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Communications

Platinum-Mediated Coupling of Alkynols and α-Diazoesters. Pseudocatalytic Synthesis of Tetrahydrofuranylidene Esters via Alkyl Migration to a Coordinated Carbene

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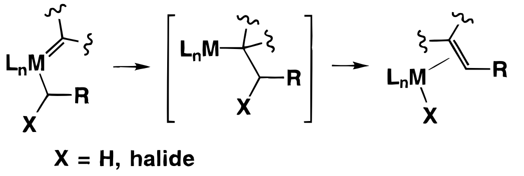
Summary: A novel combination of metal-mediated transformations is reported, which together constitute a new organic reaction: the coupling of 3-alkynols and α-diazoesters to yield tetrahydrofuranylidene esters. The process involves the migratory insertion of a coordinated carbene into a metal−alkyl σ-bond and, in stoichiometric form, is efficient and pseudocatalytic, starting and ending with (dppe)PtCl$_2$. The reaction, uniquely, can be made catalytic in platinum, but only poorly so.

The selective cyclization and cross-coupling of alkynols with α-diazoesters is reported, a new metal-mediated organic reaction that leads to the formation of synthetically-valuable tetrahydrofuranylidene esters. The reaction proceeds via an unprecedented combination of fundamental organometallic processes at platinum and, notwithstanding marginal turnover number, constitutes the first demonstration of a *catalytic* organic transformation based upon the migratory insertion of a coordinated carbene into a transition metal alkyl σ-bond (eq 1).[1]



(1)

The development of catalytic carbon−carbon bond forming processes incorporating this reactivity pattern suffers from the difficulty associated with regenerating

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

(1) Stoichiometric examples, see: (a) Van Leeuwen, P. W. N. M.; Roobeek, C. F.; Huis, R. *J. Organomet. Chem.* **1977**, *142*, 243. (b) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224. (c) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43. (d) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278. (e) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. Thorn, D. L. *Organometallics* **1985**, *4*, 192. (f) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3026. (g) Kletzin, H.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 46. Werner, H.; Kletzin, H.; Höhn, A.; Paul, W.; Knaup, W.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1986**, *306*, 227. Werner, H.; Roder, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 686. (h) McCrindle, R.; Arsenault, G. J.; Gupta, A.; Hampden-Smith, M. J.; Rice, R. E.; McAlees, A. J. *J. Chem. Soc., Dalton Trans.* **1991**, 949. McCrindle, R.; Arsenault, G. J.; Farwaha, R.; Hampden-Smith, M. J.; McAlees, A. J. *J. Chem. Soc., Chem. Commun.* **1986**, 943. (i) Stenstrom, Y.; Koziol, A. E.; Palenik, G. J.; Jones, W. M. *Organometallics* **1987**, *6*, 2079. See also refs in: Trace, R. L.; Sanchez, J.; Yang, J.; Yin, J.; Jones, W. M. *Organometallic,* **1992**, *11*, 1440. (j) Liebeskind, L. S.; Chidambaram, R. *J. Am. Chem. Soc.* **1987**, *109*, 5025. (k) Bly, R. S.; Bly, R. K.; Hossain, M. M.; Lebioda, L.; Raja, M. *J. Am. Chem. Soc.* **1988**, *110*, 7723. Bly, R. S.; Silverman, G. S.; Bly, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 7730. (l) Maitlis, P. M.; Bailey, N. A.; Adams, H.; Martinez, J. M. *J. Chem. Soc., Chem. Commun.* **1989**, 286. (m) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6232. (n) O'Connor, J. M.; Pu, L.; Woolard, S.; Chadha, R. K. *J. Am. Chem. Soc.* **1990**, *112*, 6730. (o) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 464. (p) Adams, H.; Bailey, N. A.; Tattershall, C. E.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1991**, 912. Adams, H.; Bailey, N. A.; Bentley, G. W.; Tattershall, C. E.; Taylor, B. F.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 533. (q) Selnau, H. E.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008. (r) Bergamini, P.; Costa, E.; Cramer, P.; Hogg, J.; Orpen, A. G.; Pringle, P. G. *Organometallics* **1994**, *13*, 1058.

