Nitration of Alkenes by Palladium Nitro Complexes

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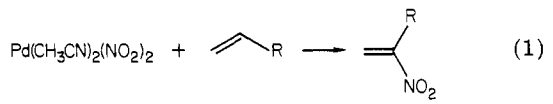
Reactions of $Pd(CH_3CN)_2ClNO_2$ (1) and $Pd(CH_3CN)_2(NO_2)_2$ (2) with alkenes lead in certain cases to nitro group transfer to the organic substrate rather than O atom transfer. Thus 2-nitro-1-alkenes are formed in good yields (based on Pd) by reaction of complex 2 with an excess of the corresponding monosubstituted alkene in dry toluene or dichloromethane. (In wet solvents, the predominate product is the 2-alkanone resulting from Wacker chemistry.) In contrast, nitroalkenes are not observed in reactions of 2 with internal or cyclic alkenes and only traces of nitroalkenes could be detected in reactions of complex 1 with monosubstituted alkenes. Evidence concerning the mechanism of nitroalkene formation is provided by the reactions of 1 with 1,5-cyclooctadiene and norbornadiene that lead to trans nitropalladation of one of the double bonds, similar to the well-known oxypalladation of the same dienes. In the course of verifying the stereochemistry of these reactions, revised NMR assignments were deduced for $[Pd(C_7H_8OCH_3)Cl]_2$ (**5b**), the product of methoxypalladation of norbornadiene.

Introduction

During the course of our investigations of the O-atom transfer oxidation of alkenes by $Pd(CH_3CN)_2ClNO_2$ (1),[1] we observed that the closely related dinitro complex $Pd(CH_3CN)_2(NO_2)_2$ (2) effects the nitration of 1-decene in the 2-position.[1a] Nitroalkenes are a valuable, but until recently, somewhat difficult to prepare class of compounds.[2] This, coupled with the remarkable sensitivity of the product distributions to the auxiliary ligand, led us to undertake the more detailed study reported here.

Results

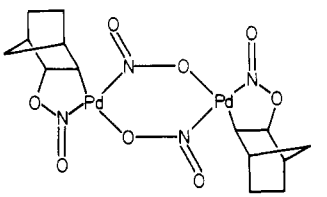
Alkene Nitration. Dinitro complex 2 reacts with excess 1-decene in either dry toluene or dichloromethane to give 2-nitro-1-decene in >85% GC yield based on Pd (eq 1).



(1)

The nitroalkene is easily separated chromatographically from the byproduct 2-decanone to give a >50% isolated yield. Although the reaction in toluene takes over a week at room temperature to reach completion due to the very low solubility of 2, the reaction proceeds with the same selectivity and yield in refluxing dichloromethane in 5 h. Propylene is also nitrated to give the known,[3] but less stable, 2-nitropropene with similar selectivities and yields. With ethylene, only traces of nitroethylene could be detected in reactions monitored spectroscopically.

The nitration reaction appears to be limited to terminal alkenes. Internal (*cis*-2-butene) and cyclic (cyclohexene, cycloheptene, and norbornene) alkenes react with dinitro complex 2 to give mainly oxidized products resulting from O atom transfer (epoxides, ketones, allyl alcohols, and α,β-unsaturated ketones). The product distributions observed in these cases are similar to those found in reactions with chloronitro complex 1.[1] In particular, no nitrocyclohexene could be detected by GC (based on an authentic sample) in the reaction of 2 with cyclohexene. The reaction of 2 with norbornene to give *exo*-epoxynorbornane proceeds via an isolable metallacyclic intermediate **3**,



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analogous to that observed in the reaction of norbornene with chloronitro complex 1.[1] The vibrational frequencies of **3** attributable to the metal nitro group (1420, 1387, 1341, 1255, and 838 cm^{-1}) are similar to those seen in $[Ni(NO_2)_3]^-$ (1435, 1202, and 852 cm^{-1}) and $[Pd(PBu)_3(NO_2)_2]_2$ (1476, 1421, 1330, and 1238 cm^{-1}),[4] suggesting that the metal nitro group in **3** is also μ-*NO* bridged as shown.

Table I gives the results of a number of experiments designed to test the effect of various reaction variables on the nitration of 1-decene. Changing the auxiliary nitrile group (run 1 vs. run 2) has very little effect on the reaction, except that the acetonitrile complex reacts about 2–3 times faster than the corresponding benzonitrile complex. Changing the concentration of the various reactants (run 5 vs. runs 8–9) seems to have very little effect on either the yield or selectivity of the reaction. Decreasing the alkene to Pd ratio (run 6 vs. run 10) or increasing the temperature of the reaction (runs 1 and 3 vs. runs 7 and 6), however, is detrimental to both the total yield and selectivity for nitroalkene.

More interesting are the selectivity changes observed as a function of solvent and auxiliary halide ligand. It initially appeared that the nitroalkene to ketone ratio was solvent dependent (runs 1, 3–5), favoring the nitroalkene in nonpolar solvents. Although we can not rule this out, the solvent effect is over shadowed by a water effect. While

(1) (a) Andrews, M. A.; Kelly, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 2894–2896. (b) Andrews, M. A.; Cheng, C.-W. F. *Ibid.* **1982**, *104*, 4268–4270. (c) Andrews, M. A.; Chang, T. C.-T.; Cheng, C.-W. F.; Emge, T. J.; Kelly, K. P.; Koetzle, T. F. *Ibid.*, in press. (d) Andrews, M. A.; Chang, T. C.-T.; Cheng, C.-W. F.; Kelly, K. P., submitted for publication in *Organometallics*.

