Oxygen-Transfer Reactions Catalyzed by Nitropalladium(II) Complexes. Reactivity of Bis(μ-chloro)bis[*exo*-3-(nitrosooxy)bicyclo[2.2.1]-hept-2-yl-*C*,*N*]dipalladium: Cleavage of the C–Pd Bond

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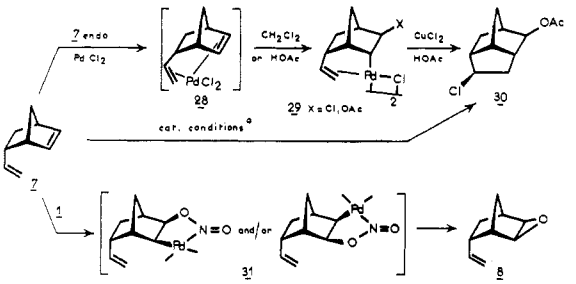
The oxidation of various norbornene derivatives and several mono- and nonconjugated diolefines with the catalyst $(CH_3CN)_2PdCl(NO_2)$ (**1**) is described. In contrast with the results previously observed with Wacker-type catalysts ($PdCl_2$–$CuCl_2$), the epoxidation process is selective for the strained norbornene double bond with dienes **5** or **7**. Methyl ketones such as **14**, **16**, **18**, and **20** are obtained with unhindered terminal olefins (e.g., **20** from **19**). The solution structure of bis(μ-chloro)bis[*exo*-3-(nitrosooxy)bicyclo[2.2.1]hept-2-yl-*C*,*N*]dipalladium (**32**) as analyzed by ^1H and ^{13}C NMR spectroscopy shows that there is a slight distortion of the palladacycle. The reactivity of isolated complex **32** has been studied. In aprotic solvents (benzene, toluene) and in the absence of any nucleophilic reagents, a pure oxygen-transfer reaction yielding epoxide **4** is the sole process. In the presence of nucleophiles or oxidants like $CuCl_2$ or $Pb(OAc)_4$ in protic or aprotic solvents (HOAc, CH_2Cl_2), the cleavage mode of the C–Pd bond is quite different. The formation of disubstituted norbornane derivatives **34** and **35** and nonrearranged products **36** and **37** are observed. The formation of various products from isolated complex **32** is discussed in terms of reaction mechanisms, particularly relative to the C–Pd bond reactivity.

During the past few years it has been well established that $PdCl_2$–$CuCl_2$ can be used as an efficient oxidation catalyst in organic synthesis,[1] particularly in the often highly selective transformation of unsaturated hydrocarbons.[2] We have shown that this bimetallic system could catalyze the oxidative formation of carbon–carbon bonds during cyclization reactions[3] as well as regio- and stereocontrolled allylic acetoxylations.[4]

Originally introduced in the Wacker process[5] as a regeneration catalyst for the active palladium species, $CuCl_2$ is now considered to have behavior far exceeding that of a simple reoxidation agent.[6] In addition to its well-known properties as a Lewis acid,[7] $CuCl_2$ is a powerful chlorinating agent.[8] The action of $CuCl_2$ on the palladium very probably involves the attack on the Pd–C σ bond[2b] rather than the oxidation of some "isolated" Pd°. Although the detailed mechanism is still unclear,[9] it is evident that such a feature markedly influences the formation of the organic products. Different mechanisms[2b,10] have been proposed, and this metal–carbon cleavage reaction can be accompanied by molecular rearrangements.[11] All these observations show that $CuCl_2$ is a powerful, but not always easily controlled, cocatalyst, and other palladium(II) reoxidant combinations[12] have been developed.[13] An interesting possibility, which was introduced by a group at Allied Chemical,[13d] is based on an oxygen-transfer process via the $NO \rightarrow NO_2$ redox couple, attached to a cobalt(II)–TPP or a Co(II)–Schiff base complex. Andrews and co-workers[14] succeeded in preparing Pd(II) catalyst $(CH_3CN)_2PdCl(NO_2)$ (**1**), which was shown to oxidize terminal olefins in a Wacker-like reaction yielding methyl ketones, while being reduced into [PdCl(NO)] (**2**). As shown with ^{18}O labeling, this was the first Pd(II)-catalyzed olefin oxidation without any participation of an external nucleophile. In other words, only the stereochemical and kinetic properties of the intermediary Pd complex—provided it is formed—could be the determining factor for the formation of the organic products. We[15] were able to show nearly simultaneously with Andrews[16] the validity of this concept by simply modifying the geometry of the intermediary palladacycle[17] and directing thereby the demetalation to a hitherto unknown epoxidation reaction. Although restricted to a few special cases, mainly in the series of (rigid) norbornane compounds, this was an important result, since it indicated that epoxidations could be achieved with molecular oxygen and catalyzed by low-valent transition metals from the platinum group and in the complete absence of any peroxidic structure element.[18]

Scheme I



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(1) (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer: Berlin, 1980. (b) Segnitz, A. In *Methoden Org. Chem.* (Houben-Weyl) *4th Ed. 1952-* **1983**, *13*(9b), 701–999.

(2) (a) Tsuji, J. *Synthesis* **1984**, 369. (b) Bäckvall, J. E. *Acc. Chem. Res.* **1983**, *16*, 335. (c) Hegedus, L. S. *Tetrahedron* **1984**, *40*, 2415.

(3) (a) Heumann, A.; Réglier, M.; Waegell, B. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 866, 867. (b) Réglier, M. Thesis, Marseille, 1980. (c) Antonsson, T.; Heumann, A.; Moberg, C. *J. Chem. Soc., Chem. Commun.* **1986**, 518. (d) Heumann, A.; Réglier, M.; Waegell, B. *Tetrahedron Lett.* **1983**, *24*, 1971.

(4) (a) Heumann, A.; Réglier, M.; Waegell, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 366. *Angew. Chem. Suppl.* **1982**, 922. (b) Blacas, J. C. Thesis, Marseille, 1982.

(5) (a) Smidt, J.; Hafner, W.; Jira, R.; Sedlmeir, J.; Sieber, R.; Rüttinger, R.; Koiger, H. *Angew. Chem.* **1959**, *71*, 176. (b) Smidt, J. *Chem. Ind. (London)* **1962**, 54. (c) Jira, R.; Freiesleben, W. *Organomet. React.* **1972**, *3*, 1.

(6) Henry, P. M. *Palladium Catalysed Oxidation of Hydrocarbons*; Academic: New York, 1980.

(7) (a) Heumann, A.; Waegell, B. *Nouv. J. Chim.* **1977**, *1*, 275. (b) Olah, G. *Friedel Crafts and Related Reactions*; Interscience: New York, 1963; Vol. 1.

(8) (a) Uemura, S.; Onoe, A.; Okano, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3702. (b) Onoe, A.; Uemura, S.; Okano, M. *Ibid.* **1976**, *49*, 345.

(9) Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.

