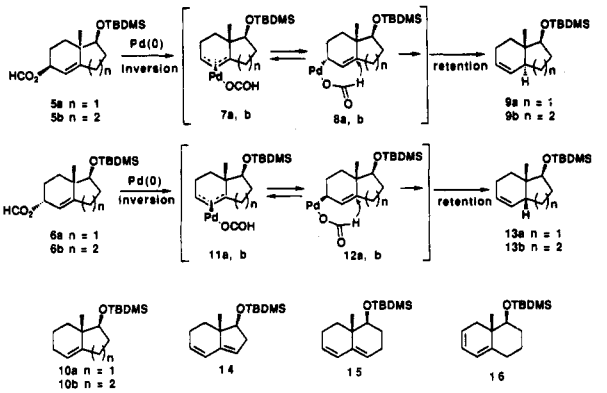
more substituted carbon of the allylic system in the bicylic systems (see **8a,b** or **12a,b**), giving the disubstituted olefins **9a,b** or **13a,b**, rather than the trisubstituted olefins **10a,b**. In addition to the regioselectivity, stereospecificity was expected based on mechanistic considerations. In palladium-catalyzed allylation reactions of nucleophiles via π-allylpalladium complexes, it is well-established that the initial step in π-allylpalladium complex formation involves inversion of stereochemistry. The subsequent addition of a soft carbon nucleophile to the π-allyl system takes place from the opposite side of palladium resulting in net retention.[3] On the other hand, the addition of a hard nucleophile to a π-allylpalladium complex proceeds from the same side as palladium, and hence overall inversion takes place. Based on the above stereochemical considerations, we expected that the attack of Pd(0) on **5a,b** or **6a,b** to form π-allylpalladium formate **7a,b** or **11a,b** would take place with inversion of stereochemistry. The subsequent migration of the hydride from the Pd formate to the angular carbon should occur with retention (**8a,b** → **9a,b**, and **12a,b** → **13a,b**). Therefore, overall inversion was expected. Thus the stereospecific formation of trans hydrindene **9a** and octahydronaphthalene **9b** is expected from the β-allylic formate **5a,b**, and the cis compounds **13a,b** would be formed from the α-allylic formate **6a,b**. We were pleased to find that these reactions in fact proceeded as expected.

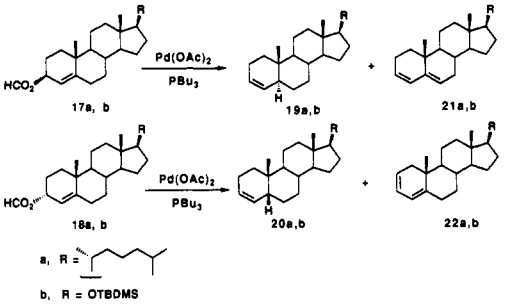
Both the α- and β-formates **6a** and **5a** were treated with the catalyst prepared from $Pd(acac)_2$ and n-Bu_3P (1:1) in THF.[4] The reactions proceeded in 30 min at room temperature to give only the 4-hydrindenes **9a** (82%) from **5a** and **13a** (57%) from **6a** with no regioisomeric 3a-hydrindene **10a** being formed. In addition, formation of the trans product **9a** (NMR, angular CH_3, $\delta = 0.73$) and *cis*-**13a** (NMR, CH_3, $\delta = 0.89$) shows that the hydrogenolysis reactions are stereospecific. As a byproduct, the heteroannular conjugated 3,4-diene **14** was formed (13% from **5a** and 38% from **6a**).[5]

In the decalin systems **5b** and **6b**, only the 3-olefins **9b** and **13b**, respectively, were formed regioselectively and stereospecifically after 1 h. As byproducts, the heteroannular-conjugated 3,5-diene **15** (3%) was produced from **5b** and the homoannular 2,4-diene **16** (6%) from **6b**.[5]

One application of this methodology is the stereoselective generation of both cis and trans AB ring junctions in steroids. The β-formates **17a,b** and the α-formates **18a,b** were prepared and subjected to the palladium catalysis