(2) (a) Knochel, P.; Seebach, D. *Synthesis* **1982**, 1017–1018. (b) Barton, D. H. R.; Motherwell, W. B.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1982**, 551–552. (c) Sakakibara, T.; Ikuta, S.-I.; Sudoh, R. *Synthesis* **1982**, 261–263. (d) Ono, N.; Miyake, H.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1982**, 33–34. (e) Sakakibara, T.; Takai, I.; Ohara, E.; Sudoh, R. *Ibid.* **1981** 261–262. (f) Knochel, P.; Seebach, D. *Tetrahedron Lett.* **1981**, *22*, 3223–3226. (g) Corey, E. J.; Estreicher, H. *Ibid.* **1980**, 1113–1116. (h) Ranganathan, D.; Rao, C. B.; Ranganathan, S.; Mehrotra, A. K.; Iyengar, R. *J. Org. Chem.* **1980**, *45*, 1185–1189. (i) Corey, E. J.; Estreicher, H. *J. Am. Chem. Soc.* **1978**, *100*, 6294–6295. (j) Miyashita, M.; Yanami, T.; Kumazawa, T.; Yoshikoshi, A. *Ibid.* **1984**, *106*, 2149–2156.

(3) (a) Buckley, G. D.; Scaife, C. W. *J. Chem. Soc.* **1947**, 1471–1472. (b) Miyashita, M.; Yanami, T.; Yoshikoshi, A. *Org. Synth.* **1981**, *60*, 101–103.

(4) Hitchman, M. A.; Rowbottom, G. L. *Coord. Chem. Rev.* **1982**, *42*, 55–132.

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Table I. Product Distributions in Reactions of $Pd(RCN)_2XNO_2$ with 1-Decene[a]

run	X	R	solvent	[Pd][b]/ mM	alkene/ equiv	T/°C	time/ days	product yields[c]/% nitrodecene	decanone
				Reference					
1	NO_2	Me	PhMe	5	10	25	7	92	16
				Variable = R					
2	NO_2	Ph	PhMe	5	10	25	8	89	17
				Variable = Solvent					
3	NO_2	Me	CH_2Cl_2	5	12	25	1	105	12
4	NO_2	Me	EtOAc	7	12	25	4	74	18
5	NO_2	Ph	acetone	5	10	25	2	52	54
				Variable = Temperature					
6	NO_2	Ph	CH_2Cl_2	5	10	40	0.2	91	17
7	NO_2	Ph	PhMe	5	10	60	2	18	22
				Variable = Concentrations/Ratios					
8	NO_2	Ph	acetone	1	55	25	2	52	51
9	NO_2	Ph[d]	acetone	5	10	25	2	57	55
10	NO_2	Me	CH_2Cl_2	5	1.2	40	4	23	27[e]
				Variable = Water					
11	Cl_2[f]	Ph	acetone[g]	5	10	25	3	0	<3
12	NO_2	Ph	acetone[g]	5	10	25	2	30	114
				Variable = Auxiliary Halide					
13	OAc[h]	Me	PhMe	7	12	25	10	18	44
14	SCN[h]	Me	PhMe	8	11	25	4	13	55
15	Br	Me	PhMe	5	10	25	3	~1	92
16	Cl	Me	PhMe	5	10	25	2	~0.5	97
				Variable = Chloride Catalyst					
17	NO_2[i]	Ph	CH_2Cl_2	3	9	25	2	80	17

[a] Reactions conducted under nitrogen. [b] The concentrations given correspond to those that would result from complete dissolution under the reaction conditions. Complex **2** is readily soluble in acetone and acetonitrile but nearly insoluble in less polar solvents. [c] Based on Pd. [d] 8 equiv of PhCN added. [e] 0.29 equiv of 1-decene remained unreacted. [f] Reagent = $Pd(PhCN)_2Cl_2$. [g] 11 equiv of water added. [h] Reagent incompletely characterized. [i] 0.1 equiv of $Pd(CH_3CN)_2ClNO_2$ added.

the Wacker reaction[5] of alkenes with water in the presence of $Pd(CH_3CN)_2Cl_2$ to give ketones is minimal (run 11), in the presence of dinitro complex **2**, ketone formation is very rapid (run 5 vs. run 12). The lower selectivity for nitroalkene in "dry" acetone vs. toluene may be a true solvent effect or more likely a residual water effect since acetone is very hard to dry thoroughly. Consistent with the latter hypothesis is the observation that ketone formation is always faster than nitroalkene formation during the early part of the reaction but levels out sooner, presumably when the residual water has been scavenged. The higher Wacker reactivity of dinitro complex **2** vs. chloronitro complex **1** and the dichloride is a reasonable consequence of the higher electron-withdrawing effect of the nitro groups.