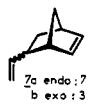
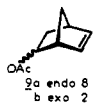
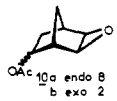
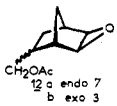
(10) Reductive elimination: Heck, R. F. *Organotransition Metal Chemistry*; Academic: New York, 1974. Radical cleavage: Budnik, R. A.; Kochi, J. K. *J. Organomet. Chem.* **1976**, *116*, C3. Nucleophilic displacement: Bäckvall, J. E.; Akermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411. Heumann, A.; Waegell, B. *Nouv. J. Chim.* **1977**, *1*, 277.

(11) Heumann, A.; Bäckvall, J. E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 207 and references cited.

(12) Henry, P. M. *J. Org. Chem.* **1973**, *38*, 1681.

0022-3263/87/1952-1916$01.50/0

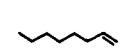
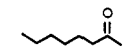
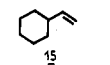
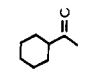
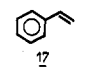
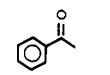
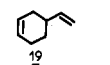
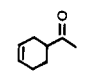
Table I. Catalytic Epoxidation of Norbornene Derivatives with $(MeCN)_2PdCl(NO_2)$ (1)

starting mater	condn 1: 8–8.5 mol %	convn, %	oxidn prod
 3	air, C_6H_6 60 °C, 6 days	37	 4
 5	air, C_6H_6 60 °C, 6 days	51	 6
 7a endo : 7 b exo : 3	air, C_6H_6 60 °C, 6 days	44	 8a endo 7 b exo 3
 9a endo 8 b exo 2	air, C_6H_6 40 °C, 6 days	61	 10a endo 8 b exo 2
 11 a endo 7 b exo 3	air, C_6H_6 60 °C, 6 days	80	 12 a endo 7 b exo 3

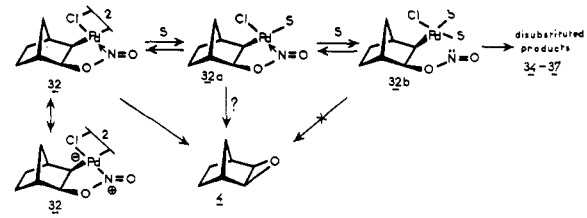
Results

Compared to the more classical Wacker oxidation system[5] (Pd(II) salt, $CuCl_2$, nucleophile, protic solvent), the palladium nitro complex $(CH_3CN)_2PdCl(NO_2)$ (1) acts as a pure oxygen-transfer catalyst.[19] While Andrews essentially studied stoichiometric and catalytic oxidations of monoolefins,[14,16,20] including the mechanism(s) of oxygen-transfer reactions,[21] we[22] focused our attention on the possibilities of this catalyst as a reagent in organic synthesis in essentially catalytic reactions. Our interest in the molecular reactivity of the carbon–palladium bond and the unexpected stability of the Pd σ complex derived from norbornene and 1 provided the opportunity to study the oxidative cleavage of an isolated C–Pd unit. In the catalytic reactions we observe either the oxidation to methyl ketones or epoxidation.[23] In the stoichiometric degradation reaction of σ-complex **32** it will be shown that external reagents (nucleophile, ligands, oxidant) considerably modify the cleavage mechanism of the Pd–C bond in such a way as to suppress completely the epoxide or ketone formation.

Table II. Catalytic Oxidation of Terminal Olefins into Methyl Ketones with Complex 1

entries	starting mater	condn	convn %/substrate	oxidn prod
1	 13	1: 8 mol % air, $C_6H_5CH_3$ 40 °C, 4 days	27	 14
2	 15	1: 8.5 mol % air, $C_6H_5CH_3$ 60 °C, 5 days	75	 16
3	 17	1: 8 mol % air, C_6H_6 40 °C, 6 days	14	 18
4	 19	1: 8.5 mol % air, $C_6H_5CH_3$ 60 °C, 5 days	50	 20

Scheme II



Catalytic Oxidation with $(RCN)_2PdCl(NO_2)$

The oxidation of different alkenes is reported in Tables I and II. One important observation is the marked difference in reactivity between the norbornene double bond and a vinyl group (Scheme I). Thus in vinylnorbornene **7**, where both of these structure elements are present together, the selectivity is complete. A similar observation has already been made with $PdCl_2$ in acetic acid; however, in this case the vinyl group of the endo isomer **7a**, via chelation, is the stereocontrolling element. The products formed, σ–π complex **29**[24] and (after cyclization) the brendane derivatives **30**,[3] are the result of an endo-metal–norbornene interaction.

It is interesting to note that a chelation effect is not operative in the case of the palladium nitro catalyst **1** and is thus comparable with (π-allyl)palladium chemistry.[25] The products we observe are due to the reaction of an isolated norbornene double bond (exo attack). With norbornadiene (NBD), the chelating diene "par excellence",[26] we could never isolate reaction products from a catalytic oxygen-transfer reaction.[27]

In aliphatic and nonstrained alicyclic compounds (Table II) a preferential oxidation of the vinyl group to methyl ketones takes place. However compounds **21**, **22**, and **23**

(13) Some palladium(II)–reoxidant combinations for catalytic oxidations are the following. (a) $Pb(OAc)_4$: Bäckvall, J. E. *Tetrahedron Lett.* **1975**, 2225. Henry, P. M.; Davies, M.; Ferguson, G.; Phillip, S.; Restivo, R. *J. Chem. Soc., Chem. Commun.* **1974**, 112. Chung, S. K.; Scott, A. I. *Tetrahedron Lett.* **1975**, 49. (b) Benzoquinone: Brown, R. G.; Davidson, J. M. *J. Chem. Soc. A* **1971**, 1321. Bäckvall, J. E.; Nyström, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 3676. (c) Benzoquinone–MnO_2: Heumann, A.; Akermark, B. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 453. Bäckvall, J. E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619. (d) py–Co–TPP–NO_2 or py–Co(saloph)–NO_2: Tovrog, B. S.; Mares, F.; Diamond, S. E. *J. Am. Chem. Soc.* **1980**, *102*, 6616.

(14) Andrews, M. A.; Kelly, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 2894.

(15) (a) Heumann, A.; Chauvet, F.; Waegell, B. *Tetrahedron Lett.* **1982**, *23*, 2767. (b) The work described in the present paper is part of F. Chauvet's Doctorat es-Sciences Thesis, Marseille, June 25, 1985.

(16) Andrews, M. A.; Cheng, C. W. F. *J. Am. Chem. Soc.* **1982**, *104*, 4268.

(17) Such palladacycles have been isolated and the X-ray structure analysis provided full support: Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F.; Emge, T. J.; Kelly, K. P.; Koetzle, T. F. *J. Am. Chem. Soc.* **1984**, *106*, 5913.