[$Pd(OAc)_2$ and n-Bu_3P (1:1)] at room temperature for 1.5–2 h. The β-formates **17a,b** were converted to the AB *trans*-cholestene (**19a**)[6] (80%) and *trans*-androstene derivative **19b** (94%) with high regioselectivity and stereospecificity. Also the heteroannular conjugated 3,5-dienes **21a,b** (15% and 5%) were byproducts. The AB *cis*-cholestene **20a**[7] (89%) and *cis*-androstene derivative **20b** (87%) were obtained cleanly from the α-formates **18a,b**. The homoannular 2,4-dienes **22a,b** (7% and 8%) were byproducts in these reactions. The steroids **19a**, **20a**, and **19b**, **20b** (after desilylation) are known and were identified by comparison of their optical rotations and mps with reported data. Also unequivocal stereochemical assignments were made by ^1H NMR analysis at 400 MHz.



Supplementary Material Available: Experimental procedures for main steps and physical data including NMR spectra for important compounds (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(3) (a) Trost, B. M.; Verhoeven, T. R. *J. Org. Chem.* **1976**, *41*, 3215. (b) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730.

(4) The use of pure n-Bu_3P was critical for consistent results. n-Bu_3P in a Sure-Seal bottle, purchased from Aldrich, was used.

(5) Studies on the palladium-catalyzed regioselective formation of the homo- and heteroannular conjugated dienes from the corresponding α- and β-allylic carbonates will be reported.

(6) Preparation of 5α-cholestene (**19a**) by the hydroboration of cholest-4-en-3-one has been reported: Caglioti, L.; Cainelli, G.; Maina, G.; Selva, A. *Tetrahedron* **1964**, *20*, 957.

(7) Preparation of *cis*-cholestene (**20a**) from cholest-4-en-3-one has been reported: Kabalka, G. W.; Hutchins, R.; Natale, N. R.; Yang, D. T. C.; Broach, V. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, p 293.

Titanium-Mediated Carbonyl Olefinations. 2. Benzylidenations of Carbonyl Compounds with Dibenzyltitanocene

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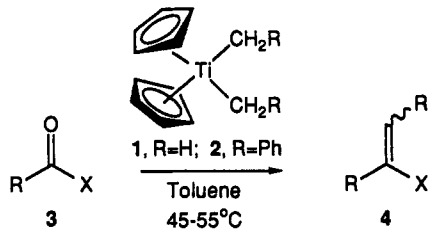
Summary: Mild thermolysis of carbonyl compounds with dibenzyltitanocene affords phenyl-substituted olefins, enol ethers, and enamines.

Several complexes of Ti,[1-3] Ta,[4] Zr,[5] Mo,[6] or W[7] were shown to perform Wittig-like olefinations of carbonyl compounds. While some of these[1-3] have found applica-

(1) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer-Verlag: Berlin, 1986.

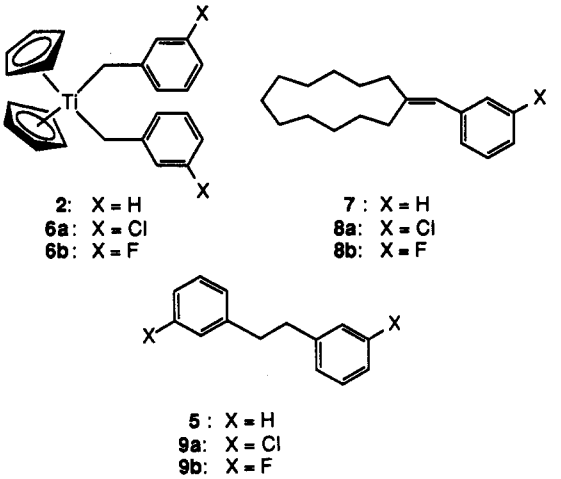
0022-3263/92/1957-1327$03.00/0

tions in organic synthesis, others are limited by structural restrictions and the requirement for special experimental procedures. We recently reported[8] that dimethyltitanocene (1) is a convenient and synthetically useful reagent for the methylenations of aldehydes, ketones, esters, and lactones. Herein we demonstrate the applicability of this new olefination procedure[9,10] to the synthesis of other types of olefins by using dialkyltitanocenes,[11] readily prepared from organolithium or organomagnesium precursors.[12] Thus, dibenzyltitanocene (2), a stable compound readily prepared from titanocene dichloride and benzylmagnesium chloride,[13] reacts with carbonyl compounds 3 to give phenyl-substituted olefins, enol ethers, and enamines 4.[14]



