Cationic Palladium Nitro Complexes as Catalysts for the Oxygen-based Oxidation of Alkenes to Ketones, and for the Oxydehydrogenation of Ketones and Aldehydes to the α,β-Unsaturated Analogues

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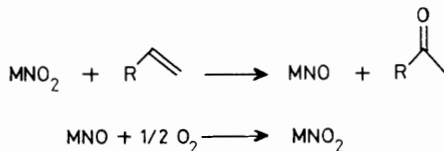*Union Carbide Corporation, PO Box 8361, South Charleston, WV 25303, U.S.A.*

Cationic palladium nitro complexes permit more rapid and more selective oxidation of alkenes to ketones than existing metal nitro catalysts; they also oxidatively dehydrogenate ketones and aldehydes to the corresponding α,β-unsaturated analogues under extremely mild conditions.

Catalysts that permit direct air oxidation of alkenes, without co-product formation, are of great importance to the chemical industry. Several metal nitro complexes have recently been shown to oxidize alkenes to ketones by using a nitro–nitrosyl couple (Scheme 1). These catalysts can be divided into two categories; (i) those that employ a metal nitro complex for oxygen atom transfer and a Lewis acid to activate the alkene,[1] and (ii) those that contain both the nitro group and the alkene activation site within the same complex.[2] We reasoned that the reactivity of either system might be increased by increasing the strength of the Lewis acid.

We achieved this by using cationic palladium complexes to activate the alkenes. The resulting systems have much faster rates, and in certain cases higher selectivities, than the corresponding neutral systems. They also catalyse the oxy-dehydrogenation of ketones or aldehydes to the corresponding α,β-unsaturated analogues under extremely mild condi-tions. This potentially valuable route to important unsatu-rated monomers has not previously been reported for metal–nitro catalysts.[3]

We began by adding 1 equiv. of AgBF$_4$ to the Co(pyr)(TPP)(NO$_2$) (pyr = pyridine, TPP = tetraphenylpor-phine)/(PhCN)$_2$PdCl$_2$ system.[1] We found that the rate of oxidation of oct-1-ene to a mixture of octanones was increased by a factor of eight, presumably because the silver abstracted chloride from the palladium complex and made it a better alkene activator. However, the cationic palladium complex also isomerized the alkenes at a much faster rate than the neutral palladium complex.

In order to increase the selectivity for oxidation over isomerization, we turned to the monometallic system [Pd]Cl{[Pd] = (CH$_3$CN)$_2$Pd(NO$_2$)}, which contains both the NO$_2$ group and the alkene-activating site in the same complex.[2] This maximizes the opportunity for O-atom trans-fer before substantial alkene isomerization can occur. By treating [Pd]Cl with various silver salts of non-co-ordinating anions, we discovered greatly improved rate and selectivity over any other known metal nitro oxidation catalyst.† With

MNO$_2$ + R⌒⌒ ⟶ MNO + R⌒C(=O)⌒

MNO + 1/2 O$_2$ ⟶ MNO$_2$

Scheme 1

AgSbF$_6$ in tetrahydrofuran (THF) solvent, we observed greater than a 20-fold increase in initial rate, and a 15-fold increase in the selectivity, over the neutral chloro complex for the oxygenation of oct-1-ene to octan-2-one (Table 1).

There were substantial differences in both the rate and the selectivity depending on the counterion of [Pd]$^+$, even among the so-called non-co-ordinating anions. For example, the SbF$_6$$^-$ salt was nearly 10 times faster than the BF$_4$$^-$ analogue (Table 1). This prompted us to investigate the effect of other anions, both co-ordinating and non-co-ordinating, by similar metathesis with the corresponding silver salt. The fastest rates were obtained with the least co-ordinating anions. The highest
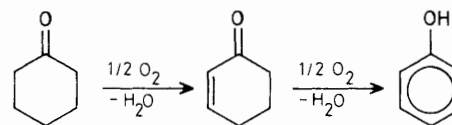
Scheme 2

Table 1. Catalytic oxidation of oct-1-ene to octan-2-one.

Conditions[a]	Turnover number[b]		Selectivity[c] after 1 h
	10 min	24 h	
no Ag	0.3	1.7	1.6
AgSbF$_6$	6.2	18.1	23.6
AgOTf, 83 equiv. H$_2$O	1.3	11.3	24.5
AgReO$_4$	6.1	10.4	18.9
AgReO$_4$ @ 0 °C	1.1	10.3	10.5
AgBF$_4$	0.7	9.6	28.8
AgOTf	3.6	9.6	14.3
AgPF$_6$	0.8	9.5	8.0
BF$_3$·(Et$_2$O)	0.7	8.1	12.1
AgClO$_4$	1.2	7.2	4.0
AgCN	0.3	5.8	2.4
Ag(S$_2$CNMe$_2$) 73 h @ 70 °C	0.1	5.4	20.9
Ag$_3$PO$_4$	0.5	4.0	5.2
AgNO$_3$	0.6	3.4	9.5
AgO$_2$CCF$_3$	0.5	2.8	60.2
Ag(acac)[d]	0.3	1.9	39.0
Ag$_2$CrO$_2$	0.4	1.8	6.5
Ag$_2$WO$_4$	0.3	1.6	12.3
AgO$_2$CMe	0.1	1.4	8.6
AgMnO$_4$	0.5	1.4	5.3
AgSCN	0.3	1.0	4.1
Ag(acac-F$_3$)[e]	0.2	0.7	37.4

[a] *Reaction conditions*: 0.046 M [Pd]Cl in THF, 1 atm dry O$_2$, room temp., 1 equiv. silver salt (or BF$_3$), and 55 equiv. dry oct-1-ene per mole Pd. THF was used immediately after distillation from sodium/benzophenone. [b] Moles octanone products per mole of palladium complex, as determined by capillary g.c. *vs.* undecane internal standard. [c] Selectivity defined as moles of octan-2-one/(moles of other octanones + moles of octene isomers), as determined by capillary g.c. [d] acac = acetylacetonate. [e] acac-F$_3$ = 1,1,1-trifluoroacetylacetonate.