(18) Epoxidation with peroxo complexes or in the presence of peroxy compounds. Pt: Chen, M. J. Y.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1977**, 204. Pt: Strukul, G.; Michelin, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1538. *J. Am. Chem. Soc.* **1985**, *107*, 7563. Pd: Nagata, R.; Matsuura, T.; Saito, I. *Tetrahedron Lett.* **1984**, *25*, 2691. See also: Tai, A. F.; Margerum, L. D.; Valentine, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 5006.

(19) In some cases (stoichiometric) nitro transfer rather than oxygen transfer has been observed: Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F.; Kapustay, L. V.; Kelly, K. P.; Zweifel, M. J. *Organometallics* **1984**, *3*, 1479.

(20) Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F.; Kelly, K. P. *Organometallics* **1984**, *3*, 1777.

(21) Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F. *Organometallics* **1985**, *4*, 268.

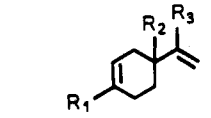
(22) With the exception of norbornene **3**, findings that parallel the results of Andrews and co-workers[20] (oxidation of cyclopentene ...) will not be reported.

(23) Pd–π-allyl complexes can be formed with **1**; however, catalytic allylic oxidation products have only been observed with cyclopentene and cycloheptene.[20,22]

(24) Wipke, W. T.; Goeke, G. L. *J. Am. Chem. Soc.* **1974**, *96*, 4244.

(25) Hughes, R. P.; Powell, J. J. *J. Organomet. Chem.* **1971**, *30*, C45; **1973**, *60*, 387 and 427.

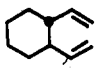
(26) (a) Rybinskaya, N. I.; Krivykh, V. V. *Russ. Chem. Rev.* **1984**, *53*, 825. (b) Omae, I. *Coord. Chem. Rev.* **1983**, *51*, 1.



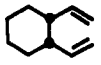
21 $R_1 = R_2 = H$, $R_3 = CH_3$

22 $R_1 = R_3 = CH_3$, $R_2 = H$

23 $R_1 = R_2 = CH_3$, $R_3 = H$



trans 24

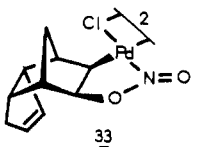


cis 25

remain unchanged under similar conditions. This observation shows that the steric influence completely inhibits the ketone formation. In this respect the palladium–nitro catalyst compares to Tsuji's $PdCl_2$–CuCl–O_2–H_2O–DMF system.[28,29] Other possible transformations of the dienic compounds, the allylic acetoxylation of cyclohexene derivatives[4,13c,23] and chelate-assisted cyclization of divinyl compounds **24** and **25**,[3a-c] have not been observed with $L_2Pd(NO_2)Cl$.

In all cases studied, the norbornene double bond[30] showed elevated nucleophilic reactivity toward the different palladium(II) species. In contrast to the acetoxypalladation reaction[31] the oxopalladated product **32** (see Scheme II) from norbornene **3** and $(CH_3CN)_2PdCl(NO_2)$ is fairly stable and can be isolated as the bis(μ-chloro) isomer.

As we proposed in a preliminary paper,[15] this complex is effectively the principal intermediate in the catalytic epoxidation reaction. The demetalation of **32** can be rationalized by a syn elimination mechanism.[32] This apparently is a result of the restricted rotation about the C_2–C_3 σ bond, thus freezing the metallacycle in a nearly eclipsed conformation. In this conformation the usual methyl ketone forming 1,2-hydrogen shift[1,2,5] is less favored (i.e., the opposite situation) than in freely rotating 1,2-oxopalladated terminal olefins.[33] X-ray analysis of **33**



33

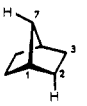
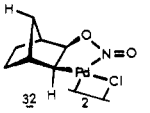
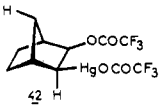
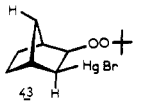
shows that the palladacycle is rather flat;[17] this geometry is also a prerequisite for the successful epoxidation of olefins with peroxomolybdenum(VI) complexes.[34] The catalytic epoxidation can be improved by modifying the oxygen-transfer catalyst. The best results have been observed with $(i\text{-PrCN})_2PdCl(NO_2)$, but nevertheless the turnover number did not exceed nine cycles.[35]

Structure and Reactivity of the Isolated Complex 32

Complex **32**, a yellow, stable solid, is easily prepared by mixing $(CH_3CN)_2PdCl(NO_2)$ with an excess of norbornene **3** in acetone or methylene chloride at 0 °C. While Andrews[17] investigated its structure in the solid state (almost planar geometry of the oxa-2-azapalladacyclopentane), we were interested in its structure in solution. Additionally we considered **32** to be a suitable model for investigations of the oxidative cleavage of the Pd–C σ bond.[11,36]

In interpreting the ^1H NMR spectra we postulate slight distortions—similar to those observed in the solid

Table III. ^1H NMR Values of 32 and Some *cis*-*exo*-Norbornane Compounds

anti	δH_2	H_3, ppm	J_{2n-7a}, Hz	J_{3n-7a}	ref
			1.5–4		37
 32	4.28	4.32	2.6	1.0	this work
 42	3.0	5.11	2.7		38
 43	2.54	5.11	2.7		38

(27) In the stoichiometric reaction. M. A. Andrews and co-workers[19] could identify two different reaction products from NBD and 1: an exo addition σ-complex formed in a rapid reaction (3 min), which rearranged within 1 h to an endo σ–π-complex and an aldehyde.

(28) Tsuji, J.; Kaito, M.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 547.

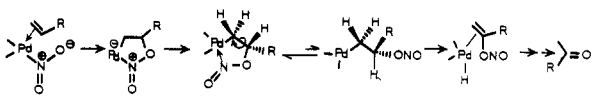
(29) Heumann, A., unpublished results.

(30) Wipff, G.; Morokuma, K. *Tetrahedron Lett.* **1980**, *21*, 4445. Spanget-Larsen, J.; Gleiter, R. *Tetrahedron Lett.* **1982**, *23*, 2435.

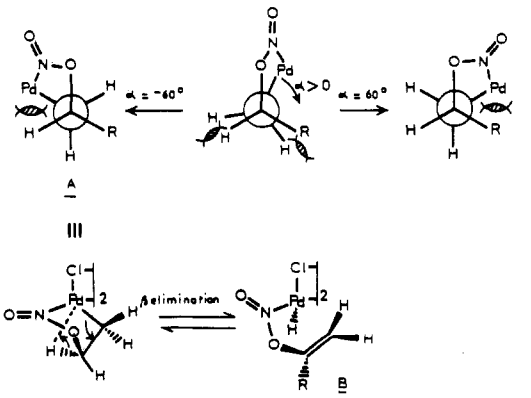
(31) Baird, W. C. *J. Org. Chem.* **1966**, *31*, 2411.