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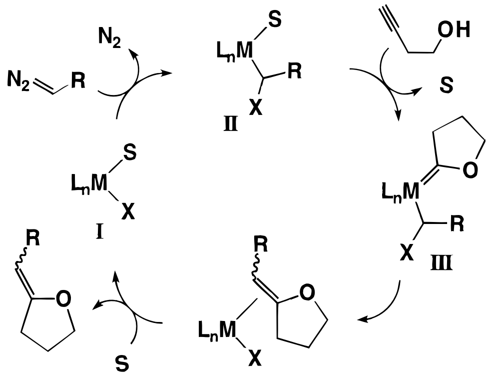
the alkyl and carbene ligands following the migration event. The β-hydride elimination anticipated subsequent to migration of a simple alkyl ligand,[1i,m,o] for example (eq 1, X = H), returns a metal−hydride fragment which is not readily converted to a new alkyl ligand.[2] A more direct alternative is β-halide elimination (eq 1, X = halide): the conversion of metal halides into haloalkyl complexes via α-diazoalkane transfer is precedented for both main group and late transition metals.[3−5] The incorporation of the halide further controls the regioselectivity of the β-elimination reaction.

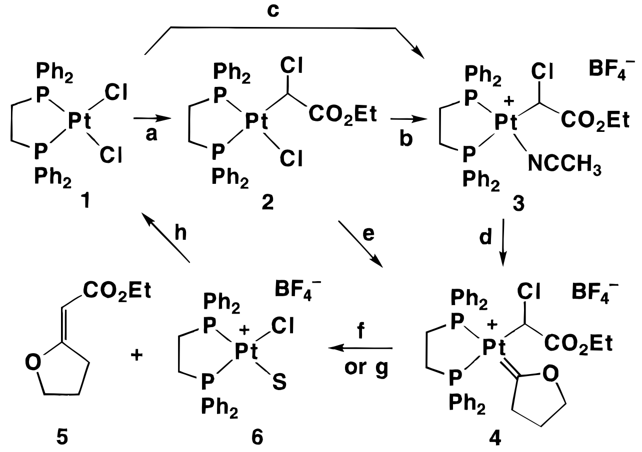
Although installation of the carbene ligand is also potentially problematic, classical alkynol cyclization[6] is an attractive option, providing single component methodology and producing a synthetically attractive oxacyclic fragment.[7,8] This procedure, however, is not without potential incompatibilities: the cycloisomerization proceeds via alkyne and vinylidene intermediates which may suffer competitive migratory insertion prior to oxacycloalkylidene formation. This may limit the range of compatible haloalkyl ligands to those having relatively low migratory aptitude.[9]

In this communication, we report a demonstration of the fundamental transformations required to close a proposed catalytic cycle, illustrated in highly simplified form (Scheme 1): haloester ligand formation via α-diazoester insertion (**I** → **II**), carbene generation by alkynol cyclization (**II** → **III**), and the critical migratory insertion/β-halide elimination reaction (**III** → **IV**),[10] releasing the tetrahydrofuranylidene ester and regenerating the metal template. Stoichiometrically, a high-yield pseudocatalytic transformation has been developed, mediated by (dppe)PtCl$_2$ (dppe = 1,2-bis(diphenylphosphino)ethane). Preliminary development of a true catalytic process is also reported, limited, however, by decomposition of one intermediate in the temperature range necessary for turnover.