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† Complex [Pd]$^+$ReO$_4$$^-$ was isolated and characterized. The i.r. spectrum as a mull showed a shift in the asymmetric N–O stretch upon converting [Pd]Cl to [Pd]$^+$ReO$_4$$^-$ (from 1451 cm^{-1} in the chloride, to 1493 cm^{-1} in the perrhenate), whereas the symmetric stretch was unchanged. There was little difference between the spectra of the chloride and the perrhenate in THF solution.

Table 2. Catalytic oxydehydrogenation by cationic palladium nitro complexes.[a]

Substrate	Catalyst	Solvent	[Pd]/M	[Substrate] /M	Turnover number[b]		Comment
					(1 h)	(24 h)	
cyclopentanone	[Pd]OTf	THF	0.035	3.2	3.0	12.1	
cyclopentanone	[Pd]OTf	THF	0.022	0.9	1.0	8.1	
cyclopentanone	[Pd]ReO$_4$	THF	0.022	0.9	3.9	9.1	
cyclopentanone	[Pd]Cl	THF	0.035	3.2	<0.1	0.2	
cyclopentanone	[Pd]Cl	toluene	0.035	3.2	<0.1	0.1	
cyclohexanone	[Pd]OTf	THF	0.036	2.8	4.9	4.6	aldol formation
cyclohexanone	[Pd]OTf	THF	0.022	0.9	1.1	11.0	phenol formation[c]
cyclohexanone	[Pd]OTf	THF	0.036	2.8	0.9	0.9	reaction under N$_2$
cycloheptanone	[Pd]OTf	THF	0.022	0.9	0.1	1.0	
isobutyraldehyde	[Pd]OTf	glyme	0.022	0.9	0.7	2.6	[BHT] = 0.01 M[d]
butan-2-one	[Pd]OTf	glyme	0.050	4.5	—	0.5	

[a] Catalyst solutions were generated by mixing [Pd]Cl with AgOTf or AgReO$_4$ in the appropriate solvent. The substrate was then added and the mixture stirred at room temp. under 1 atm dry O$_2$. [b] Moles α,β-unsaturated product per mole of palladium complex, as determined by capillary g.c. *vs.* undecane internal standard. [c] Phenol = 0.26 turnovers at 24 h. [d] BHT (2,6-di-t-butyl-4-methylphenol) prevented aldehyde autoxidation.

selectivities were achieved with potentially chelating anions, such as trifluoroacetate or acetylacetonates, although their rates were extremely slow. Note that the replacement of chloride by another ligand increased both the selectivity and productivity in nearly every case.

Deactivation of the [Pd]$^+$ system appears to occur by precipitation of palladium metal. The black solids and metallic mirrors that formed during the reaction exhibited no i.r. absorptions. Potentially oxidizing anions, such as CrO$_4^{2-}$, NO$_3^-$, MnO$_4^-$, and ReO$_4^-$, had little effect on the catalyst lifetime.

Cyclic monoalkenes such as cyclohexene were also readily oxidized, but the corresponding ketone product was catalytically oxydehydrogenated to the α,β-unsaturated ketone. For instance, the addition of cyclohexanone to a solution of [Pd]$^+$OTf$^-$ (OTf$^-$ = CF$_3$SO$_3^-$) in THF under one atmosphere of oxygen at room temperature resulted in the smooth catalytic conversion to cyclohex-2-en-1-one. At longer reaction times (>6 h), phenol was formed (Scheme 2). Only 0.9 turnovers were achieved with cyclohexanone under an inert atmosphere, proving that the reaction is truly an oxidative dehydrogenation.

As in the alkene oxidation studies, the ReO$_4^-$ salt exhibited a faster reaction rate than OTf$^-$, although the final yield for each was similar (Table 2). In contrast, the parent chloride [Pd]Cl was barely active for oxydehydrogenation. The reaction is restricted to a rather narrow temperature range, with the best results being obtained near room temperature. Temperatures near 0 °C gave rates that were too slow, while temperatures between 40 and 60 °C caused rapid catalyst deactivation in solvents other than acetonitrile. More dilute solutions in the case of cyclohexanone prevented aldol condensation and increased the turnover number.

The range of substrates examined, and their respective turnover numbers, are given in Table 2. The most active substrates were cyclic ketones, while acyclic ketones and

aldehydes gave much poorer yields. There was a very distinct ring size effect for the oxydehydrogenations of the cyclic ketones. The fastest rates were obtained with cyclopentanone and cyclohexanone, while cycloheptanone was very slow. Esters, nitriles, and nitroalkanes were unreactive, even on prolonged heating at 80 °C.

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