Platinum-Catalyzed Cycloisomerization Reactions of Enynes

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Received April 11, 2001

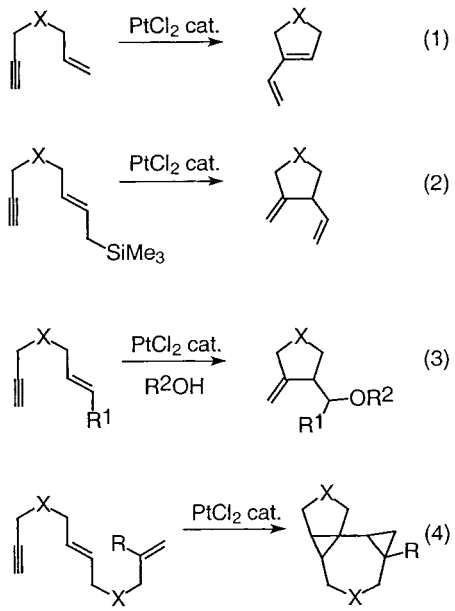
Abstract: $PtCl_2$ constitutes an efficient and practical catalyst for a set of different atom economical rearrangement reactions of enynes. This includes (i) a formal enyne metathesis reaction delivering 1,3-dienes, (ii) the formation of polycyclic vinylcyclopropane derivatives, and (iii) an unprecedented O→C allyl shift reaction if unsaturated ethers are employed. Although these transformations produce significantly different structural motifs, they share a common mechanism comprising a cationic manifold triggered by the π-complexation of Pt(II) onto the alkyne unit of the substrates. Strong experimental support for the proposed mechanism comes from deuterium-labeling studies, a careful analysis of the product distribution pattern, and the fact that in some cases $PtCl_2$ can be replaced by simple Lewis or Brønsted acids as the catalysts.

Introduction

Chemical reactions proceeding with total mass transfer from the substrates to the products are inherently attractive.[1] To gain practical importance, however, such "atom economical" transformations must be accompanied by a significant increase in structural complexity, they should require only catalytic amounts of reagents, and they must be scalable and user-friendly. Cycloisomerization reactions of enynes catalyzed by $PtCl_2$ seem to meet these stringent criteria. Since the pioneering studies of Murai et al.,[2,3] four different reaction modes have been discovered (Scheme 1) which convert the substrates either to (i) 1,3-dienes via a formal metathesis pathway (eq 1),[2] (ii) 1,4-dienes if the substrate contains an allylsilane (stannane) entity (eq 2),[4] (iii) unsaturated ethers if the reactions are performed in alcoholic media (eq 3),[5] or (iv) complex polycyclic arrays if compounds with more than one double bond are employed (eq 4).[6,7]

In the following we summarize our investigations in this field.[8,9] During the course of a study aimed at a better understanding of the platinum-catalyzed enyne metathesis process, two additional cycloisomerization processes have been discovered. Although these transformations generate quite diverse structural motifs, they seem to share a common mechanism and represent just different productive outlets of a complex but highly versatile cationic manifold.

Scheme 1



Results and Discussion

Enyne Metathesis versus the Formation of Bicyclo[4.1.0]-heptenes. Driven by a program aimed at the total synthesis of the immunosuppressive prodigiosin alkaloid streptorubin and congeners, we investigated if enyne metathesis[10] opens an entry into the azabicyclic pyrrolophane core of this target.[11,12] For

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(1) Trost, B. M. *Angew. Chem.* **1995**, *107*, 285−307; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259−281.

(2) (a) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901−903. (b) For similar reactions catalyzed by Ru catalysts see: Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049−6050.

(3) In independent work, Trost et al. have pursued similar transformations using palladol complexes as catalysts, cf.: (a) Trost, B. M.; Trost, M. K. *J. Am. Chem. Soc.* **1991**, *113*, 1850−1852. (b) Trost, B. M.; Yanai, M.; Hoogsteen, K. *J. Am. Chem. Soc.* **1993**, *115*, 5294−5295. (c) Trost, B. M.; Chang, V. K. *Synthesis* **1993**, 824−832.

(4) Fernández-Rivas, C.; Méndez, M.; Echavarren, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 1221−1222.

(5) Méndez, M.; Muñoz, M. P.; Echavarren, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 11549−11550.

(6) Chatani, N.; Kataoka, K.; Murai, S.; Furukawa, N.; Seki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9104−9105.

(7) For related reactions of ω-aryl-1-alkynes see: Chatani, N.; Inoue, H.; Ikeda, T.; Murai, S. *J. Org. Chem.* **2000**, *65*, 4913−4918.

(8) For a preliminary communication see: Fürstner, A.; Szillat, H.; Stelzer, F. *J. Am. Chem. Soc.* **2000**, *122*, 6785−6786.

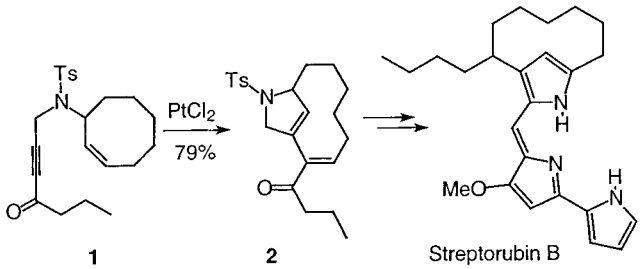
(9) For studies from our laboratory on other Pt(II)-catalyzed C−C-bond formations see: (a) Fürstner, A.; Voigtländer, D.; Schrader, W.; Giebel, D.; Reetz, M. T. *Org. Lett.* **2001**, *3*, 417−420. (b) Fürstner, A.; Voigtländer, D. *Synthesis* **2000**, 959−969.

(10) For general discussions of metathesis see the following for timely reviews: (a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29. (b) Fürstner, A. *Angew. Chem.* **2000**, *112*, 3140−3172; *Angew. Chem., Int. Ed.* **2000**, *39*, 3012−3043. (c) For a review on enyne metathesis see: Mori, M. *Top. Organomet. Chem.* **1998**, *1*, 133−154.