The reaction variable with the strongest effect on product selectivity is the auxiliary halide ligand present in the $Pd(CH_3CN)_2XNO_2$ reagent (runs 1, 13–16). When X = Cl or Br, ketone formation is favored over nitration by about 100:1. When X = NO_2, the ratio is reversed and ketone formation is disfavored by about 1:6. When complexes where X is presumably thiocyanate or acetate are employed, the selectivity is intermediate with ketone formation favored by about 4–2.5:1. A possible catalytic role for chloride ion (eq 2 and 3) in the formation of ketone

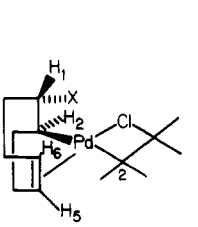
$$Pd(CH_3CN)_2ClNO_2 + CH_2{=}CHR \rightarrow PdNOCl + RCOCH_3 \quad (2)$$

$$PdNOCl + Pd(CH_3CN)_2(NO_2)_2 \rightarrow PdNONO_2 + Pd(CH_3CN)_2ClNO_2 \quad (3)$$

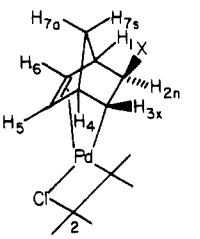
(5) Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sieber, R.; Ruttinger, R.; Kojer, H. *Angew. Chem.* **1959**, *71*, 176–182.

was examined, since the dinitro complex generally contained trace (<5 mol %) amounts of chloride. The purposeful addition of 0.1 equiv of chloro nitro complex **1** had very little effect on the yield of ketone (run 3 vs. run 17), however, indicating that such catalysis is minimal.

Alkene Nitropalladation. The reaction of chloro nitro complex **1** with the chelating dialkenes 1,5-cyclooctadiene (COD) and norbornadiene (NBD) leads to the nitropalladated complexes **4a** and **5a**, respectively. With COD,



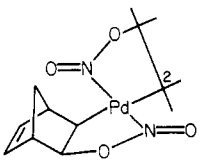
4a–c



5a–c

a, X = NO_2; b, = OCH_3; c, X = OCD_3

the 15-min reaction is quantitative and shows no evidence for observable intermediates (except possibly the chelated dialkene complex $(COD)PdNO_2Cl$). With NBD, the reaction proceeds within 3 min to the metallacyclic intermediate **6** that then decomposes over a period of about an hour to a mixture of complex **5a** and an unidentified aldehyde. The ratio of **5a** to aldehyde formed is markedly concentration dependent, favoring complex **5a** at high reaction concentrations. Complex **4a** and **5a** were identified by their characteristic NO_2 stretching vibrations (1540 and 1377 cm^{-1} for **4a** vs. ~1560 and 1350 cm^{-1} for



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nitroalkanes[6]) and by the strong similarity of their ^1H NMR spectra to those of the well-known methoxy analogues **4b**[7] and **5b**[8], respectively. The basis for the trans substitution stereochemistry shown is described in the Discussion. In contrast to methoxy complexes **4b** and **5b** that undergo bridge cleavage by donor ligands,[7a,8a] complex **4a** is rapidly quenched by triphenylphosphine back to COD (plus presumably $[Pd(PPh_3)ClNO_2]_2$). Thermolysis of **4a** did not lead to any readily identifiable organic products such as 1-nitro-1,5-cyclooctadiene.

Discussion

Synthetic Methodology Prospects. Dinitro complex **2** would appear to have limited application as a reagent for the nitration of alkenes. The reaction appears to be restricted to monosubstituted alkenes and does not appear to proceed well under stoichiometric conditions. Since an extensive investigation of the reaction as a function of reactant ratios was not carried out, it is possible that satisfactory results might be obtained with a 50–100% excess of either alkene or Pd. Since the nitration reagent and reaction conditions are very mild, complex **2** might prove to be a useful specialty reagent for alkene nitration.

Mechanism of Nitration. There are at least two mechanisms that could be envisioned to explain the formation of nitroalkenes from dinitro complex **2** and terminal alkenes (Scheme I). The first (path 1) involves a linkage isomerism preequilibrium between a dinitro complex and a nitro nitrito complex. Although no clear IR evidence for the presence of an O-bonded nitrite ligand in **2** was found, facile linkage isomerism has been seen in dinitrobis(phosphine)nickel(II) complexes.[9] The nitrito nitrogen atom could then nucleophilically attack an adjacent coordinated alkene to give the metallacyclic chelated nitroalkyl complex i. The Pd–O bond in metallacycle i would be expected to be very weak,[10] leading to ring opening to give nitroalkyl complex ii, followed by facile β-hydrogen elimination with formation of the nitroalkene. Aside from the linkage isomerization step, this mechanism is directly analogous to that proposed for the formation of ketones in reactions of chloro nitro complex **1** with terminal alkenes.[1] An alternative mechanism (path 2) would involve dissociation of NO_2^- from a dinitro complex. The nitrite anion could then attack a coordinated alkene to give nitroalkyl complex ii that would then undergo β-hydrogen elimination to yield nitroalkene in the same manner as in the linkage isomerization mechanism.[11]

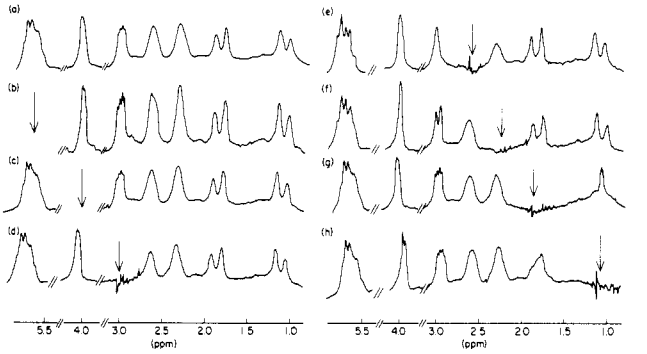
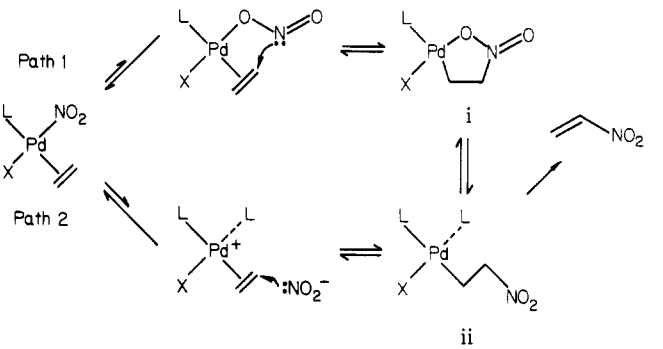