Some mechanistic aspects of this thermally-induced benzylidenation process are noteworthy. In contrast to the analogous reaction of 1, heating of 2 (1 equiv) with methyl benzoate in toluene-d_8 indicated ca. 30% increase in the amount of partially deuterated toluene.[15] This increase may result from abstraction of deuterium from the solvent methyl group by a reactive benzyl intermediate such as a benzyl radical. However, in some earlier reports[16] dealing with the thermal behavior of 2 in the solid state and in solution, it was postulated that 2 decomposes via a non-radical pathway involving conversion of the σ-Ti–C bond to an allylic π-complex, followed by intermolecular H-abstraction from the Cp rings.[16c]

While the thermolysis of 2 alone was previously reported[16b,d] to form only traces of dibenzyl (5) under our reaction conditions substantial amounts of 5 were produced. In an NMR experiment involving heating a benzene-d_6 solution of 2 at 54 °C for 22 h, we obtained a 9.4:1 mixture of toluene and 5. Variable amounts of 5 were also obtained during most of the benzylidenations with 2 reported below.



Similar reactions with various substituted dibenzyltitanocenes indicated that the presence of electron-withdrawing groups enhances the efficiency of the olefination. For example, while olefination of cyclododecanone with 2 (3 equiv, toluene, 60 °C, 27 h) gave 7 and 5 in a 4:1 ratio, the analogous reactions with **6ab** produced nearly quantitative amounts of **8ab**, with ratios of **8ab** and **9ab** of 14:1 and 10:1, respectively.[17] Furthermore, with **6ab** substantial amounts (0.1–0.2 equiv) of dibenzyltitanocene remained unreacted whereas all of 2 was consumed.

The formation of dibenzyl byproducts may be attributed to a reductive elimination process or to a homolytic cleavage of the Ti–C bond which would form the stabilized benzyl radical.[18] However, this is probably a competing decomposition pathway and does not preclude an alternative mechanism for the olefination process. Thus, the intermediacy of benzylidenetitanocene ($Cp_2Ti{=}CHAr$) or

(2) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270. (c) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733. (d) Pine, S. H.; Pettit, R. J.; Geib, G. D.; Cruz, S. G.; Gallego, C. H.; Tijerina, T.; Pine, R. D. *J. Org. Chem.* **1985**, *50*, 1212. (e) Cannizzo, L. F.; Grubbs, R. H. *J. Org. Chem.* **1985**, *50*, 2316. (f) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907.

(3) (a) Takai, K.; Hotta, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1978**, 2417; **1985**, *26*, 5579, 5581; *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1698. (b) Lombardo, L. *Tetrahedron Lett.* **1982**, *23*, 4293. (c) Okazoe, T.; Takai, K.; Oshima, K.; Utimoto, K. *J. Org. Chem.* **1987**, *52*, 4410. (d) Takai, K.; Fujimura, O.; Kataoka, Y.; Utimoto, K. *Tetrahedron Lett* **1989**, *30*, 211.

(4) (a) Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399. (b) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(5) (a) Hartner, F. W. J.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 4979. (b) Hartner, F. W. J.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640. (c) Clift, S. M.; Schwartz, J. *J. Am. Chem. Soc.* **1984**, *106*, 8300. (d) Arvanitis, G. M.; Schwartz, J. *Organometallics* **1987**, *6*, 421. (e) Schwartz, J.; Arvanitis, G. M.; Smegel, J. A.; Meier, I. K.; Clift, S. M.; Van Engen, D. *Pure Appl. Chem.* **1988**, *60*, 65. (f) Tour, J. M.; Bedworth, P. V.; Wu, R. *Tetrahedron Lett.* **1989**, *30*, 3927.