(11) Fürstner, A.; Szillat, H.; Gabor, B.; Mynott, R. *J. Am. Chem. Soc.* **1998**, *120*, 8305−8314.

10.1021/ja0109343 CCC: $20.00
Published on Web 11/07/2001

Scheme 2



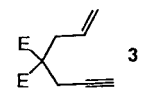
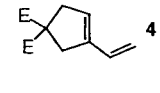
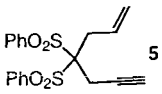
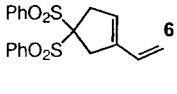
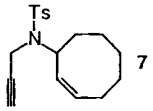
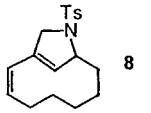
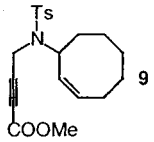
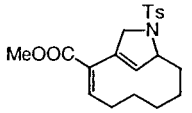
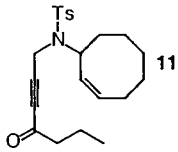
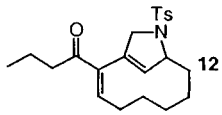
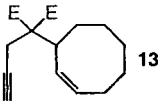
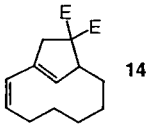
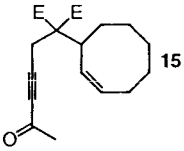
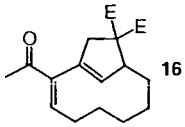
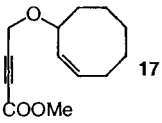
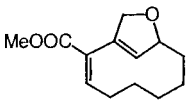
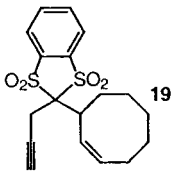
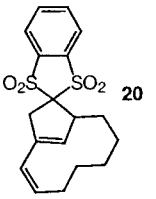
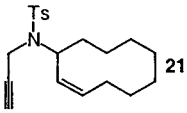
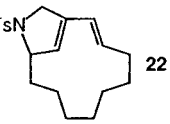
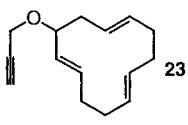
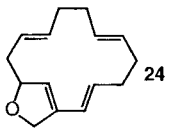
this purpose, the rearrangement of the readily available substrate **1** to product **2** was investigated (Scheme 2). Among the different catalysts screened, $PtCl_2$ turned out to be by far the most efficient and convenient one, delivering the desired key building block in excellent yield.[13] In structural terms, this transformation is quite remarkable as one C−C bond must be broken and two new ones formed while forging a bicyclic system that incorporates a bridgehead alkene moiety. Despite this significant increase in molecular complexity, the reaction is distinguished by its "low-tech" character and directly scales-up to multigram quantities without need for any further optimization.[11,14]

Subsequently, many other enyne derivatives were found to undergo equally facile and efficient "metathesis" to the corresponding 1,3-diene products under the same reaction conditions.[15] As can be seen from Table 1, substantial structural variations are accommodated and different functional groups were found to be compatible, including ethers, esters, sulfones, ketones, and sulfonamides. The rearrangement process is not limited to compounds in which the alkene group is part of a (strained) preexisting ring. Electron-withdrawing groups on the alkyne facilitate the reaction, and a regular cyclization was observed even with the polyunsaturated substrate **23**.

Surprisingly, however, it was noticed that some closely related 1,6-enynes deviate from the expected course and populate an entirely different pathway. This striking dichotomy is obvious by comparing the behavior of sulfone **5** with that of the corresponding tosylamide derivative **25** (Scheme 3). While the former undergoes an essentially quantitative conversion to the expected "metathesis" product **6**, the latter delivers only 2% of the corresponding 1,3-diene **27** together with the previously unknown cyclopropane derivative **26** as the major product. If enyne **28** is exposed to $PtCl_2$ in toluene at 80 °C, both reactions are operative to a similar extent, thus leading to diene **30** and the tricyclic derivative **29**. The unusual structure of the latter was unequivocally deduced from 2D NMR experiments (see the Experimental Section in the Supporting Information) and was confirmed by X-ray analysis (Figure 1).

As can be seen from Table 2, many other substrates containing heteroelements in the tether between the alkene and the alkyne moiety also lead to bicyclo[4.1.0]heptene derivatives in reasonable to excellent yields.[16] This includes even allylsilane

Table 1. Enyne Metathesis Reactions Catalyzed by $PtCl_2$[a,b]

Nr	Substrate	Product	Yield
1	 **3**	 **4**	91%
2	 **5**	 **6**	96%
3	 **7**	 **8**	96%
4	 **9**	 **10**	85%
5	 **11**	 **12**	79%
6	 **13**	 **14**	83%
7	 **15**	 **16**	63%
8	 **17**	 **18**	70%
9	 **19**	 **20**	60%
10	 **21**	 **22**	80%
11	 **23**	 **24**	54%

[a] In toluene at 80 °C with 4−10 mol % of $PtCl_2$. [b] E = COOEt.

(12) For the syntheses of other prodigiosins and related alkaloids see: (a) Fürstner, A.; Grabowski, J.; Lehmann, C. W. *J. Org. Chem.* **1999**, *64*, 8275−8280. (b) Fürstner, A.; Krause, H. *J. Org. Chem.* **1999**, *64*, 8281−8286. (c) Fürstner, A.; Weintritt, H. *J. Am. Chem. Soc.* **1998**, *120*, 2817−2825. (d) Fürstner, A.; Grabowski, J.; Lehmann, C. W.; Kataoka, T.; Nagai, K. *ChemBioChem* **2001**, *2*, 60−68. (e) Fürstner, A.; Grabowski, E. J. *ChemBioChem* **2001**, *2*, 706−709.

