski, A.F.; Izumi, A.N. Moore, S.S.; Brown, D.W.; Staudt, E.M. *Organometallics* **1985**, *4*, 1819.
6. Lewis, L.N. *J. Am. Chem. Soc.* **1990**, *112*, 5998.
7. Citron, J.B. *J. Org. Chem.* **1969**, *34*, 1977.
8. (a) Brown, H.C.; Heydkamp, W.R.; Breuer, E.; Murphy, W.S. *Am. Soc.* **1964**, 3365. (b) Burgess, K.; Ohlmeyer, M.J. *Tetrahedron Lett.* **1989**, *30*, 395. (c) Yamashite, J.; Catellani, M.; Tanaka, M.; *Chemistry Lett.* **1991**, 241. (d) Heck, R.F.; Nolley Jr., J.P.; *J. Org. Chem.* **1972**, *37*, 2320. (e) Heck, R.F. *Accts. Chem. Res.* **1979**, *12*, 146. (f) Cook, N.C.; Lyons, J.E. *J. Am. Chem. Soc.* **1965**, *87*, 3283. (g) Crabtree, R.H.' Davis, M.W.; *J. Org. Chem.* **1986**, *51*, 2655. (h) Evans, D.A.; Fu, G.C. *J. Am. Chem. Soc.* **1991**, *113*, 4042. Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712. (i) Tamao, K.; Tohma, T. *Tetrahedron Lett.* **1990**, *31*, 7353.
9. Giordano, G.; Crabtree, R.H. *Inorg. Synthesis* **1979**, *19*, 218.

(Received in USA 13 January 1993; accepted 8 March 1993)