(6) (a) Kauffmann, T.; Ennen, B.; Sander, J.; Wieschollek, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 244. (b) Kauffmann, T.; Fiegenbaum, P.; Wieschollek, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 531. (c) Kauffmann, T.; Kieper, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 532. (d) Kauffmann, T.; Enk, M.; Kaschube, W.; Toliopoulos, E.; Wingbermuehle, D. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 910.

(7) (a) Kauffmann, T.; Abeln, R.; Welke, S.; Wingbermuehle, D. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 909. (b) Aguero, A.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 531.

(8) Petasis, N. A.; Bzowej, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 6392.

(9) Petasis, N. A.; Bzowej, E. I. U.S. patent pending.

(10) For synthetic applications see: (a) Petasis, N. A.; Patane, M. A. *Tetrahedron Lett.* **1990**, *31*, 6799. (b) Csuk, R.; Glanzer, B. I. *Tetrahedron*, **1991**, *47*, 1655. (c) DeShong, P.; Rybczynski, P. J. *J. Org. Chem.* **1991**, *56*, 3207.

(11) Dialkyltitanocenes susceptible to facile β-hydride elimination, are not expected to undergo this reaction under the usual conditions. See, for example: McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

(12) For a review of the chemistry of titanocene derivatives see: Bottrill, M.; Gavens, P. D.; Kelland, J. W.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 3, pp 331.

(13) (a) Razuvaev, G. A.; Latyaeva, V. N.; Vyshinskaya, L. I. *Dokl. Akad. Nauk SSSR* **1969**, *189*, 103. (b) Glivicky, A.; McCowan, J. D. *Can. J. Chem.* **1973**, *51*, 2609. (c) Scholz, J.; Schlegel, M.; Thiele, K. H. *Chem. Ber.* **1987**, *120*, 1369.

(14) In a typical experiment, a solution of 2 (1.45g, 4 mmol, 4 equiv) in toluene (8 mL) was mixed with dodecyl acetate (228 mg, 1 mmol) and heated at 55 °C for 20 h while stirring under argon in the dark. After cooling, the reaction mixture was diluted with petroleum ether (200 mL), and the resulting yellow-orange precipitate that formed was removed by filtration. Removal of the solvent in vacuo, followed by flash column chromatography (basic alumina, 5% diethyl ether/petroleum ether) yielded the vinyl ether as a colorless oil (212 mg, 70%).

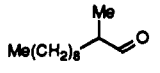
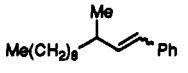
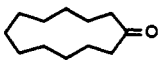
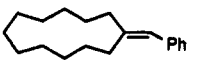
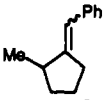
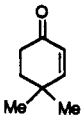
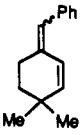
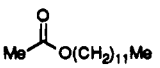
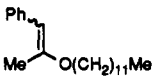
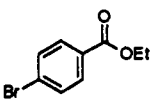
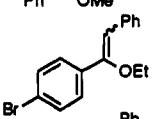
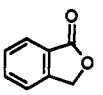
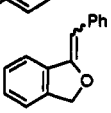
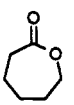
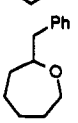
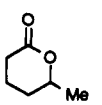
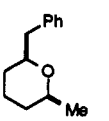
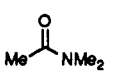
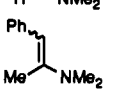
(15) This was determined by the integration of the CH_2D/CHD_2 peak relative to the OCH_3 peak of the substrate and product.

(16) (a) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1972**, 654. (b) Boekel, C. P.; Teuben, J. H.; Liefdemeijer, H. J. D. *J. Organomet. Chem.* **1974**, *81*, 371. (c) Boekel, C. P.; Teuben, J. H.; LiefdeMeijer, H. J. D. *J. Organomet. Chem.* **1975**, *102*, 317. (d) Latyaeva, V. N.; Vyshinskaya, L. I.; Mar'in, V. P. *Zh. Obshch. Khim.* **1976**, *46*, 628.

(17) Similar results were obtained with other regioisomers and with the *m*-methoxy derivative, while the *p*-methoxy analogue underwent rapid self-decomposition. The details of this work will be reported in due course.