(13) $PtCl_4$ shows similar catalytic activity as $PtCl_2$. In sharp contrast, the following platinum compounds have been found to be totally inactive: $PtCl_2(COD)$, $PtCl_2(PhCN)_2$, PtO_2, $H_2Pt(OH)_6$, $Pt(acac)_2$, $Pt_2(dba)_3$, $K_2[PtCl_6]$. Moreover, $PdCl_2$, $NiCl_2$, $CoCl_2$, $RhCl_3$, $CrCl_2$, and $MnCl_2 \cdot 4H_2O$ showed no catalytic activity in toluene at 80 °C. The palladol complex **56** described by Trost et al. produced a complex mixture from which the desired product could be isolated in only 18% yield.

(14) For a short discussion of our strategic goals see: Fürstner, A. *Synlett* **1999**, 1523−1533.

(15) For a related application to a formal total synthesis of roseophilin see: Trost, B. M.; Doherty, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 3801−3810.

(16) A similar transformation catalyzed by $PtCl_4$ was described for allyl propargyl ethers; in most cases, however, the yields obtained were rather low. Conversion of the alkyne into an allene followed by formation of a metallacycle was proposed as the reaction mechanism, cf.: Blum, J.; Beer-Kraft, H.; Badrieh, Y. *J. Org. Chem.* **1995**, *60*, 5567−5569.

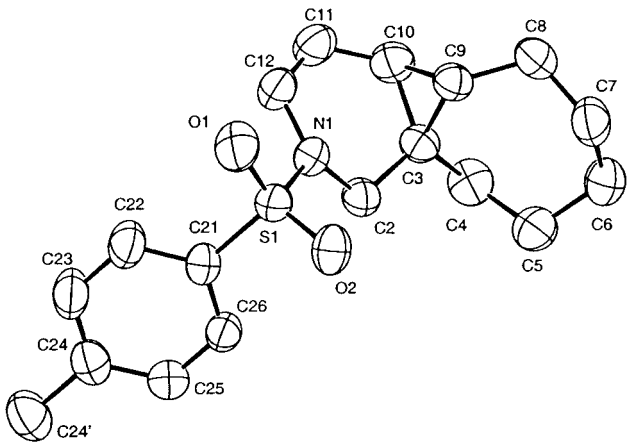
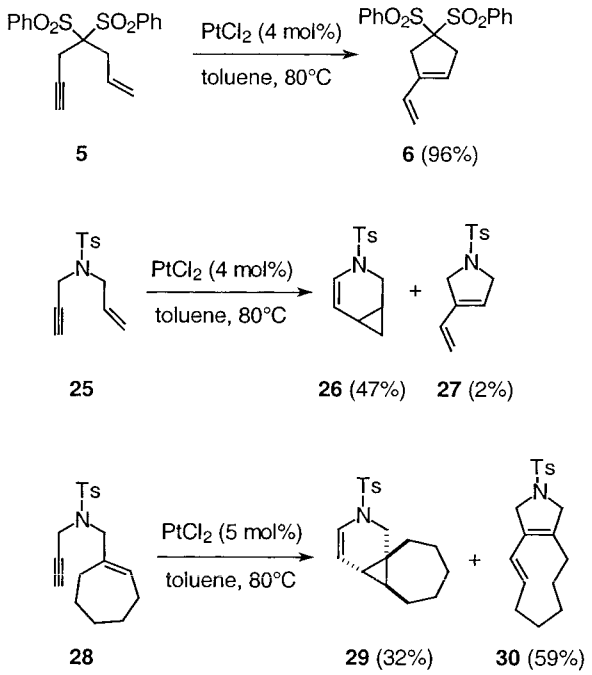


Figure 1. ORTEP diagram of the molecular structure of compound **29**. Anisotropic displacement parameter ellipsoids are drawn at 50% probability, hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (deg): N1−C2 1.475(2), N1−C12 1.421(2), C2−C3 1.512(2), C12−C11 1.316(3), C11−C10 1.469(3), C3−C10 1.514(3), C3−C9 1.491(2), C9−C10 1.525(3), C9−C3−C10 60.99(12), C3−C9−C10 60.24(12), C3−C10−C9 58.77(11).

Scheme 3

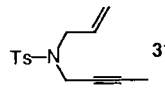
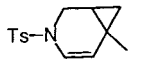
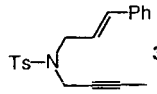
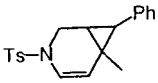
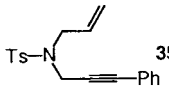
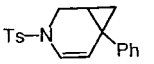
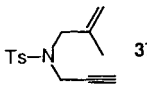
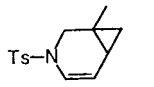
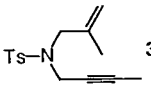
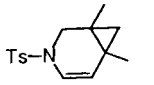
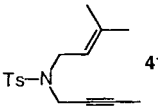
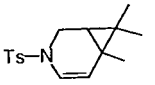
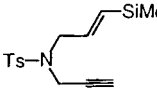
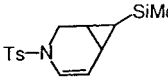
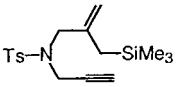
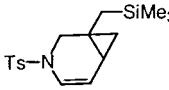
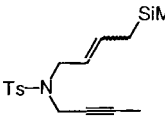
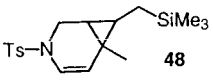
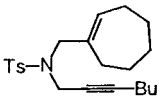
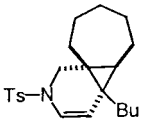
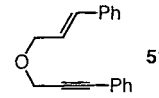
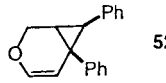
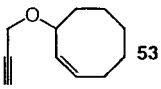
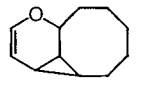


47, although substrates of this type lacking the heteroatom were previously shown to undergo $PtCl_2$-catalyzed transformations into 1,4-dienes.[4] It is important to note, however, that in most entries shown in Table 2, minor amounts (1−15%) of the corresponding 1,3-diene products originating from the formal metathesis pathway accompany the cyclopropane derivatives formed as the major reaction products. This may be interpreted in terms of common reactive intermediates which can stabilize along two different pathways (vide infra).