Scheme 1



Scheme 2[a]



[a] Conditions: (a) N$_2$CHCO$_2$Et, CH$_2$Cl$_2$, 20 °C, 80%, ref 5d; (b) AgBF$_4$, CH$_2$Cl$_2$/CH$_3$CN, 0 °C, 5 h, 95%; (c) AgBF$_4$, N$_2$CHCO$_2$Et, CH$_3$CN, 0−20 °C, ~50%; (d) HC≡C(CH$_2$)$_2$OH, CH$_2$Cl$_2$, 20 °C, 15 h, quant; (e) AgBF$_4$, CH$_2$Cl$_2$/(CH$_3$)$_2$CO, −78 to 20 °C, 9 h, 92%; (f) 80 °C, CH$_3$CN, 3 h, **5**, quant (**6** (S = CH$_3$CN) not observed); (g) 50 °C, CH$_2$Cl$_2$/CH$_3$CN or CDCl$_3$, 2,6-lutidine (5 equiv), 6 h, **5** and **6** (S = 2,6-lutidine), quant; (h) [PPN]Cl, CH$_2$Cl$_2$, quant.

To evaluate carbene construction and migratory insertion, platinum(II) chloroester chloride complex **2**[5d] was prepared by treatment of (dppe)PtCl$_2$ with ethyldiazoacetate and converted in high yield to the cationic acetonitrile complex **3** by AgBF$_4$-assisted ionization, using a mixed acetonitrile/dichloromethane solvent for improved solubility (Scheme 2).[11] Alkynol coordination and cycloisomerization occurs quantitatively at room temperature with 3-butynol, yielding chloroester oxacyclopentylidene complex **4**[11] with no competitive insertion of intermediate alkyne or alkylidene complexes. Ionization and carbene formation (*i.e.*, **2** → **4**) can be conducted in one operation either at low temperature or room temperature without significant loss in yield. The migratory insertion and β-chloride elimination proceed efficiently in acetonitrile, dichloromethane, or in mixtures of the two solvents. Temperatures above ambient temperature are required; the reaction is run most conveniently at 80 °C in acetonitrile (Scheme 2). The organic product is formed quantitatively and identified

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(2) Provided the reaction could be induced efficiently, reductive elimination of the hydride (*e.g.*, by deprotonation) followed by oxidative addition to "reload" the alkyl ligand provides a reasonable alternative pathway, currently under investigation.

(3) Main group metals: (a) Seyferth, D. *Chem. Rev.* **1955**, *55*, 1155. (b) Barluenga, J.; Campers, P. J.; Garcia-Martin, J. C.; Roy, M. A.; Asenio, G. *Synthesis* **1979**, 893 and references therein.

(4) Comprehensive list of references to transition metal halide/diazoalkane insertions, see: McCrindle, R.; McAlees, A. J. *Organometallics* **1993**, *12*, 2445.

(5) Platinum systems: (a) reference 4. McCrindle, R.; Arsenault, G. J.; Farwaha, R.; Hampden-Smith, M. J.; Rice, R. E.; McAlees, A. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1773 and references therein. (b) Hanks, T. W.; Ekeland, R. A.; Emerson, K.; Larsen, R. D.; Jennings, P. W. *Organometallics* **1987**, *6*, 28. (c) Alcock, N. W.; Pringle, P. G.; Bergamini, P.; Sostero, S.; Traverso, O. *J. Chem. Soc., Dalton Trans.* **1990**, 1553. (d) Bergamini, P.; Costa, E.; Sostero, S.; Orpen, A. G.; Pringle, P. G. *Organometallics* **1991**, *10*, 2989.

(6) Chisholm, M. H.; Clark, H. C. *Acc. Chem. Res.* **1973**, *6*, 202 and references therein.

(7) Alkynol cyclization without concomitant carbon−carbon bond formation has recently been developed in the context of two catalytic organic transformations. (a) Dihydrofuran synthesis: McDonald, F. E.; Connolly, C. B.; Gleason, M. M.; Towne, T. B.; Treiber, K. D. *J. Org. Chem.* **1993**, *58*, 6952. McDonald, F. E.; Schultz, C. C. *J. Am. Chem. Soc.* **1994**, *116*, 9363. McDonald, F. E.; Gleason, M. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 350. (b) α-Stannyl−dihydrofuran synthesis: McDonald, F. E.; Schultz, C. C.; Chatterjee, A. K. *Organometallics* **1995**, *14*, 3628.