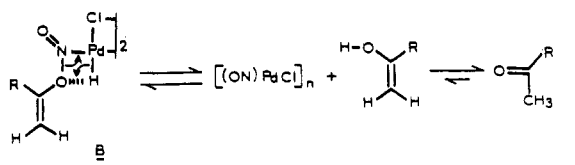
(32) Sicher, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 200. Cf. also the decomposition of peroxometallacycles: Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734.

(33) Andrews[17,20] proposes a mechanism for the ketone formation that involves nucleophilic attack of the oxygen atom on the coordinated alkene followed by cleavage and conformational reorientation of the resulting palladacycle by rotation around the terminal C–C bond: This process,



which aligns the β-H atom in the cis position, is not possible in palladacycle **32**. We have suggested an alternative for this mechanism:[15b] the most favorable skewed conformation A of the intermediate palladacycle undergoes a β-elimination, which yields B. Ketones are then formed from the latter via a four-centered mechanism:





(34) Chaumette, P.; Mimoun, H.; Saussine, S.; Fischer, J.; Mitcheler, A. *J. Organomet. Chem.* **1983**, *250*, 291.

(35) Chauvet, F.; Heumann, A.; Waegell, B., unpublished results.

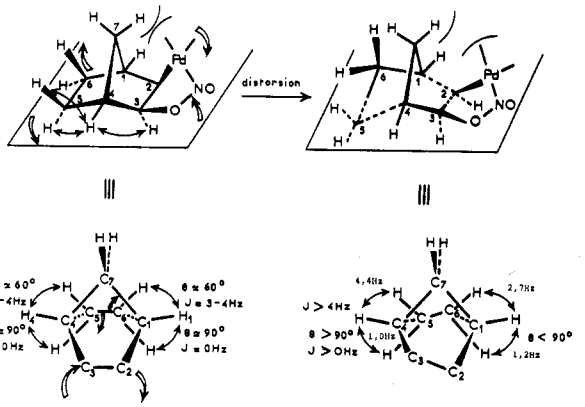
(36) A preliminary account has been published: Chauvet, F.; Heumann, A.; Waegell, B. *Tetrahedron Lett.* **1984**, *25*, 4393.

Table IV. Decomposition[a] of Palladacycle 32 at 25 °C

entry	32	solvent	reagents[b]	time, h	34	35	36	37	NI[c]	total yield, %
1	0.5	CH_3CN	$CuCl_2$ (2)	24	85		5	7.5	2.5	77
2	0.5		$CuCl_2$ (2) + LiCl (5)		57		23	6	14	57
3	0.5		$CuCl_2$ (2) + LiOAc (5)		91		4.5	1.5	3	62
4	0.5		$Pb(OAc)_4$		45	32	8	4	11	78
5	0.5		LiCl (5)	48		no reaction				
6	1	CH_2Cl_2	$CuCl_2$ (2)		58			traces	not determined	
7	1		$CuCl_2$ (2) + LiCl (5)		80			20		75
8	1	HOAc		24	94			6		30
9	1		$CuCl_2$ (2)		64	21	9			40
10	1		$CuCl_2$ (2) + LiCl (5)		80	8	5		7	35–40
11	1		$Pb(OAc)_4$		67	22			11	25
12	1		LiCl (5)		87				13	40
13	1		$CuCl_2$ (2) + LiOAc (5) + Ac_2O		33	49			18	65–70

[a] Product composition determined by glass capillary GLC (CW 20M or OV-1); the yields correspond to isolated products with respect of $C_7H_{11}ClO$. [b] Numbers in parentheses correspond to the molar ratio/Pd; for lead tetraacetate, the ratio Pb:Pd is 1:1. [c] Nonidentified products.

state[17]—due to the steric interaction between Pd and H_7 syn:



In rigid molecules like norbornane ^4J couplings are quite significant for stereochemical modifications.[37] Thus two different long-range coupling constants H_{2endo}–H_{7anti} (J = 2.6 Hz) and H_{3endo}–H_{7anti} (J = 1.0 Hz) are not conceivable with the completely symmetric structure of **32**. The signal assignments could be made by comparison with organometallic derivatives **42** and **43**[38] which possess a cis exo structure comparable to **32** (Table III). A structural resemblance, and most probably the same kind of distortion, can be concluded from the different ^{13}C NMR spectra of **32**, **43**, **44**, and **45**.[39a,b]

Complex **32** is very soluble in acetonitrile, dichloromethane, and benzene, but much less so in $CHCl_3$, CCl_4, or acetone. Like Andrews,[17] we have observed that norbornene metallacycle **32** gives back **1** and norbornene **3** in the presence of an excess of acetonitrile. This ring cleavage[40] via β-elimination can be followed by ^1H NMR in CD_3CN (Figure 1), i.e., using the integration of the olefinic and bridgehead protons in norbornene (δ 6.0 and 2.85) and the characteristic signals in complex **32** (δ 4.28 and 4.32). The equilibrium described in Figure 1 is reached in less than 1 h.

However, in CD_2Cl_2, complex **32** is much more stable than in CD_3CN or even C_6D_6:[17] at 0 °C no decomposition is observed during 24 h.

A very different behavior is observed with palladacycle **32** under oxidative conditions in the presence of $CuCl_2$ or $Pb(OAc)_4$. Only slight solvent effects are recognizable between acetonitrile (perfectly homogeneous solution) and CH_2Cl_2 or acetic acid (partly heterogeneous) (Table IV).

In all reactions studied so far, we oberved as main products chloro alcohol **34** and chloroacetate **35**, formed via a Wagner–Meerwein-type rearrangement. The epoxidation cleavage (benzene, 60 °C) seems to be suppressed completely, even in the absence of any external oxidant. The solvolysis reaction of anhydrous acetic acid leads mainly to rearranged **34**, but in somewhat lower yields probably due to a slower reaction. This is certainly a result of the reduced nucleophilic power of pure HOAc compared to solvent mixtures containing copper, lithium, or lead salts. The ratio of rearranged acetate **35** to alcohol **34** depends on the concentration of free OAc anions, and a higher concentration of **35** in the product mixture is only found in the presence of $Pb(OAc)_4$ (Table IV, entries 4 and 11) and in acetic acid, in the presence of either $CuCl_2$ (entry 9) or LiOAc (entry 13).[41] However, acetoxylation of **34** under the reaction conditions has been excluded by blank experiments: alcohol **34** submitted to $Pb(OAc)_4$ in HOAc or $CuCl_2$–LiOAc in HOAc remained unchanged after 26–27 h at room temperature.

All compounds isolated from the degradation of **32** have been characterized by spectroscopic data and by comparison with authentic samples.[31,42,43] The structure of the new compound **36** is confirmed by the observation of two intense stretches at 1550 and 1375 cm^{-1} in the IR spectra that are characteristic for nitroalkanes (ν–NO_2 asymmetric and ν–NO_2 symmetric).[44] No molecular peak is detectable in the mass spectra,[45] but some characteristic ions are observed: M – NO_2 m/e 129 (48.3%); NO^+ 30 (19.4%); NO_2^+ 46 (8.7%); and 131/133 (14.3%) for the

(37) Gaudemer, A. In *Stereochemistry*; Kagan, H. B., Ed.; G. Thieme: Stuttgart, 1977; Vol. 1, p 108. Günther, H. *NMR Spektroscopie*, 2nd ed.; G. Thieme: Stuttgart, 1983; p 114.