Mechanistic Considerations. All attempts to gain insights into the reaction mechanism by spectroscopic means were unsuccessful. No intermediates are observed when the reaction is carried out in an NMR tube even if equimolar amounts of $PtCl_2$ are employed. However, a set of experimental data has accumulated that contains substantial indirect evidence for the elementary steps of these reactions.

Different scenarios can be envisaged for cycloisomerization reactions of enynes mediated by Pt(II) or electrophilic Pd(II)

Table 2. Formation of Cyclopropane Derivatives Catalyzed by $PtCl_2$[a]

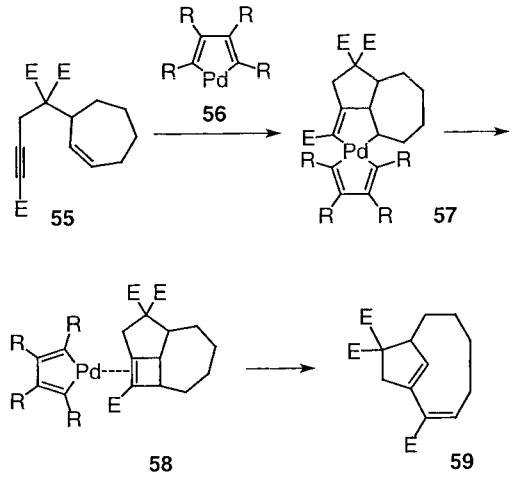
Nr	Substrate	Product	Yield[b]
1	 **31**	 **32**	59%
2	 **33**	 **34**	62%
3	 **35**	 **36**	78%
4	 **37**	 **38**	68%
5	 **39**	 **40**	69%
6	 **41**	 **42**	47%
7	 **43**	 **44**	50%
8	 **45**	 **46**	73%
9	 **47**	 **48**	76%
10	 **49**	 **50**	87%
11	 **51**	 **52**	83%[16]
12	 **53**	 **54**	39%[c]

[a] In toluene at 60−80 °C with 4−10 mol % of $PtCl_2$. [b] Small amounts (1−15%) of the corresponding 1,3-dienes resulting from formal enyne metathesis of the substrates were obtained as byproducts in many cases. [c] The lower yield is partly due to losses during workup caused by the lability of the product which is formed as two diastereoisomers, cf. Supporting Information.

complexes, respectively. One of them was launched to explain the behavior of the electron-deficient palladol complex **56** (R = $COOCH_2CF_3$), which was previously shown to effect similar enyne metathesis reactions.[3,13,17] In this particular case, a truly organometallic pathway was proposed involving metallacyclopentene derivatives such as **57** as key intermediates of a Pd(II)/Pd(IV) manifold (Scheme 4). The occasional isolation of cyclobutenes of type **58** that may originate from **57** by reductive elimination lends experimental support for this assumption.

(17) See also: Trost, B. M.; Hashmi, A. S. K. *Angew. Chem.* **1993**, *105*, 1130−1132; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1085−1087.

Scheme 4

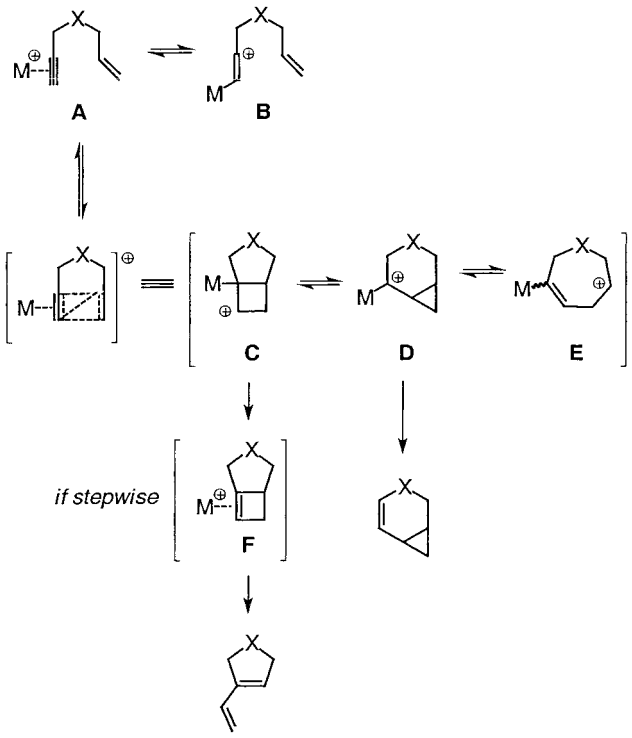


Decomplexation followed by an electrocyclic ring opening of the cyclobutene affords the final product and regenerates the catalyst.

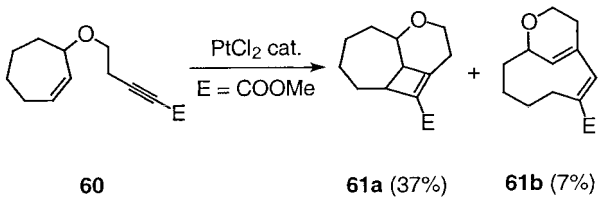
Alternatively, simple π-complexes formed by coordination of the transition metal cation onto the alkyne moieties of the substrates may trigger the rearrangement process. It is well established that Pt(II)−alkyne complexes are very electrophilic and are readily attacked by a variety of nucleophiles.[18,19] There is, however, some ambiguity as to whether the π-complex **A** itself or the zwitterionic vinylmetal complex **B** derived thereof constitutes the actual reactive intermediate.[20] No rigorous distinction between these tautomeric forms has been made so far. If the nucleophilic reaction partner is a tethered alkene group, a *delocalized cation* results which can also be represented by the forms **C**−**E**. As shown in Scheme 5, such species stabilize along different pathways. The preference for either of these reaction channels will ultimately depend on which of the possible resonance forms gains more weight, e.g. by stabilization via the heteroatom X in the tether and/or the presence of annellated ring systems.