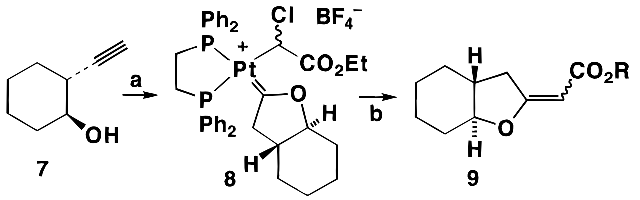
(8) No synthetically useful carbon−carbon bond forming reactions involving alkynol cyclization have been reported. Oxacyclopentylidene migratory insertion into σ-vinyl[1n] and alkylphosphonium[1o] (phosphonium ylide) ligands have, however, been recently reported.

(9) An investigation of alkyl and substituted alkyl migration to oxacyclopentylidene complexes of platinum(II) will be reported in a full account: Casty, G. L.; Stryker, J. M. Unpublished results.

(10) 1,2-Migration of an α-chloromethyl ligand to coordinated methylene is strongly implicated in the formation of ethylene from *cis*-bis(chloromethyl) complexes, see: (a) Pt: ref 1h. (b) Ru: Hubbard, J. L.; Morneau, A.; Burns, R. M.; Nadeau, O. W. *J. Am. Chem. Soc.* **1991**, *113*, 9180.

(11) Experimental details, spectroscopic characterization, and elemental analyses are provided as Supporting Information.

Scheme 3[a]

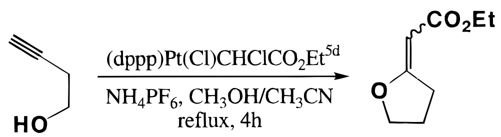


[a] Conditions: (a) complex **2**, $AgBF_4$, CH_2Cl_2 or CH_2Cl_2/$(CH_3)_2CO$, −78 to 0 °C, 12 h, 95% (1:1); (b) 40 °C, CH_2Cl_2, 4 h, 84% (*E*:*Z* = 8.5:1).

as the known tetrahydrofuranylidene ester **5**,[12] obtained exclusively as the *E*-stereoisomer.[13,14] The expected platinum byproduct from this reaction, cationic chloro solvate **6** (S = CH_3CN), is not observed. Instead, dichloride complex **1** is recovered in low yield as the only identifiable metal-containing product.[15] Cationic complex **6** (S = 2,6-lutidine),[11] however, is recovered quantitatively from reactions run in the presence of the more basic scavenger 2,6-lutidine (5 equiv).[16] Cationic complex **6** affords (dppe)$PtCl_2$ (**1**) cleanly upon treatment with PPN^+Cl^- in dichloromethane, completing the pseudocatalytic cycle.

In a second series, bicyclic chloroester carbene complexes **8**[11] (1:1 mixture of diastereomers) were similarly prepared and converted to the bicyclic tetrahydrofuranylidene ester **9**,[11] isolated in high yield as a readily separable 8.5:1 mixture of double bond isomers, which have been assigned tentatively by spectroscopic comparison with the unambiguously assigned monocyclic esters **5** (Scheme 3). In this series, the migration occurs under somewhat milder conditions (CH_2Cl_2, 40 °C, 4 h), perhaps reflective of increased steric demands in intermediate complex **8**.

In more polar reaction media, solvolytic ionization of the chloroester chloride complex can be accomplished without the use of silver ion assistance and the entire reaction sequence after the diazoester insertion step can be run in one operation: in the 1,2-bis(diphenylphosphino)propane (dppp) series, for example, direct conversion of 3-butynol to tetrahydrofuranylidene ester **5** is obtained in high yield at reflux in a mixture of methanol and acetonitrile (eq 2).