Figure 1. ^1H NMR spectra of trideuteriomethoxy complex **5c** in C_6D_6: a, undecoupled; b–h, homonuclear decoupled by double irradiation of proton(s) indicated by arrows.

Scheme I. Possible Mechanisms for Alkene Nitration by $Pd(RCN)_2XNO_2$



The nitropalladated complexes **4a** and **5a** provide potential models for the intermediate nitroalkyl complex ii proposed in both of the above mechanisms, the subsequent β-hydrogen elimination being inhibited by the chelating alkene group present. The intramolecular linkage isomerism mechanism of path 1 would necessarily predict cis nitropalladation, while the nitrite anion mechanism of path 2 would be expected to occur with a trans stereochemistry.[8,12] A determination of the stereochemistry of complexes **4a** and **5a** therefore seemed important.

Stereochemistry of Complexes 4a–5b. The sterochemical assignments in nitropalladated complexes **4a** and **5a** are almost certainly the same as those in the corresponding methoxy complexes **4b** and **5b** since, aside from some expected chemical shift differences, the NMR spectra of the nitro and previously known methoxy-substituted complexes[7,8] are almost identical (Tables II and III). In both COD complexes, double irradiation of all the methylene hydrogens leads to a low-field AB quartet ($J \approx 9.5$ Hz) due to the vinylic protons H_5 and H_6 and to two mid-field doublets ($J = 2.5$ Hz) due to the mutually coupled vicinal H_1 and H_2 methine protons. No detailed study of the stereochemistry of the methoxy COD complex appears to have been made, but the small value of the vicinal methine coupling constant and the now well-established trans geometry for methoxypalladation reactions[8,12] are consistent with a trans stereochemistry for both **4a** and **4b**.

A more detailed analysis of the stereochemistry of the NBD complexes is possible due to the rigid geometry present. The methoxy NBD complex has been assigned a trans stereochemistry by two sets of workers,[8] but they disagreed on the assignment of the methine protons. In

(6) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 194.

(7) (a) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413–3416. (b) Robinson, S. D.; Shaw, B. L. *Ibid.* **1964**, 5002–5008.

(8) (a) Stille, J. K.; Morgan, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5135–5141. (b) Green, M.; Hancock, R. I. *J. Chem. Soc. A* **1967**, 2054–2057.

(9) Kriege-Simondsen, J.; Bailey, T. D.; Feltham, R. D. *Inorg. Chem.* **1983**, *22*, 3318–3323.

(10) Davies, J. A.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 79–90.

(11) Nitrite ion dissociation from palladium nitro complexes may also be occurring in reactions of nitro complexes **1** and **2** with organic halides (especially allylic and benzylic) that give the corresponding palladium halide complex and mixtures of organic nitro and nitrite compounds. Halide exchange reactions between (nitrile)halopalladium(II) complexes and organic halides (with concomitant isomerization in the case of some allylic halides) have also been observed. (Andrews, M. A.; Chang, T. C.-T.; Kapustay, L. V., unpublished work.)

(12) (a) Bäckvall, J.-E. *Acc. Chem. Res.* **1983**, *16*, 335–342. (b) Kurosawa, H.; Majima, T.; Asada, N. *J. Am. Chem. Soc.* **1980**, *102*, 6996–7003. (c) Stille, J. K.; James, D. E. *J. Organomet. Chem.* **1976**, *108*, 401–408.

Table II. ^{1}H NMR Data for 4a and 4b

proton	$CDCl_3$ solution		C_6D_6 solution	
	4a	4b	4a[a]	4b
	Chemical Shifts (ppm)			
H_1	4.8 (1 H, m)	3.60 (2 H, ~t)	4.55	3.60 (1 H, m)[b]
H_2	3.68 (1 H, m)		3.80	3.95 (1 H, m)[b]
H_3, H_4, H_7, H_8	2.7-2.3 (7 H, m), 1.5 (1 H, m)	2.60 (2 H, ~t), 2.3-1.8 (5 H, m), 1.45 (1 H, m)	1.85-0.95	2.2-1.3 (8 H, m)
H_5, H_6	6.1 (1 H, m), 5.6 (1 H, m)	5.90 (1 H, m), 5.55 (1 H, m)	5.50, 5.25	5.65 (1 H, m), 5.45 (1 H, m)
OCH_3		3.26 (3 H, s)		3.10 (3 H, s)
	Selected Coupling Constants (Hz)			
J_{1-2}	2.5			2.5
J_{5-6}	9.1			9.5

[a] Solubility too low to permit detailed analysis. [b] Assignments based on comparison of peak shapes with those of 4a.