(38) Bloodworth, A. J.; Griffin, I. M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 195.

(39) See paragraph at the end of the paper about supplementary material. (a) Bloodworth, A. J.; Courtneidge, J. L. *J. Chem. Soc., Perkin Trans. 1* **1981**, 3258. (b) Morishima, I.; Inubushi, T.; Uemura, S.; Miyoshi, H. *J. Am. Chem. Soc.* **1978**, *100*, 354.

(40) The cleavage equilibrium of the bis(μ-2-chloride) bridge in **32**, another cleavage reaction, however, not affecting the C–Pd or C–O units can be followed at −80 °C in the ^1H NMR experiment.[17]

(41) Ionic dissociation of $Pb(OAc)_4$, $Pb(OAc)_4 \rightleftharpoons Pb(OAc)_3^+ + (OAc)^-$, is observed in complexing solvents such as acetic acid: Mihailovic, M. L. J.; Patch, R. C. In *Selective Organic Transformations*; Thyagarajan, B. S., Ed.; Wiley Interscience: New York, 1972; Vol. 2, p 97.

(42) McDonald, R. N.; Taber, T. E. *J. Org. Chem.* **1968**, *33*, 2934.

(43) Loreto, M. A.; Pellacani, L.; Tordella, P. A. *Synth. Commun.* **1981**, *11*, 287.

(44) Hediger, H. J. *Infrarotspektroskopie*; Akademische: Frankfurt am Main, 1971.

$C_7H_{10}Cl$ ion. As can be deduced from the NMR spectra, **36** is structurally closely related to chlorohydrin **37**. Both protons in the bridgehead position are well separated (2.89 and 2.62 ppm, respectively) and markedly deshielded compared to rearranged molecules like **34** or **35** (2.16–2.44 ppm). The signal at 4.80 ppm corresponds to H_{3endo}, geminated to the nitro group[46] and enlarged by supplementary quadrupole coupling to NO_2. The splitting pattern at 4.30 ppm (C_1–C_2 H_{exo}; dd J_1 = 2 Hz, J_2 = 3.6 Hz) confirms the structure of a 2,3-trans disubstituted norbornane. The endo stereochemistry of the C–Cl bond is deduced from the coupling constants J_1 = 2 Hz, H_{2exo}–H_1 (bridgehead), and J_2 = 3.6 Hz, H_{2exo}–H_{3endo}. Consequently, the nitro group exhibits the exo stereochemistry. The attributions made by ^1H NMR are fully confirmed by the ^{13}C spectra of **36** and **37** (see Experimental Section).

The question arises whether the products **34** and **37** could have been formed from (intermediary) epoxynorbornane **4** or norbornene **3**. Indeed, compound **4** can be obtained from **32**, and **3** has been shown to be in equilibrium with **32** (Figure 1). We have excluded these possibilities by reacting **3** and **4** under comparable conditions over prolonged periods (6 days and more). In all cases (e.g., in the presence of $CuCl_2$, $CuCl_2$–LiCl, and $Pb(OAc)_4$ in solvents such as CH_3CN, HOAc, or CH_2Cl_2) we could discover at best traces of the compounds **34** and **37**. This means that the latter are effectively the exclusive primary reaction products issued from the nucleophilic degradation of bis(μ-chloro)bis[*exo*-3-(nitrosooxy)bicyclo[2.2.1]hept-2-yl-*C*,*N*]dipalladium (**32**).

Discussion

While the epoxide formation from **32** may be discussed in terms of a pure oxygen-transfer mechanism,[47] the formation of bifunctionalized compounds (Table IV) can only be rationalized by oxido reduction processes in the coordination sphere of the palladium–carbon unit. As the organic products are metal free and do not contain a nitroso group, we must consider different kinds of C–Pd bond cleavage reactions (Scheme III).

A. Cleavage of the Carbon–Palladium Bond Associated with Wagner–Meerwein Rearrangement. Normally palladium σ complexes are not stable enough to be isolated. But in complex **32** two stabilizing factors are operative: the bis(μ-2-chloride) bridge as well as the existence of a five-membered heteropalladacyclic ring which can be represented by mesomeric formulas (zwitterion and intramolecular chelate)[26,48] (Scheme II). The epoxide formation from **32** is likely to occur[21] from such a metallacycle structure, as shown by its reactivity in a noncoordinating solvent (benzene, toluene). However, any reagent capable of influencing this cyclic structure in **32**

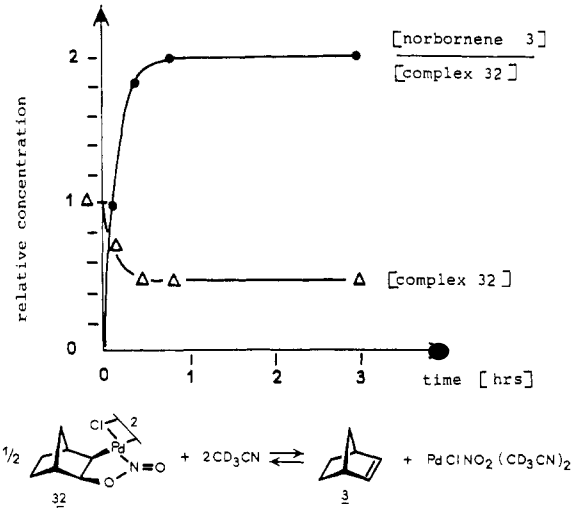
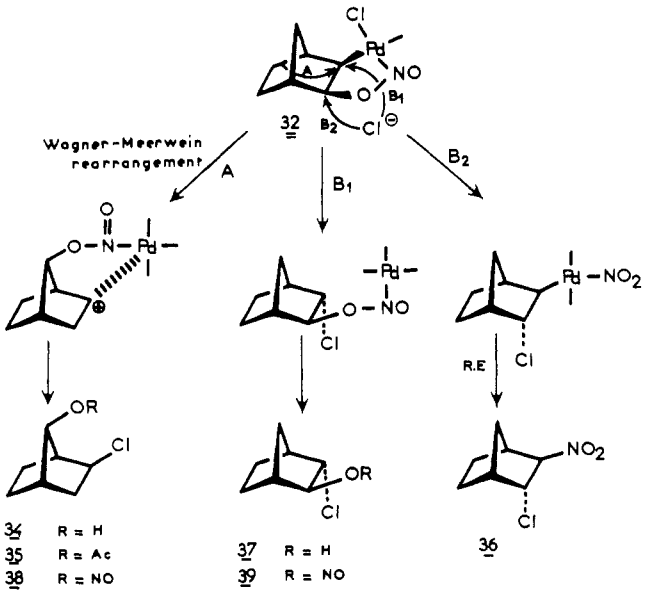


Figure 1. Equilibrium between palladacycle **32** and norbornene **3** in deuterioacetonitrile.