Specifically, the evolution of the cyclobutyl cation **C**[21] leads to 1,3-dienes as the products of a formal enyne metathesis. This may occur either in a concerted or in a stepwise fashion with formation of a cyclobutene derivative **F**[21] that subsequently undergoes an electrocyclic ring opening. This facet is important as it provides an alternative explanation for the possible intervention of cyclobutenes in these reactions (vide supra). Upon treatment of enyne **60** with $PtCl_2$, such a compound (**61a**) has in fact been isolated; the low yields obtained in this reaction are mainly due to the poor stability of products **61a**,**b** (Scheme 6). In contrast, the "cyclopropyl-methyl" cation resonance form **D** is "carbenoid" in nature, suffering a rapid 1,2-hydrogen shift to give bicyclo[4.1.0]heptane derivatives.[22]

Scheme 5



Scheme 6



Since this rationale explains the observed dichotomy without difficulty, further experiments have been carried out to corroborate this mechanistic interpretation. First, the assumed stabilization of the carbenoid resonance form **D** by rapid 1,2-hydrogen shift has been probed by deuterium labeling studies (Scheme 7).

For this purpose, the *gem*-dideuterated enyne **62** was prepared, which rearranges into product **63** bearing deuterium labels at the *vicinal* positions. This finding provides strong evidence for the assumed pathway. The deuterium incorporation at C-3 is high, yet incomplete (**63**:**64** $\approx$ 3:1). The unlabeled product **64** may originate from a competing insertion of the carbene into traces of water that may be present in the reaction mixture. Therefore, a control experiment has been carried out in which the unlabeled analogue **31** was reacted with $PtCl_2$ under the standard conditions in the presence of D_2O (1 eq). As expected, the product formed was largely unlabeled; interestingly though, the ratio of isotopomeres is in the same range as above (**32**:**65** $\approx$ 3:1) and the deuterium incorporation occurs selectively at C-3 as evident from an appropriate set of NMR (^1H, ^2H, ^{13}C) experiments. Taken together, these data are fully consistent with the assumed intervention of carbenoid species that stabilize preferentially by an intramolecular 1,2-hydrogen (deuterium)

(18) For reviews on the carbocation-like behavior of Pt(II)−alkyne complexes see: (a) Chisholm, M. H.; Clark, H. C. *Acc. Chem. Res*. **1973**, *6*, 202−209. (b) Belluco, U.; Bertani, R.; Michelin, R. A.; Mozzon, M. *J. Organomet. Chem*. **2000**, *600*, 37−55.

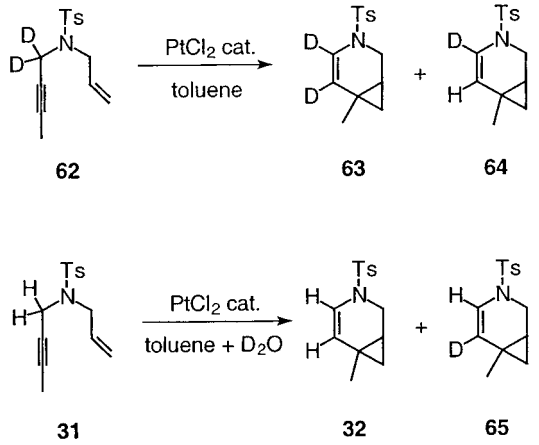
(19) For prototype examples of reactions of alkynes π-complexed to platinum or Lewis acids with various nucleophiles see the following for leading references: (a) Kataoka, Y.; Matsumoto, O.; Tani, K. *Organometallics* **1996**, *15*, 5246−5249. (b) Baidossi, W.; Lahav, M.; Blum, J. *J. Org. Chem*. **1997**, *62*, 669−672. (c) Murata, T.; Mizobe, Y.; Gao, H.; Ishii, Y.; Wakabayashi, T.; Nakano, F.; Tanase, T.; Yano, S.; Hidai, M.; Echizen, I.; Nanikawa, H.; Motomura, S. *J. Am. Chem. Soc*. **1994**, *116*, 3389−3398. (d) Neveux, M.; Seiller, B.; Hagedorn, F.; Bruneau, C.; Dixneuf, P. H. *J. Organomet. Chem*. **1993**, *451*, 133−138. (e) Yeon, S. H.; Han, J. S.; Hong, E.; Do, Y.; Jung, I. N. *J. Organomet. Chem*. **1995**, *499*, 159−165. (f) Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc*. **1997**, *119*, 6781−6786. (g) Asao, N.; Shimada, T.; Yamamoto, Y. *J. Am. Chem. Soc*. **1999**, *121*, 3797−3798 and literature cited therein.

(20) A detailed discussion of this issue is found in ref 7.

(21) It is emphasized that structures **C** and **F** are resonance forms that represent two extremes of the same intermediate.

(22) For a general treatise of the reactivity of carbenes see: Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971.

Scheme 7



shift as the dominant pathway, which is faster than a competing insertion into water (D_2O).

The analysis of the byproducts formed in the $PtCl_2$-catalyzed reaction of substrate **1** also strongly advocates the proposed cationic scenario. Enyne metathesis of **1** is a clean process delivering product **2** in 79% yield; however, if the reaction was carried out on a multigram scale (>7 g), we were able to isolate minute amounts of compounds **66**−**68** formed as byproducts. As has been discussed earlier in more detail,[11] the formation of all of these unusual derivatives is straightforward by assuming a delocalized carbocation as the key intermediate that originates from the attack of the alkene onto the π-complexed alkyne moiety of the substrate. Its possible resonance forms **G**−**J** engender the four different reaction channels featured in Scheme 8 and explain the observed product distribution pattern without difficulty.