(18) The addition of 2,4,6-tri-*tert*-butylphenol did not have any significant effect, indicating that a radical chain process is not involved.

Table I. Carbonyl Olefinations with Dibenzyltitanocene (2)

entry	carbonyl compd	product[a]	yield[b] (%)	E:Z ratio[c]
1			20[d]	67:33
2			86	
3			75	50:50
4			15	48:52
5			35	74:26
6			70	60:40
7			84	14:86
8			75	15:85
9			70	16:84
10			55[e]	
11			60[e]	
12			48[f]	>99:1
13			45[f]	71:29

[a] Reactions were run in toluene with 3–4 equiv of 2 at 45–55 °C over 16–26 h on a 1 mmol scale.[24] [b] Yields were determined after chromatographic purification and were corrected for dibenzyl contaminant (entries 5–8, 12–13). [c] Determined by ^{1}H- and ^{13}C-NMR spectroscopy[20] on the purified products. [d] 2 equiv of 2 were used. [e] After hydrogenation over Pd/C. [f] After distillation.

a mechanism similar to the one we postulated for 1,[8] involving carbonyl complexation followed by migratory insertion and elimination, may operate here as well. The substituent effects on the titanocenes noted above may be consistent with such mechanisms.[19]

Synthetically, this is a convenient and quite efficient process with certain carbonyl compounds. For most substrates the best benzylidenation yields were obtained when 3–4 equiv of a toluene solution of the reagent 2 were used. Other solvents such as THF or hexane were less effective. Table I shows the results of the benzylidenation of various carbonyl derivatives with 2. In general, moderate stereoselectivities in the olefin geometry have been observed in these olefinations. The more stable isomer predominates, particularly with aromatic carbonyl derivatives.

Although several aldehydes (e.g., entry 1) reacted rather sluggishly with 2, the reaction worked well with saturated ketones (entries 2,3). With α,β-unsaturated ketones (entry 4), however, only small amounts of the expected olefin were obtained, possibly due to a competitive polymerization process.

The olefination was quite effective with esters (entries 5, 6, 7, 8) and lactones (entry 9) which gave the corresponding enol ethers[20] as a mixture of stereoisomers.[21] Although these acid-sensitive systems can be isolated by chromatography on basic alumina, this process often results in some loss of product. It is also possible to hydrogenate the crude reaction mixture over Pd/C to afford directly the corresponding ethers (entries 10 and 11). The product[22] derived from the olefination of phthalide (entry 9) is of special interest since it can serve as a precursor to the highly reactive isobenzofurans.[23]

Amides also react to give phenyl-substituted enamines. Since chromatographic purification was difficult with these products they were best isolated by distillation (entries 12 and 13). These enamines had predominantly the *E*-geometry which would be expected to be more stable for steric reasons.

The use of functionalized dibenzyltitanocenes in this olefination enhance the synthetic utility of this process. Thus, olefination of phthalide with 3 equiv of **6a** gave **10** in quantitative conversion as a single geometrical isomer. This direct conversion of lactones to aryl-substituted exocyclic enol ethers may be useful for the synthesis of bioactive prostacyclin analogues[25] such as taprostene[26] (**11**) that have enhanced stability toward acid-catalyzed hydrolysis.[27]

(19) The presence of electron-withdrawing substituents may increase the acidity of the benzylic hydrogen, facilitating the formation of the titanium–benzylidene complex and resulting in higher amounts of olefination. Alternatively, the decrease of the electron-density of the aromatic ring may increase the Lewis acidity of the titanium and lead to a higher concentration of a carbonyl complex with dibenzyltitanocene. This may facilitate the olefination and/or prevent self-decomposition of the reagent which results in decreased amounts of dibenzyl byproducts.

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(21) While the benzylidenation of formic or acetic esters led predominately to the *E*-enol ether, this was reversed in the case of aromatic esters and lactones. The *Z*-isomer was the major product in these substrates, as indicated by ^{1}H- and ^{13}C-NMR chemical shifts and coupling constants.