Scheme III

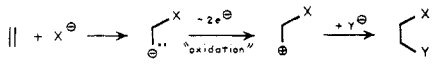


should prevent the epoxide formation and consequently give rise to products due to the usual bond breaking of the C–Pd unit. Effectively, the sole common denominator of such different reagents such as acetic acid and, e.g., $CuCl_2$, is their nucleophilic capacity to cleave bis(μ-2-chloro) bridges and to disrupt chelated stabilized organopalladium complexes. In **32** these processes lead to the polarization of the C–Pd bond, thus rendering the palladium framework a good leaving group. The resulting partially cationic norbornane is particularly prone to undergo Wagner–Meerwein-type rearrangements and/or nucleophilic substitutions at C_2 and C_3.[49] Although the beginning and the determination of the nonepoxidative reaction is due to a common reactivity, the attack on the C–Pd bond is now really reagent substrate specific (Table IV). All reagents and various combinations lead preferentially to the skeletal rearranged chlorides **34** and **35**. This means that the main process in the heterolytic cleavage of this norbornane carbon–palladium bond is a Wagner–Meerwein-type rearrangement as occurs in solvolytic reactions.[49] The formation of alcohol **34** is easily explained by simple hydrolysis of the (nonisolated) nitro ester **38**. The formation of acetate **35** (Scheme III) might be due to the acetylation of alcohol **34**. However, the absence of any acetate during

(45) Silverstein, R. M.; Bassler, G. C. *Spectroscopic Identification of Organic Compounds*; Wiley: New York, 1963.

(46) For some related nitroso compounds in the bicyclo[2.2.1]heptane series, see: Francisco, C. G.; Freire, R.; Hernandez, R.; Melian, D.; Salazar, J. A.; Suarez, E. *J. Chem. Soc., Perkin Trans. 1* **1984**, 459. Cf. also: Borisenko, A. A.; Nikulin, A. V.; Wolfe, S.; Zefirov, N. S.; Zyk, N. V. *J. Am. Chem. Soc.* **1984**, *106*, 1074.

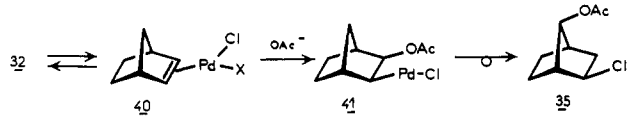
(47) Without considering any mechanistic details, the epoxidation or ketone formation with palladium–nitro complexes corresponds very simply to the addition of one (uncharged) oxygen atom to one alkene double bond. Formally this is the simplest kind of an oxidation process. The most important consequence is that the palladium(II) does not act as an oxidant. However, disubstituted compounds like **34** or **37** have been formed by the addition of two nucleophilic species, Cl^- and OH^-. This is only possible after a $2e^-$ oxidation at the hydrocarbon. In this case, Pd(II) acts as a real oxidant:



(48) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic: New York, 1971; Vol. 1.

(49) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426.

the reaction of **34** with $Pb(OAc)_4$/HOAc or LiOAc/HOAc, as well as the observation of significant amounts of alcohol **34** in highly concentrated AcO^- medium (Table IV), suggests that the acetate **35** is formed by a different mechanism and probably directly from **32**. Equilibrium of **32** with π-complex **40** is followed by readdition of a palladium(II) species and an acetate ion. Intermediate **41** undergoes a known[31] rearrangement to give chloro acetate **35**.



B. S_N2 Type Cleavage of the C–Pd Bond (B_1) and Nucleophilic Attack on the Metallacyclic Carbon Bearing the Oxygen (B_2). Nonnegligible amounts of 2,3-disubstituted compounds **36** and **37** are observed in addition, mainly in the presence of higher LiCl concentrations. This is in agreement with poorly understood prospectives of this salt, i.e., favoring the direct (S_N2 type) cleavage of the C–Pd bond.[11] Here again, the hydrolysis of nitro ester **39** yields the alcohol **37**.

However, the formation of nitro chloride **36** with a nonrearranged norbornane skeleton should follow some different mechanistic pathways. Andrews showed that palladium–nitro complexes could transfer the nitro group to an alkene double bond.[19] However, the nitration reaction failed with cycloalkenes. We suggest that the nitration reaction via the isolated complex **32** is the result of the direct nucleophilic attack on the C–O bond which (1) does not lead to Wagner–Meerwein rearrangement and (2) liberates the coordinated nitro group for a reductive elimination process. Indeed, the weakness of the C–O bond in **32** (cf. equilibrium in CD_3CN; Figure 1) and the relatively large amount of **36** formed in this solvent (CH_3CN) in the presence of LiCl may support this mechanistic picture (Table IV, entry 2). At this point, it is interesting to note that the formation of ring-opened derivatives **36** and **37** from metallacycle **32** constitutes in fact a chemical structural proof of the latter.

One point that merits some comment concerns the stereochemistry of the palladium–nucleophile addition to norbornene.[30] In palladacycle **32**, the addition product is a cis-exo-2,3-disubstituted norbornane. This has been proven by NMR spectroscopy and by X-ray structure analysis. The close relationship of the nonepoxidative rearrangement of **32** with respect to the Baird reaction,[31] i.e., the chloroacetoxylation of norbornene in the presence of $PdCl_2$–$CuCl_2$, and formation of **35** is obvious, and we might assume that the acetoxypalladation[50] of norbornene **3** is a cis process. This apparently is in disagreement with the results of Bäckvall,[2b] Stille,[51] and Henry,[6] who have observed that with hard nucleophiles such as acetates the organopalladation of simple olefins in a trans process. It is generally understood that the hard nucleophile does not enter the coordination sphere of the soft palladium. However, coordination of OAc at the palladium prior to the reaction with carbon has been observed with π-allyl systems,[2b,52] and we may conclude that cis acetoxypalladium at **3** may be the first really clear-cut exception of the trans addition rule.

(50) In his original paper Baird[31] does not specify the stereochemistry of the C–Pd bond in the first acetoxypalladium intermediate.
(51) Stille, J. K.; Divakarvni, R. *J. Organomet. Chem.* **1979**, *169*, 239.
(52) (a) Bäckvall, J. E. *Pure Appl. Chem.* **1983**, *55*, 1669. (b) Hosokawa, T.; Yasushi, I.; Murahashi, S. I. *Tetrahedron Lett.* **1982**, 3373.