(2)

In the presence of substoichiometric platinum, tetrahydrofuranylidene formation becomes catalytic,[11] but at best only modestly so. Thus, treatment of ethyldiazoacetate and 3-butynol with a catalytic amount (10 mol %) of chloroester complex **3** or **4** in CH_2Cl_2 or $CHCl_3$ containing acetonitrile (between 2 equiv/Pt and cosolvent level) at 40−80 °C produces tetrahydrofuranylidene ester **5** with *at most* 2 catalyst turnovers.[17] The limited catalyst lifetime is attributed to the reaction of catalytic intermediate **6** (S = CH_3CN) with the diazoester (*i.e.*, Scheme 1, **I** → **II**), which is strongly temperature dependent. At room temperature, for example, treatment of dichloride complex **1** with $AgBF_4$ and ethyldiazoacetate produces none of the chloroester complex **3**, but instead returns a new material that has, unfortunately, resisted characterization. At 0 °C, however, formation of this byproduct is completely suppressed; chloroester complex **3** is obtained in ca. 50% yield (Scheme 2, step **c**). Similarly, the reaction of (dppe)-$PtCl_2$ (**1**) and $AgBF_4$ in in $CDCl_3$/CD_3CN at −78 °C gives a material spectroscopically consistent with the cationic solvate **6**, which upon treatment with ethyldiazoacetate and 3-butynol followed by warming to room temperature produces chloroester carbene complex **4**, also in about 50% yield. Attempts to improve this conversion, *e.g.*, by the incorporation of 2,6-lutidine into complex **6**, have been unsuccessful.[18]

Despite the marginal performance of the catalytic transformation, this work provides a model for the further development of catalytic carbon−carbon bond-forming processes involving the formation and functionalization of transition metal carbene complexes.

Acknowledgment. Financial support from the NSERC of Canada and the University of Alberta is gratefully acknowledged, as is Johnson Matthey Aesar/Alfa for a generous loan of precious metals.

Supporting Information Available: Text giving the experimental procedures and complete spectroscopic and analytical data for all new compounds (7 pages). Ordering information is given on any current masthead page.

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(12) (a) Bryson, T. A. *J. Org. Chem.* **1973**, *38*, 3428. Swendsen, A.; Boll, O. M. *Acta Chem. Scand., Ser. B* **1975**, *29*, 197. Lambert, P. H.; Vauties, M.; Carrier, R. *J. Org. Chem.* **1985**, *50*, 5352. Michael, J. P.; Gladys, H. D.; Howard, A. S. *Tetrahedron* **1988**, *10*, 3025. (b) For other preparations and synthetic applications of tetrahydrofuranylidene esters, see: Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 7550, 7557. Bartlett, P. A.; Meadows, J. D.; Ottow, E. *J. Am. Chem. Soc.* **1984**, *106*, 5304 and references therein.

(13) The yield of this volatile product was determined by ^1H NMR spectroscopy at long pulse delay by integration against an internal standard. The product can be isolated in analytically pure form by chromatography with substantial material loss (50−60% yield).

(14) The stereoselectivity is the result of *E*/*Z*-equilibration[12a] under the reaction conditions, as determined by monitoring the reaction using ^1H NMR spectroscopy. At short reaction times (5−10% conversion), the product consists of the expected 1:1 mixture of stereoisomers.

(15) We speculate that ligand disproportionation may occur to give **1** and the dicationic bis(acetonitrile) complex $[(dppe)Pt(NCCH_3)_2]^{+2}$, which is unstable under the reaction conditions.

(16) $[(dppe)PtCl(2,6\text{-lutidine})]^+BF_4^-$ is prepared independently and quantitatively from (dppe)$PtCl_2$ by treatment with $AgBF_4$ in acetonitrile at 0−23 °C.[11]

(17) In all catalytic reactions, an unquantified amount of diethylfumarate and diethylmaleate are also detected as byproducts. In preliminary experiments, catalytic diazoester dimerization is also a problem in reactions mediated by the corresponding palladium complexes. For a discussion of metal-mediated dimerization of diazoalkanes, see ref 4 and refs cited therein. See also: da Silva, M. F. C. G.; da Silva, J. J. R. F.; Pombeiro, A. J. L.; Bertani, R.; Michelin, R. A.; Mozzon, M.; Benetollo, P.; Bombieri, G. *Inorg. Chim. Acta* **1993**, *214*, 85.

(18) The reaction of ethyldiazoacetate with (dppe)$PtCl_2$ does not proceed cleanly at elevated temperatures.