Table III. ^{1}H NMR Data for 5a, 5b, and 5c

Chemical Shifts (ppm)

proton	$CDCl_3$ solution		C_6D_6 solution	
	5a	5b	5a	5c
H_1				2.29 (1 H, br s)
H_3	3.56 (2 H, br s), 3.40 (1 H, m)	3.23 (1 H, br s), 2.85 (2 H, m)	2.65 (2 H, br s), 2.53 (1 H, m)	2.97 (1 H, m)
H_4				2.60 (1 H, br s)
H_2	5.17 (1 H, s)	4.17 (1 H, s)	4.45 (1 H, s)	4.02 (1 H, s)
H_5	6.19 (m)[a]	6.12 (1 H, ~t), 5.93 (1 H, m)	5.35 (m)[a]	5.67 (2 H, m)
H_6				
H_{7s}	1.80 (d),[a] 1.55 (d)[a]	1.97 (1 H, d), 1.63 (1 H, d)	~1.3 (m)[a]	1.81 (1 H, d)
H_{7a}				1.07 (1 H, d)
OCH_3		3.29 (3 H, s)		

Coupling Constants (Hz) for 5c in C_6D_6 [b]

	H_2	H_3	H_4	H_5/H_6	H_{7s}	H_{7a}
H_1	2.3	2.0	(1)	(2)	(0.5)	(0.5)
H_2		(0)	(0.5)	(0.5)	(0)	(1)
H_3			4.3	(0.5)	(0)	(0)
H_4				(1)	(0.5)	(0)
H_5/H_6				(3.5)	(0)	(0)
H_{7s}						9.1

[a] Partially obscured by impurities. [b] Values in parentheses estimated from changes in width at half-height on double irradiation; others actually observed.

the course of our present investigation we found it helpful to reanalyze the NMR of **5b** for comparison with **5a**. While our undecoupled spectra of **5b** in both $CDCl_3$ and C_6D_6 exactly match those reported in the literature,[8b] our decoupling experiments show marked discrepancies with those in the literature.[8b] Our 80-MHz FT NMR spectra of the trideuteriomethoxy complex **5c** (Figure 1) have slightly less resolution than the previously reported 100-MHz CW NMR spectra (Figure 3 of ref 8b) but have significantly better signal to noise ratios.

The vinyl (H_5 and H_6) and bridging methylene (H_7) hydrogens of deuterio complex **5c** are readily assigned to the multiplet at ~5.67 ppm and the AB quartet at 1.81 and 1.07 ppm, respectively (C_6D_6 solution). This leaves three closely spaced (2.97, 2.60, and 2.29 ppm), broad (~10-Hz width at half-height) multiplets and a narrower (~6-Hz width at half-height) multiplet at 4.02 ppm. We concur with the original workers that the 2.60 and 2.29 ppm multiplets are the bridgehead protons (vide infra). In marked contrast with the literature which states that "double irradiation of either of the two bridgehead protons has no effect on the band centered at τ 7.09 [δ 2.97 here]",[8b] we find that double irradiation of the high-field bridgehead proton collapses the 2.97 ppm multiplet (J = 4.3, 2, <1 Hz) to a 4.3-Hz doublet (Figure 1f) and irradiation of the low-field bridgehead proton collapses the 2.97 ppm multiplet to an unresolved singlet whose half-width has decreased by ~3–4 Hz (Figure 1e). Furthermore, the narrow downfield 4.02 ppm multiplet (J = 2.3, 1, <1 Hz) is observed to be coupled to the high-field bridgehead (J = 2.3 Hz) not the low-field bridgehead as reported.[8b] This is shown by the ~2 Hz narrowing in the 4.02 ppm resonance that occurs on irradiation of the high-field bridgehead proton (Figure 1f vs. 1a and 1e) (and vice versa Figure 1c) to which it is coupled. Finally, irradiation of the 2.97 ppm multiplet had only a very slight effect on the 4.02 ppm signal (Figure 1d) (and vice versa, Figure 1c), indicating a coupling between them of <1 Hz, not 2.6 Hz as previously reported.[8b] We have no good explanation for the irreconcilable decoupling results obtained by the two groups.

Our assignments for the four mid-field protons are derived as follows. If (endo) cis methoxypalladation had occurred, there should be three couplings >3 Hz, two between the bridgehead and adjacent exomethine protons (3–5 Hz) and one large one between the two exo methine protons (8–12 Hz).[8b,13] In contrast the trans configuration shown for **5c** would be expected to have just one bridgehead–exo coupling (3–5 Hz) and a small (2–5 Hz) exo-

(13) (a) Marshall, J. L.; Walter, S. R.; Barfield, M.; Marchand, A. P.; Marchand, N. W.; Segre, A. L. *Tetrahedron* **1976**, *32*, 537–542. (b) Marshall, J. L.; Walter, S. R. *J. Am. Chem. Soc.* **1974**, *96*, 6358–6362.

methine–endo methine coupling.[8b,13] The only coupling constant >2.5 Hz observed (excluding the vicinal vinyl and geminal methylene couplings) is the 4.3 Hz one between the 2.97 and 2.60 ppm multiplets. This requires that the Pd and the methoxy groups have a trans configuration. By analogy, nitropalladated complex **5a** is also deduced to have a trans stereochemistry.