Conclusion

The unusual stability of the palladium–carbon σ bond[53] in complex **32** (issued from the reaction of norbornene and $PdCl(NO_2)(CH_3CN)_2$ allowed the investigation of two different oxidation reactions of the bicyclic norbornene system. In aprotic solvents (benzene, toluene) and in the absence of any nucleophilic reagents, a pure oxygen-transfer reaction is observed, yielding epoxides as reaction products. These compounds are formed most probably by a syn elimination process of the perfectly eclipsed five-membered palladacyclic ring. The oxidation can be performed in a catalytic manner; however, the turnover number does not exceed 9–10 cycles. When complex **32** is treated with nucleophiles or oxidants like $CuCl_2$ and $Pb(OAC)_4$ in protic or aprotic solvents (HOAc, CH_2Cl_2), the cleavage mode of the C–Pd bond is found to be quite different. Under these conditions disubstituted norbornane compounds with a rearranged skeleton (syn-2,7 compounds **34** and **35**) and a nonrearranged norbornane ring (trans-2,3 compounds **36** and **37**) are the organic reaction products. The latter transformations are not catalytic, and the isolation of complex **32** is necessary. These reactions show—for the first time on the same organopalladation product—the importance of the reaction conditions, stereochemistry, and cleavage mode on the proceedings, of two completely different Pd-catalyzed oxidation reactions.

Experimental Section

General Information. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer; all absorptions are given in reciprocal centimeters. ^1H and ^{13}C NMR spectra were recorded on a Varian XL 200 in solution by using tetramethylsilane as an internal standard. The substitution of carbons in ^{13}C NMR spectra is determined with the Attached Proton Test technique (APT, spin–echo sequence). Analyses were performed by the Service de Microanalyse du Département de Chimie Organique de la Faculté des Sciences de St-Jérôme.

The reaction mixtures were analyzed on a Carlo Erba Fractovap 2150 Series gas chromatograph equipped with glass capillary columns: CW 20M 25 and 50 m and OV-1 50 m. Column chromatography was performed on silica gel 60 (Merck 70–230 mesh; eluents, hexane–ether or hexane–CH_2Cl_2). Solvents were dried over molecular sieves or basic alumina; reagents were used as received. *cis*-bis(acetonitrile)chloronitropalladium(II) (**1**) and and 2-*endo*-chloro-3-*exo*-hydroxybicyclo[2.2.1]heptane (**37**) were prepared according to published procedures. 5-(Acetoxymethyl)bicyclo[2.2.1]hept-2-ene (**11**) (exo/endo = 3/7) was prepared by acetylation (Ac_2O/py) of 5-(hydroxymethyl)bicyclo[2.2.1]hept-2-ene (Hüls).[54] Most of the oxidation products have been described in the literature: acetylcyclohexane **16**;[55] 4-acetylcyclohex-1-ene **20**;[56] *exo*-2,3-epoxybicyclo[2.2.1]heptane **4**;[57] *exo*-2,3-epoxy-5-methylenebicyclo[2.2.1]heptane **6**;[58] *exo*-2,3-epoxy-5-vinylbicyclo[2.2.1]heptane (exo/endo = 3/7) **8**.[59]

Catalytic Oxidation Reactions with *cis*-Bis(acetonitrile)chloronitropalladium(II) (1). A solution of **1** (43.2 mg, 0.16 mmol) in 20 mL of dry benzene is heated to the desired temperature (see Tables I and II), and 2 mmol of the corresponding olefin is added rapidly. The solution, which rapidly turns

(53) Cf. also: Akermark, B.; Arnek, R.; Zetterberg, K. Presented at the XII I.C.O.M.C., Vienna, Austria, Sept 8–13, 1985, (0 352). The "abnormal" stability of 4-membered alkylazapalladacycles is rationalized by the rigidity of this cyclic framework. The system cannot rotate into the position where elimination reactions (e.g., β-elimination) are favored.
(54) We thank the Chemische Werke Hüls, Marl, West Germany, for a sample of 5-(hydroxymethyl)bicyclo[2.2.1]hept-2-ene.
(55) Blanchard, E. P.; Büchi, G. *J. Am. Chem. Soc.* **1963**, *85*, 955.
(56) Robinson, R.; Fray, G. J. *J. Am. Chem. Soc.* **1961**, *83*, 249.
(57) Budnick, R. A.; Kochi, J. K. *J. Org. Chem.* **1976**, *41*, 1384.
(58) Tinsley, S. W.; MacPeek, D. L. U.S. Patent 3 238 227; *Chem. Abstr.* **1966**, *64*, 19 557g.
(59) Wiesse, H. K. U.S. Patent 3 183 249; *Chem. Abstr.* **1965**, *63*, 1767d. Kim, Y. H.; Chung, B. C. *J. Org. Chem.* **1983**, *48*, 1562.

dark, is stirred under atmospheric pressure in the presence of air. After quenching with water (30 mL), the solution is extracted with pentane or hexane (3-4 × 10 mL), and the organic phases are washed with brine and dried with $MgSO_4$. The GLC analysis is usually made directly from the pentane or hexane solution of the reaction product(s). After evaporation or distillation of the solvent (by means of a 10-15-cm Vigreux column), the product is purified by column chromatography or distillation.

5-Acetoxy-*exo*-2,3-epoxybicyclo[2.2.1]heptane (exo/endo = 2/8) (10): yield 61%; IR (CCl_4) 1735, 849 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.04 (m, $^1/_2W$ = 18 Hz, 0.8 H C_5-H_{exo}), 4.64 (d, J = 6 Hz, 0.2 H C_5-H_{endo}), 3.29 (dd, J = 19 and 3 Hz) and 3.06 (dd, J = 10 and 3 Hz) ratio 8:2 (2 H, C_2-H and C_3-H_{endo}); 2.76 and 2.58 (2 br s, ratio 8:2, 1 H, C_4-H), 2.49 (br s, 1 H, C_1-H), 1.95-2.15 (m, 1 H), 2.02 and 2.00 (2 s, 3 H, OCCCH_3 endo and exo), 1.26-1.50 (m, part of an AB, J = 10.4 Hz, 1 H, C_7-H anti to epoxide), 1.08 (dt, J = 13 and 3 Hz, 1 H, C_6-H_{endo}), 0.79 (d, J = 10.4 Hz, part of an AB, 1 H, C_7-H syn to epoxide); ^{13}C NMR ($CDCl_3$) **10** endo (≃80%) δ 170.89 (CO), 76.41 (C_5), 50.92 and 48.22 (C_2/C_3), 40.39 (C_4), 36.81 (C_1), 33.0 (C_6), 24.7 (C_7), 20.97 (CH_3); **10** exo (≃20%) δ 170.89 (CO), 73.25 (C_5), 51.69 and 48.08 (C_2/C_3), 42.56 (C_4), 36.45 (C_1), 35.75 (C_6), 23.41 (C_7), 21.15 (CH_3). Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.35; H, 7.18.