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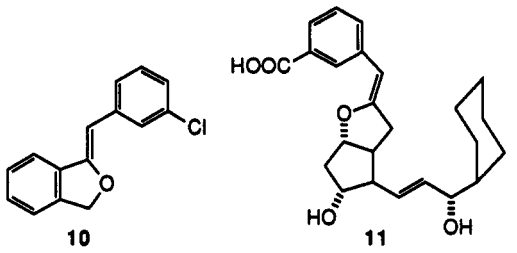

10 11

In summary, we have shown that dibenzyltitanocene (2) may serve as a convenient and synthetically useful reagent for the benzylidenation of ketones, esters, lactones, and amides. Substitution on the phenyl ring of the titanocene increases both the efficiency and the synthetic utility of the olefination. Further work with this and other titanocene derivatives and other types of substrates is currently under way.

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Supplementary Material Available: Detailed experimental procedures and ^1H and ^{13}C NMR spectra of titanium reagents and benzylidene products (49 pages). Ordering information is given on any current masthead page.

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Control of Chemoselectivity in the Rhodium(II)-Catalyzed Alkyne Insertion Reaction of α-Diazo Ketones

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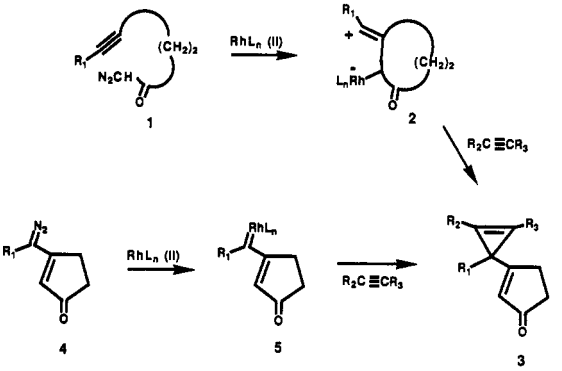
Summary: Chemoselectivity in the rhodium(II) catalyzed reaction of an acetylenic α-diazo ketone was found to be markedly influenced by the solvent used. Cyclopropenyl indenones are formed in pentane whereas alkenyl-substituted indenones are produced when CH_2Cl_2 is used as the solvent.

The insertion of alkynes into transition-metal–carbon bonds is a well-documented reaction and has been observed in nearly all of the triads of transition metals.[1-12] Recently, Hoye and Dinsmore reported on the Rh(II)-catalyzed double internal–external alkyne insertion reaction of an acetylenic α-diazo ketone.[13] The initially formed rhodium carbenoid intermediate was suggested to undergo internal insertion into the tethered alkyne unit followed by a second external addition to produce a cyclopropenyl-substituted cyclopentenone derivative (i.e., **3**). Migration of the rhodium metal to the remote alkyne carbon via a [2 + 2]-cycloaddition/cycloreversion path (i.e., **1** → **5**) was discounted on the basis that the distribution of products derived from **1** differed significantly from those obtained from the rhodium carbenoid species **5** generated from the vinylogous diazo ketone precursor **4**.[14] Instead, the results were rationalized via the intermediacy of



1 2 4 5 3

zwitterion **2**. In this paper, we describe our related observations dealing with a double internal/internal alkyne insertion. Our results establish that the reaction mechanism is markedly dependent on the solvent employed in these Rh(II)-catalyzed insertion reactions.

Our previous findings that *o*-alkynyl-substituted α-diazoacetophenone derivatives produce vinyl carbenoids[15] suggested to us that these species might undergo intramolecular addition to a neighboring acetylenic π-bond. Initial efforts focused on the rhodium(II)-catalyzed reaction of α-diazo ketone **6**. Treatment of **6** with a catalytic quantity of rhodium(II) octanoate in pentane at 25 °C afforded dimer **10** (51%) derived from a transient indenone intermediate (i.e., **9**). The structure of **10** was unequivocally established by an X-ray crystal structure analysis. That the reactive indenone **9** is the primary product of reaction follows from its interception by diphenylisobenzofuran (DPIBF). Cycloadduct **11** was obtained as the exclusive cycloadduct in 73% isolated yield. Formation of indenone **9** can be explained in terms of insertion of the initially formed rhodium carbenoid **7** (vide infra) onto the

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