We, as did Stille,[8a] assign the methoxy-substituted methine proton H_{2n} to the downfield multiplet at 4.02 ppm. This is consistent with the larger downfield shift in this resonance that is observed on going into nitro complex **5a** ($\Delta\delta$ = 1.00 ppm in $CDCl_3$ and $\Delta\delta$ = 0.45 ppm in C_6D_6) vs. all the other resonances. The one large 4.3-Hz coupling between the 2.97 and 2.60 ppm resonances is attributed to the exo palladium methine H_{3x} to H_4 bridgehead coupling, leaving the H_1 bridgehead adjacent to the methoxy group to be the resonance at 2.29 ppm. The H_{2n} methine to H_{3x} methine coupling constant is therefore <1 Hz regardless of whether the 2.97 or 2.60 ppm proton is assigned to H_{3x}. (We assign the 2.97 ppm resonance to H_{3x} and the 2.60 ppm resonance to the H_4 bridgehead based on the multiple small couplings observed.) The small value of the H_{2n}–H_{3x} methine coupling constant (<1 Hz vs. a ~3 Hz normal value) and the large values of both the H_1 bridgehead to H_{2n} methine vicinal coupling (2.3 Hz vs. a normal 0 Hz) and the H_1 bridgehead to H_{3x} methine W coupling (2 Hz vs. a normal 0.5 Hz) can all be attributed to a twist about the C2–C3 bond resulting from coordination of the palladium to the double bond. Molecular models suggest that this twist decreases the H_{2n}–C–C–H_{3x} dihedral angle from 117° to ~90° and the H_1–C–C–H_{2n} dihedral angle from 75° to ~60° (decreasing $J_{2n\text{-}3x}$ and increasing $J_{1\text{-}2n}$) and increases the planarity of the H_1–C–C–C–H_{3x} W group (increasing $J_{1\text{-}3x}$). It also decreases the H_{3x}–C–C–H_4 dihedral angle from 44° to ~30°. The fairly normal 4.3-Hz value observed for this coupling may result from a cancellation of substituent and dihedral angle effects. All the other couplings observed in the molecule are quite typical of a norbornane system.[8b,13]

Conclusions. The trans stereochemistry observed for nitropalladation in **4a** and **5a** supports a dissociative nitrite ion mechanism (path 2, Scheme I) for their formation and by extension for the formation of nitroalkenes in the reaction of dinitro complex **2** with terminal alkenes. The origin of the auxiliary halide and monoene vs. diene effects on the partitioning between O atom and nitro group transfer is not certain. Nitro groups and alkenes have a high trans effect, however, and may facilitate nitrite ion dissociation and hence nitro group transfer when they are present as auxiliary ligands.

Experimental Section

General Data. Infrared spectra were recorded on a Nicolet MX-1 Fourier transform spectrometer. NMR spectra were recorded on a Varian CFT-20 spectrometer equipped with a dual ^1H–^{13}C probe. GC analyses were performed on a Perkin-Elmer Sigma 3B gas chromatograph equipped with $^1/_8$ in. × 6 ft stainless steel columns and a flame ionization detector linked to a Sigma 10B data station that performed electronic integrations.

Reagent grade solvents were dried over molecular sieves, except for acetone which was distilled under nitrogen from anhydrous calcium sulfate. 1-Decene was distilled from sodium under nitrogen; other alkenes were used as received. Chloronitro complex **1**[1] and methoxy complexes **4b**,[7] **5b**,[8b] and **5c**[8b] were prepared as described in the literature. The benzonitrile analogues of **1** and **2** were prepared by ligand exchange and characterized by IR and NMR spectroscopy and by GC analysis (for benzonitrile stoichiometry).

Bis(acetonitrile)dinitropalladium(II) (2). A suspension of $Pd(CH_3CN)_2Cl_2$ (1.50 g, 5.78 mmol) (conveniently prepared in situ from $PdCl_2$ and acetonitrile) in acetonitrile (30 mL) was treated with a solution of silver nitrite (1.78 g, 11.6 mmol) in acetonitrile (20 mL) resulting in the immediate precipitation of silver chloride. The mixture was stirred for about 1 h and then filtered without difficulty. The solvent was removed under vacuum from the deep yellow filtrate to give **2** as a yellow solid (1.64 g, 100%). The material tended to darken upon extended drying under vacuum or upon recrystallation (acetonitrile–toluene): ^1H NMR (acetone-d_6) 2.16 ppm (s); IR (Nujol/Fluorolube mull, KBr for ν_{NO_2}) 2999 (w, ν_{CH} (E)), 2935 (m, ν_{CH} (A_1)), 2333 (ms, ν_{CN}), 2303 (m, $\delta_{CH} + \nu_{CC}$), 1406 (s, ν_{NO_2}), 1388 (s, ν_{NO_2}), 1347 (s, ν_{NO_2}), 1029 (m, ρ_{CH_3}), 945 (m, ν_{CC}), 828 (s, δ_{NO_2}), 820 (s, δ_{NO_2}), 583 (w, ρ_{NO_2}) cm^{-1}. Anal. Calcd for $C_4H_6N_4O_4Pd$: C, 17.13; H, 2.16; Cl, 0.00; N, 19.97. Found: C, 16.74, H, 2.17; Cl, 0.56; N, 18.20.