5-(Acetoxymethyl)-*exo*-2,3-epoxybicyclo[2.2.1]heptane (exo/endo = 3/7) (12): yield 80%; ^1H NMR ($CDCl_3$) δ 3.95-4.12 and 3.77-3.95 (2m, ratio ≃8:2, 2 H, CH_2OAc), 3.15 (dd, J = 12.5 and 3 Hz) and 3.08 (s) ratio ≃8:2 (2 H, C_2-H and C_3-H_{endo}), 2.49 and 2.39 (2br s) ratio ≃8:2 (2 H, C_1-H and C_4-H), 2.17-2.37 (m, 1 H), 2.03 and 2.04 (2s, 3 H, $OCOCH_3$), 0.72-1.9 (3br m and several small m, 4 H (br m are centered at 1.72 ($^1/_2W$ = 27 Hz), at 1.37 (dm, J = 10 Hz), and at 0.79 ($^1/_2W$ = 20 Hz)); ^{13}C NMR ($CDCl_3$) **12** endo (≃70%) δ 170.96 (CO), 65.03 (C_8), 51.06 and 49.07 (C_2/C_3), 39.92 (C_5), 38.19 and 37.16 (C_1/C_4), 28.65 and 27.19 (C_6/C_7), 20.92 (CH_3); **12** exo (≃30%) δ 170.96 (CO), 66.58 (C_8), 51.62 and 51.19 (C_2/C_3), 39.92 (C_5), 36.91 and 37.25 (C_1/C_4), 30.02 (C_6), 23.27 (C_7), 20.92 (CH_3). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.88; H, 7.71.

Preparation of Palladacycle 32. A solution of *cis*-bis(acetonitrile)chloronitrilopalladium(II) (1) (1.34 g, 5 mmol) in 50 mL of acetone was stirred and cooled to 0 °C, and 4 equiv of norbornene (1.88g, 20 mmol) were added rapidly. After a few minutes, a yellow precipitate was formed, and the mixture was stirred until completion of the reaction in the absence of light (≃15 min). The yellow solid was filtered, washed with cold acetone, and dried carefully: yield 1.21 g (86%). The product **32**[17] was used immediately for the different decomposition studies (cf. Table IV).

Oxidation of 32 with $CuCl_2$-LiCl in CH_3CN. A mixture of palladacycle **32** (1.41 g, 5 mmol equiv), $CuCl_2$ (1.34 g, 10 mmol), and LiCl (1.059 g, 25 mmol) (ratio Pd:Cu:Li = 1:2:5) in 50 mL of CH_3CN was stirred at room temperature for 2 days. Water (50 mL) was added and the aqueous solution extracted with ether (4 × 20 mL). The combined organic phases were washed with brine and dried with $MgSO_4$. Removal of the solvent gave a slightly colored liquid (467 mg, 64% with respect to $C_7H_{11}OCl$). The separation, which gave three main products, **34** (57%), **36** (23%), and **37** (6%), could be achieved by preparative column chromatography on silica gel (elution with hexane-CH_2Cl_2 = 95:5).

***exo*-2-Chloro-*syn*-7-hydroxybicyclo[2.2.1]heptane (34)**:[42] IR ($CHCl_3$) 3600, 3450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.08 (s, 1 H, C_7-H_{anti}), 4.07 (partially hidden d of d, 1 H, J = 6.6 and 4.0 Hz, C_2-H_{endo}), 2.74 (s, 1 H, OH), 2.44-2.16 (m, 4 H), 1.8-1.48 (m, 2 H), 1.26-1.02 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 80.39 (C_7), 60.97 (C_2), 48.34 (C_1), 41.75 (C_4), 41.16 (C_3), 25.18 and 24.49 (C_6 + C_5). Anal. Calcd for $C_7H_{11}ClO$: C, 57.34; H, 7.56; Cl, 24.18. Found: C, 57.38; H, 7.68; Cl, 24.05.

***endo*-2-Chloro-*exo*-3-hydroxybicyclo[2.2.1]heptane (37)**:[43] IR ($CHCl_3$) 3600, 3400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (m, 1 H, $^1/_2W$ = 8.8 Hz, C_2-H_{exo}), 3.66 (t, 1 H, J = 2.2 Hz, C_3-H_{endo}), 2.42 (m, 1 H, $^1/_2W$ = 11 Hz, C_4-H), 2.16 (m, d, 1 H, J = 3.5 Hz, $^1/_2W$ = 8.8 Hz, C_1-H), 1.80-1.16 (2m, 6 H), 1.86 (t, 1 H); ^{13}C NMR ($CDCl_3$) δ 83.63 (C_3), 69.87 (C_2), 44.57 (C_4), 42.90 (C_1), 34.52 (C_7), 24.80 (C_5), 21.26 (C_6).

***endo*-2-Chloro-*exo*-3-nitrobicyclo[2.2.1]heptane (36)**: IR ($CHCl_3$) 1550, 1375, 905, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.80 (m, 1 H, $^1/_2W$ = 10 Hz, C_3-H_{endo}), (d, d, 1 H, J = 3.6 and 2 Hz, C_2-H_{exo}), 2.89 (d, m, 1 H, J = 3.6 Hz, C_1-H), 2.62 (m, 1 H, $^1/_2W$ = 9 Hz, C_4-H), 2.05-1.19 (2m, 5 H), 0.86 (m, 1 H, $^1/_2W$ = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 95.47 (C_3), 61.71 (C_2), 44.51 (C_4), 43.40 (C_1), 35.58 (C_7), 26.75 (C_5), 21.16 (C_6). Anal. Calcd for $C_7H_{10}NO_2Cl$: C, 47.88; H, 5.74; N, 7.97; Cl, 20.19. Found: C, 47.89; H, 5.66; N, 7.89; Cl, 20.3.

The other reactions reported in Table IV were carried on **32** in a similar fashion to the one reported above using $CuCl_2$/LiCl in CH_3CN.

Supplementary Material Available: ^{13}C NMR data of cis exo substituted organometallic 2,3-norbornane derivatives **43**, **44**, and **45** and independent preparation of disubstituted norbornene reference compounds **34-37** (1 page). Ordering information is given on any current masthead page.

Iododediazoniation of Arenediazonium Salts Accompanied by Aryl Radical Ring Closure[1]

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Treatment of *o*-(allyloxy)benzenediazonium tetrafluoroborate (**1a**) with sodium iodide in acetone affords the cyclized iodide **2a** in good yield by a mechanism involving the generation and exo cyclization of the aryl radical **6a**. Other diazonium salts (**1b-i**) containing suitable unsaturated side chains behave similarly, but those (**1l**, **1m**) in which there is an *N*-allylsulfonamido group yield mainly products formed by endo cyclization. The diazonium salts **1j** and **1k** do not give cyclized products. Factors affecting the mechanism, rates, and regiochemistry of the reaction are discussed.

Recently, we described experiments involving the use of thiolate ions or copper(II) halides to effect cyclization in the exo mode[2] of aryl radicals derived from *o*-(2-propenyloxy)benzenediazonium tetrafluoroborate (**1a**) or *o*-[(2-methyl-2-propenyl)oxy]benzenediazonium tetrafluoroborate (**1b**).[3] The reactions afforded dihydrobenzofuran derivatives which were functionalized at the

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