If the reaction mechanism is cationic in nature, it may well be triggered by catalysts other than $PtCl_2$. In fact, substrate **1** (and related electron deficient enynes) rearranges quite efficiently to the corresponding "metathesis" product **2** in the presence of either $BF_3{\cdot}Et_2O$ (5 mol %) or HBF_4 (Scheme 9). This finding is mechanistically relevant since no organometallic pathway can be operative under these conditions and only a cationic "Wagner−Meerwein" type process similar to the one discussed above can account for the observed results. Therefore, the overall reaction is reminiscent of the Lewis acid-catalyzed cyclotrimerization of internal alkynes to substituted Dewarbenzenes, which is initiated by an analogous π-complexation of the substrates to a metal cation and proceeds via related metal−cyclobutadiene complexes as reactive intermediates.[23]

Taken together, these data provide compelling evidence that the skeletal reorganizations of enynes catalyzed by Pt(II) involve delocalized cations as the key intermediates.[24] This scenario readily explains the dichotomy of the reaction pathway, is consistent with the observed product distribution patterns and the isotope labeling studies, and explains why in some cases Pt(II) may even be replaced by simple Lewis or Brønsted acids without changing the course of the reaction.

Platinum-Catalyzed O→C Allyl Shift Reactions. On the basis of this mechanistic interpretation, we were trying to extend the concept by intercepting the assumed electrophilic Pt(II)−alkyne complexes with nucleophiles other than alkenes. For this purpose, unsaturated ether derivatives of the general structure shown in Scheme 10 have been designed in which the coordination of the metal may trigger a cascade comprising a 1,4-addition of the ether oxygen onto the π-complexed alkyne and simultaneous release of a (presumably metal complexed) allyl cation. Recapturing of this fragment by the emerging organoplatinum intermediate leads to a subsequent C−C-bond formation at the carbon atom adjacent to the newly formed ring.

We were pleased to see that acetylenic esters (Y = COOR) as well as acetylenic nitriles (Y = CN) smoothly undergo this previously unknown O→C allyl shift reaction on exposure to catalytic amounts of $PtCl_2$ in toluene at 80 °C. Transition metal salts other than $PtCl_2$ were either found to be totally inactive or lead to the rapid decomposition of the starting materials.[25]

The results compiled in Table 3 show the scope of this transformation and deserve several comments. Thus, remarkably high levels of stereoselectivity with regard to the newly formed tetrasubstituted double bond are obtained in all cases investigated. It is noteworthy, however, that the major products are (*E*)-configurated in the case of acetylenic ester substrates, whereas acetylenic nitriles invariably lead to (*Z*)-configurated compounds. The formal trans addition of the ether oxygen and the allyl part in the latter case is inconsistent with a concerted reaction mechanism but is well explained by the rationale depicted in Scheme 10 involving enolate intermediates **K** and **L** which can interconvert via the respective O- or N-metalated tautomers.[26] Since the different stereochemical course of the reaction in the ester and the nitrile series cannot be explained by the thermodynamic stability of the products, it must be kinetic in origin and hence arise from differences in the structure of these intermediates.[27] The fact that ester (as well as ketone) enolates of nobel metals largely prefer the C-metalated form,[28] whereas the nitrile analogues of the same metals are best described as N-metalated keteniminato complexes,[29] provides a tentative explanation for this distinct behavior. The notion that organometallic intermediates are involved in the observed transformation is also supported by the finding that the addition

(23) This transformation is similarly promiscuous with regard to the Lewis acid that can be used; for a review see: Schäfer, W.; Hellmann, H. *Angew. Chem.* **1967**, *79*, 566−573; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 518 and literature cited therein.

(24) Further support for the proposed cationic mechanism comes from a recent publication describing elegant labeling studies, cf.: Oi, S.; Tsukamoto, I.; Miyano, S.; Inoue, Y. *Organometallics* **2001**, *20*, 3704−3709.

(25) This includes $PtCl_2(PPh_3)_2$, $PdCl_2$, $Pd(PPh_3)_4$, $AgPF_6$, $ZnCl_2$, $BF_3{\cdot}Et_2O$, and a cationic platinum complex formed in situ from $PtCl_2(PPh_3)_2$/$AgPF_6$.

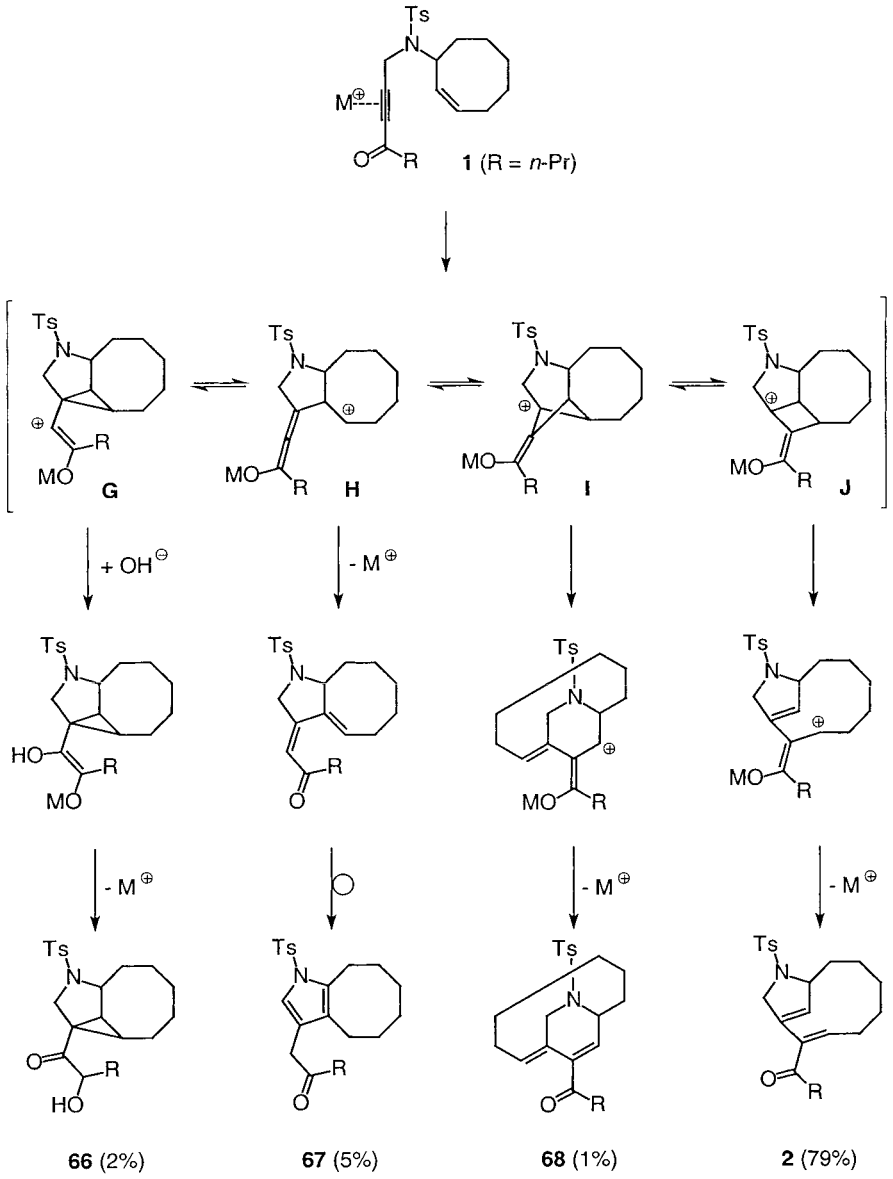
(26) The importance of metal enolates as reactive intermediates in these reactions can also be gleaned from the fact that substrates devoid of the ester or nitrile group do not undergo this rearrangement process.