Reaction of Dinitro Complex 2 with Propylene. A suspension of dinitro complex **2** (33 mg) in dichloromethane (3.5 mL) was treated with excess propylene under nitrogen. The yellow solution rapidly became olive green and then gradually deposited a black precipitate. An infrared spectrum taken of the reaction mixture after 54 h showed a peak due to acetone at 1712 (m, ν_{CO}) cm^{-1} and peaks due to 2-nitropropene at 1676 (vw, $\nu_{C=C}$), 1529 (vs, ν_{NO} asym), and 1345 (s, ν_{NO} sym) cm^{-1} (lit.[14] 1670, 1520, and 1350 cm^{-1}, respectively). GC analysis indicated that the yields of acetone and 2-nitropropene (based on Pd) were about 20 and 85%, respectively. (It was necessary to estimate the GC response factor for 2-nitropropene since the pure material polymerizes readily[3].) Most of the dichloromethane was removed with a rotary evaporator and the residual material dissolved in $CDCl_3$ and a ^1H NMR spectrum obtained that also showed peaks attributable to acetone (2.17 ppm) and 2-nitropropene (6.41 (1 H, s), 5.58 (1 H, s), and 2.26 (3 H, s) ppm (lit. (CCl_4)[14] 6.33, 5.60, and 2.21 ppm)).

Reaction of Dinitro Complex 2 with *cis*-2-Butene. A suspension of dinitro complex **2** (30 mg, 0.11 mmol) in dichloromethane (10 mL) was treated with an excess of *cis*-2-butene under nitrogen at 40 °C. After 1 day, the only significant product detected by GC was 2-butanone.

Reaction of Dinitro Complex 2 with Cyclohexene. A suspension of dinitro complex **2** (31.5 mg) in 1,2-dichloroethane (3.5 mL) was treated with 1 equiv of cyclohexene under nitrogen. After 2.5 days GC analysis showed only a trace of cyclohex-2-en-1-ol. The mixture was then heated at 60 °C for 2 h at which time GC analysis give a ~50% yield of cyclohex-2-en-1-ol that decreased on further heating with the concomitant formation of cyclohex-2-en-1-one. The absence of 1-nitrocyclohexene formation was confirmed by comparison with GC spectra of an authentic sample (Aldrich).

Reaction of Dinitro Complex 2 with Cycloheptene. A suspension of dinitro complex **2** (33 mg) in 1,2-dichlorethane (3.5 mL) was treated with 1 equiv of cycloheptene under nitrogen at 60 °C for 20 h at which time GC analysis showed the formation of epoxycycloheptane (8%), cycloheptanone (1%), cyclohept-2-en-1-ol (5%), and cyclohept-2-en-1-one (17%). A similar reaction conducted in air at 60 °C with the sequential addition of 1-equiv aliquots of cycloheptene at 0, 40, and 180 min gave the same products in yields of 27, 6, 25, and 44%, respectively (based on Pd).

Reaction of Dinitro Complex 2 with Norbornene. A suspension of dinitro complex **2** (28 mg) in dichloromethane (20 mL) was treated with 12 equiv of norbornene at room temperature in air. After 7 days GC analysis showed the formation of epoxynorbornane in 195% yield based on Pd. An intermediate can be isolated from the reaction of dinitro complex **2** and norbornene in acetone identified as metallacycle **3** by comparison of its spectral characteristics (IR (KBr) 1609 ($\nu_{N=O}$), 1420, 1387, 1341, and 1255 (ν_{NO_2}), and 838 (δ_{NO_2}) cm^{-1}; ^1H NMR acetone-d_6) δ 4.60 (1 H, d, J = 6.8 Hz), 4.30 (1 H, d of d, J = 6.8, 2.7 Hz), 2.56 (1 H, br s), 2.42 (1 H, br s), ~1.7–1.0 (6 H, m)) with those of the metallacycle derived from chloronitro complex **1** and norbornene[1] (IR 1610 cm^{-1}; NMR ($CDCl_3$) δ 4.37 (1 H, q, J = 5, ~1.5 Hz), 4.29 (1 H, q, J = 6, 2.5 Hz), 2.57 (1 H, s), 2.44 (1 H, br s), 1.8–1.2 (6 H, m)).

Reaction of Dinitro Complex 2 with 1-Decene. A. Synthesis of 2-Nitro-1-decene. A suspension of **2** (200 mg, 0.71

(14) Descotes, G.; Bahurel, Y.; Bourillot, M.; Pingeon, G.; Rostaing, R. *Bull. Soc. Chim. Fr.* **1970**, 282–302.

mmol) in toluene (160 mL) was treated with 1-decene (0.8 mL, 4.2 mmol) and stirred under nitrogen for 26 days. The reaction mixture was filtered and the cake washed with acetone. The filtrate, which contained the product and 2-decanone in GC yields of ca. 85 and 15%, respectively, was evaporated to give a dark brown oil (131 mg). The oil was flash chromatographed on silica gel (50 g) with ether–hexane (8:92) as eluant. Six 25-mL fractions were collected, and fractions 4–6 were evaporated to give 2-nitro-1-decene (69 mg, 52% based on Pd) as an almost colorless liquid. An analytical sample was prepared by rechromatography followed by microdistillation: IR (CCl_4) 2956 (m), 2929 (s), 2872 (w), 2857 (m), 1554 (w), 1531 (vs, ν_{NO} asym), 1468 (w), 1457 (w), 1432 (w), 1388 (w), 1379 (w), 1344 (s, ν_{NO} sym), 937 (m), 859 (w) cm^{-1}; ^1H NMR (CCl_4) δ 6.39 (1 H, s), 5.52 (1 H, s), 2.6 (2 H, t, J = 7 Hz), 1.8–1.1 (12 H, br s), 0.91 (3 H, br t). Anal. Calcd for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.82; H, 10.32; N, 7.80.