(27) Semiempirical calculations have shown that in both series the (*E*)-configured products are thermodynamically more stable. For an example showing slow isomerization of a (*Z*)-configured product into the more stable (*E*)-isomer see: (a) Krueger, S. A.; Bryson, T. A. *J. Org. Chem.* **1974**, *39*, 3167−3168. (b) Bryson, T. A. *J. Org. Chem.* **1973**, *38*, 3428−3429.

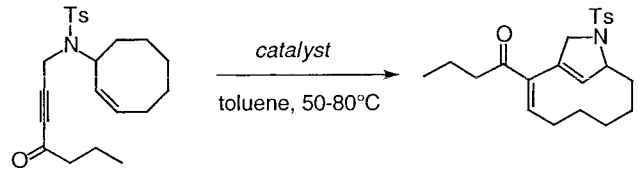
(28) See the following for leading references on structures and reactivity of ester and ketone enolates of Pt(II) and other nobel metals (Pd, Ni, Re, etc.): (a) Appleton, T. G.; Chisholm, M. H.; Clark, H. C.; Yasufuku, K. *J. Am. Chem. Soc.* **1974**, *96*, 6600−6605. (b) Chaudhury, N.; Puddephatt, R. *J. Chem. Soc., Dalton Trans.* **1976**, 915−919. (c) Ito, T.; Yamamoto, A. *J. Organomet. Chem.* **1979**, *174*, 237−245. (d) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3028−3030. (e) Burkhardt, E. R.; Bergman, R. G.; Heathcock, C. H. *Organometallics* **1990**, *9*, 30−44. (f) Stack, J. G.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *Organometallcis* **1990**, *9*, 453−466. (g) Burkhardt, E. R.; Doney, J. J.; Stack, J. G.; Heathcock, C. H.; Bergman, R. G. *J. Mol. Catal.* **1987**, *41*, 41−57. (h) Nizova, G. V.; Serdobov, M. V.; Nikitaev, A. T.; Shul'pin, G. B. *J. Organomet. Chem.* **1984**, *275*, 139−144. (i) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993−999. (j) Kurosawa, H.; Majima, T.; Asada, N. *J. Am. Chem. Soc.* **1980**, *102*, 6996−7003.

(29) See the following for leading references showing that nitrile enolates of Pt(II) and other nobel metals (Rh, Ir, Pd, etc.) exist as keteniminato complexes: (a) Lenarda, M.; Baddley, W. H. *J. Organomet. Chem.* **1972**, *39*, 217−224. (b) Chaudhury, N.; Kekre, M. G.; Puddephatt, R. J. *J. Organomet. Chem.* **1974**, *73*, C17−C19.