B. GC Studies. The reaction of dinitro complex **2** and other complexes with 1-decene under a variety of conditions was examined by GC methods. The response factors for 2-decanone and 2-nitro-1-decene were determined from authentic samples. The reaction conditions and results are given in the tables. Pd$(CH_3CN)_2BrNO_2$ was prepared by the same method as that used for complex **1** except that $PdBr_2$ was employed as the starting material. A thiocyanate complex presumed to be Pd$(CH_3CN)_2(SCN)(NO_2)$ was prepared by treating complex **1** with 1 equiv of silver thiocyanate in acetonitrile (IR (KBr) 2325 (w), 2297 (w), 2163 (m), 2112 (sh), 1406 (s), 1342 (s) cm^{-1}). An acetate complex presumed to be Pd$(CH_3CN)_2(OAc)(NO_2)$ was prepared by reacting equal quantities of Pd$(OAc)_2$ and **2** in acetonitrile.

Reaction of Chloro Nitro Complex 1 with 1,5-Cyclooctadiene. 1,5-Cyclooctadiene (65 μL, 0.53 mmol) was added to a solution of chloro nitro complex **1** (138 mg, 0.51 mmol) in dichloromethane (15 mL). The orange solution immediately turned light yellow. After 5 min, hexane (10 mL) was added and the mixture concentrated under vacuum. The mother liquor was removed from the resulting precipitate, and the precipitate was washed with hexane and dried under vacuum to give complex **4a** as a light yellow powder (129 mg, 86%). The complex is somewhat light and heat sensitive and hard to free of traces of solvent hence no analysis was obtained: IR (KBr disk, intensity, shift on ^{15}N labeling, assignment) 3011 (vw), 2949 (w), 2926 (w), 2877 (w), 2833 (w), 1541 and 1535 (vs, −31 and −35, ν_{NO} (singlet at 1543 cm^{-1} in $CDCl_3$ solution)), 1424 (s), 1377 (s, −30, ν_{NO}), 1372 (m), 1359 (m), 1330 (m), 1309 (m), 1272 (w), 1209 (s), 1139 (w), 1080 (w), 1021 (w), 1001 (w), 990 (w), 871 (w), 828 (m), 771 (m), 755 (w, −3), 692 (w), 654 (w) cm^{-1}.

Reaction of Chloro Nitro Complex 1 with Norbornadiene. In a typical reaction, norbornadiene (4.8 μL, 44.5 μmol) was added to a solution of chloro nitro complex **1** in $CDCl_3$ (1 mL) under nitrogen. Within 3 min infrared spectra showed a strong peak at 1616 (1586 for ^{15}N) cm^{-1} attributable to metallacycle **6**. Over a period of 1 h, this peak disappeared and was replaced by peaks due to the nitropalladated complex **5a** (1541 (1508 for ^{15}N) cm^{-1}) and to an unidentified aldehyde (1688 cm^{-1}). The ratio of complex **5a** to aldehyde formed was observed to be concentration dependent, complex **5a** being favored by high concentrations. Neither complex **5a** nor the aldehyde could be isolated due to further decomposition reactions. Solutions containing primarily nitro complex **5a** were obtained by sequentially adding norbornadiene (3.8 μL) and then $CDCl_3$ or C_6D_6 (25 μL) to chloro nitro complex **1** (9 mg) under nitrogen in an NMR tube. After 1 h, the mixture was diluted with further solvent (0.5 mL) and NMR spectra were obtained. Peaks attributable to complex **5a** were observed (Table III). Solutions containing primarily the unknown aldehyde were obtained by reacting dilute solutions of chloro nitro complex **1** in dichloromethane with norbornadiene for 1 h, followed by concentration on a rotary evaporator and dissolution in $CDCl_3$. NMR spectra of the latter solutions (after quenching with triphenylphosphine to remove complex **5a**) showed peaks at 9.18 (1 H, d, J = 6.4 Hz), 5.86 (~4 H, s), 2.65 (~8 H, m), and ~1.5 (?, ?, J = 6.4 Hz) ppm. Other aldehydes were sometimes observed (9.79 (s) ppm; ν_{CO} = 1662 cm^{-1}; 9.55 (s) ppm, ν_{CO} = 1670 cm^{-1}), particularly in solutions that had been allowed to stand or that were worked up.

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Registry No. **1**, 77933-52-9; **2**, 77933-53-0; **3**, 91032-27-8; **4a**, 91032-28-9; **4b**, 35502-73-9; **5a**, 91032-29-0; **5b**, 12112-61-7; **5c**, 33505-21-4; **6**, 91053-79-1; Pd$(CH_3CN)_2Cl_2$, 14592-56-4; Pd$(PhCN)_2(NO_2)_2$, 91032-30-3; Pd$(PhCN)_2ClNO_2$, 91032-31-4; Pd$(CH_3CN)_2OAcNO_2$, 91053-80-4; Pd$(CH_3CN)_2SCNNO_2$, 91032-33-6; Pd$(CH_3CN)_2BrNO_2$, 91032-32-5; $AgNO_2$, 7783-99-5; propylene, 115-07-1; *cis*-2-butene, 590-18-1; cyclohexene, 110-83-8; cycloheptene, 628-92-2; norbornene, 498-66-8; 1-decene, 872-05-9; 2-nitro-1-decene, 77934-56-6; 1,5-cyclooctadiene, 111-78-4.