Scheme 8

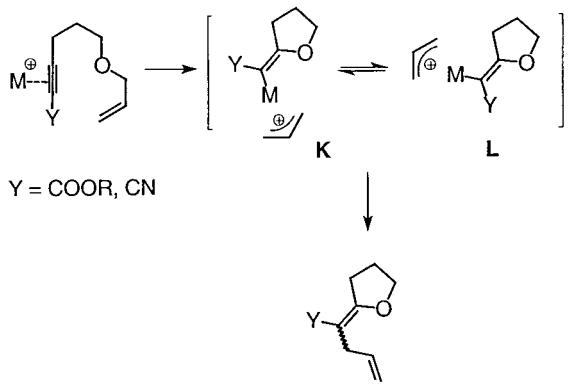


Scheme 9



catalyst	yield
$PtCl_2$	79%
$BF_3{\cdot}Et_2O$	64%
HBF_4	57%

Scheme 10

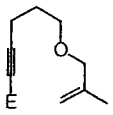
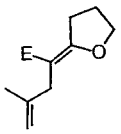
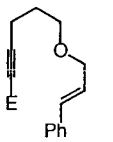
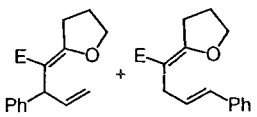
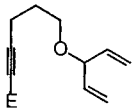
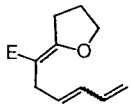
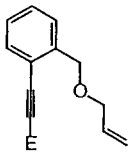
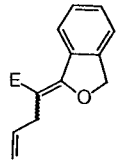
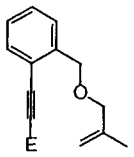
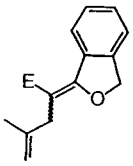
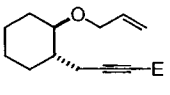
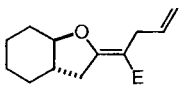
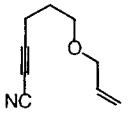
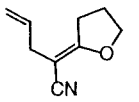
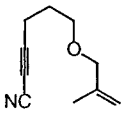
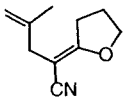
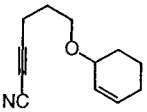
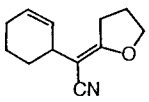
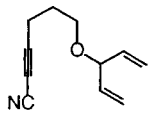
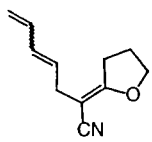
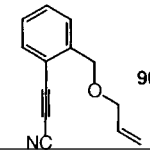
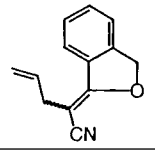


of radical scavengers such as *p*-quinone or dihydroquinone to the reaction mixture does not inhibit the Pt(II)-catalyzed allyl shift.

The results shown in entries 2, 3, and 10 provide further information. In these cases, the substitution patterns of the allyl ether entities serve as mechanistic probes which indicate if (metal complexed) allyl cation equivalents form at any stage along the pathway of the O→C allyl shift reaction. In fact, the formation of the resulting products is best explained by assuming an allyl fragment as reactive intermediate that rearranges prior to recombination at the site where the positive charge is most stabilized and/or the intermediate is sterically least encumbered.

A crossover experiment has been carried out to gain insight if the allyl group is transferred inter- or intramolecularly. Specifically, an equimolar mixture of substrates **69** and **80** has

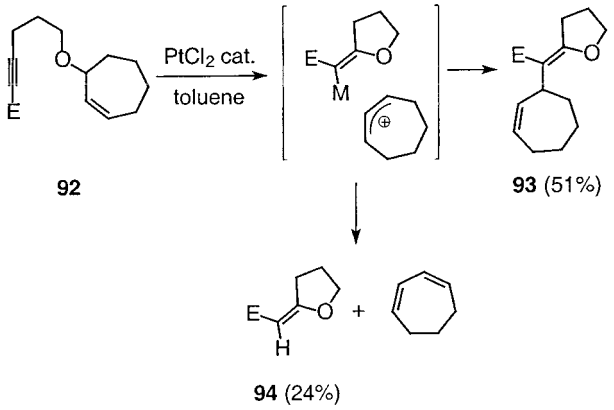
Table 3. Platinum Catalyzed O→C Allyl Shift Reactions (E = COOMe)

Nr	Substrate	Product	Yield
1	 **69**	 **70**	59%[a]
2	 **71**	 **72** (7.1) : **73** (1)	76%[a]
3	 **74**	 **75**	73%[a]
4	 **76**	 **77**	71%[b]
5	 **78**	 **79**	74%[c]
6	 **80**	 **81**	56%[a,d]
7	 **82**	 **83**	86%[e]
8	 **84**	 **85**	85%[e]
9	 **86**	 **87**	65%[e]
10	 **88**	 **89**	77%[e]
11	 **90**	 **91**	80%[f]

[a] Pure (*E*)-isomer at the exocyclic double bond. [b] *E*:*Z* = 2.4:1. [c] *E*:*Z* = 10.3:1. [d] With $PtCl_4$ instead of $PtCl_2$. [e] Pure (*Z*)-isomer at the exocyclic double bond. [f] *E*:*Z* = 1:7.9.

been exposed to catalytic amounts of $PtCl_x$ (x = 2, 4) under standard conditions. Careful inspection of the reaction mixture by GC/MS showed that compounds **70** and **81** were the only products formed in this reaction. Within the limits of detection (ca. 1%), no indications for the formation of products derived from a crossover of the allyl fragments have been found, thus strongly suggesting an intramolecular delivery of these moieties as suggested by Scheme 10.

Scheme 11



The fact that the $PtCl_2$-catalyzed reaction of compound **92** does not only provide the expected tetrasubstituted alkene **93** but also affords small amounts of the protonated congener **94** lends further credence to the notion that allyl cation equivalents intervene (Scheme 11). The cycloheptenyl cation initially formed may not only be recaptured by the organometallic entity but can also stabilize to some extent via loss of H^+, which explains the competing pathway.

Conclusions. $PtCl_2$ is shown to be an extremely effective, user-friendly, and versatile catalyst for different structural reorganizations of enynes. Among the reaction modes that were already known in the literature, the formal enyne metathesis of such compounds is particularly attractive and has already served as the key step in the total synthesis of complex bioactive targets. Two additional transformations have now been developed: One of them consists of the formation of bicyclo[4.1.0]heptene derivatives while the other one represents a previously unknown O→C allyl shift resulting in the stereoselective formation of tetrasubstituted alkene moieties. Although these processes lead to rather diverse structural motifs, strong evidence is provided that they share a common cationic mechanism. The coordination of the Pt(II) to the alkyne of the substrate likely triggers all of these events which belong to the rare category of "low-tech" yet complexity inducing and atom economical transformations and should therefore find further applications in advanced organic synthesis.

Acknowledgment. Generous financial support by the Deutsche Forschungsgemeinschaft (Leibniz award to A.F.) as well as the Fonds der Chemischen Industrie (Kekulé stipend to F.S.) is gratefully acknowledged. We thank Dr. Ch. W. Lehmann for the X-ray analysis of compound **29** and Dr. R. Mynott and coworkers for their help with the interpretation of the NMR spectra of some products. We thank the Degussa AG for a generous gift of platinum salts.

Supporting Information Available: Full experimental details, including the spectroscopic and analytical data of all new compounds and information concerning the X-ray structure of compound **29** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0109343