ometries, with these bond angles being in the range 117.3 (4)–133.0 (5)°. Interestingly, these structural data are in close agreement with the tin–tin bond lengths of 2.887 Å and the 90° bond angles predicted for the parent $\mathrm{Sn_8H_8}$ octastannacubane derivative.[1c]

At the present time, the mechanism by which the octastannacubane 1 is formed from the cyclotristannane 2 is a matter of speculation. It is reasonable to assume, however, that a highly reactive transient intermediate, such as "RSn", might be generated under thermal conditions via the disproportionation $2\mathrm{R_2Sn} \rightarrow \mathrm{RSn} + \mathrm{R_3Sn}^{\bullet}$[11] and that this species then undergoes rapid oligomerization to produce a family of $(\mathrm{RSn})_n$ compounds, of which the cubane structure ($n = 8$) is either the most thermodynamically stable or the most kinetically stabilized member. Similar mechanisms for the formation of cyclopolystannanes, $(\mathrm{R_2Sn})_n$, from the oligomerization of transient stannylenes, $\mathrm{R_2Sn}$, are well-known.[12] Given the documented stability of 1, we are currently exploring alternate, and potentially higher yielding, routes to 1 and other members of the $(\mathrm{RSn})_n$ series.

Acknowledgment. We thank Dr. Cynthia Day of Crystalytics Co. for the structural analysis of 1 and the National Science Foundation (Grant CHE-9001462) for support of this work. High-resolution mass spectra were provided by Dr. Catherine Costello of the facility supported by the National Institutes of Health (Grant R-R-00317; principal investigator Professor K. Biemann), from the Division of Research Resources.

Supplementary Material Available: Detailed information regarding the crystallographic analysis of 1, including listings of atomic coordinates, temperature factors, bond lengths, and bond angles and an ORTEP representation of 1 (11 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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[11] A similar disproportionation of $\mathrm{R_2Sn}$ [R = bis(trimethylsilyl)-methyl] has been observed under photolytic conditions; see: Hudson, A.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans.* **1976**, 2369.

[12] (a) Watta, B.; Neumann, W. P.; Sauer, J. *Organometallics* **1985**, *4*, 1954. (b) Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 6390.

Imino Carbene Complexes of Tungsten and Chromium as Synthons for Nitrile Ylides in Reactions with Alkynes, Alkenes, Nitriles, and Aldehydes

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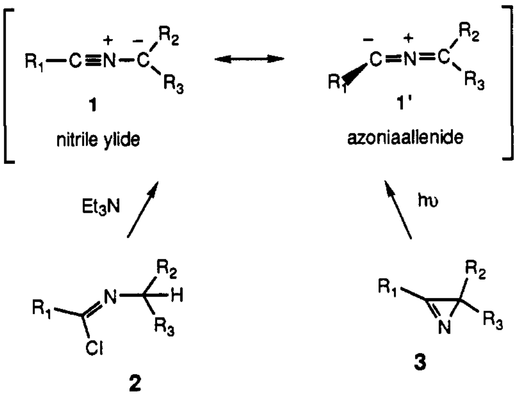
Summary: The stable and isolable imino carbene complexes of chromium and especially tungsten are found to be synthons for nitrile ylides and have the advantage that the range of 1,3-dipolarophiles is not limited to electron acceptors but is broad enough to include electronically neutral as well as electron-rich systems.

Nitrile ylides were first reported by Huisgen in 1961,[1] and since that time a variety of methods have been reported for their generation.[2] Two of the more popular methods are Huisgen's original method, consisting of elimination of hydrogen chloride from chloroimidates of the type 2 (Scheme I), and the photoinduced ring opening of 1-aziridines that was first reported by Schmid and Padwa.[3] The [3 + 2] dipolar cycloadditions of these species have been investigated in detail with a variety of π-bonded functional groups.[2,4] These cycloadditions are generally limited to dipolarophiles that are electron acceptors, and the regiochemistry observed is most consistent with the azoniaallenide structure 1′ for these intermediates.[2,5] Calculations[6] and experiment[2,4] reveal that the largest coefficient in the HOMO of these dipoles is nor-

Scheme I



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[1] (a) Huisgen, R. *Naturwiss. Rundsch.* **1961**, *14*, 43. (b) Huisgen, R. *Proc. Chem. Soc., London* **1961**, 357.

[2] For a comprehensive review up to 1983, see: Hansen, H. J.; Heimgartner, H. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Vol. 1, pp 177–290.

[3] (a) Padwa, A.; Smolanoff, J. *J. Am. Chem. Soc.* **1971**, *93*, 548. (b) Giezendanner, H.; Märky, M.; Jackson, B.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 745.

[4] For more recent citations, see: (a) De Meijere, A.; Teichmann, S.; Yu, D.; Kopf, J.; Oly, M.; Von Thienen, N. *Tetrahedron* **1989**, *45*, 2957. (b) Bozhkova, N.; Heimgartner, H. *Helv. Chim. Acta* **1989**, *72*, 825. (c) Ried, W.; Maria, F. *Helv. Chim. Acta* **1988**, *71*, 1681. (d) Wipf, P.; Prewo, R.; Bieri, J. H.; Germain, G.; Heimgartner, H. *Helv. Chim. Acta* **1988**, *71*, 1177. (e) Maerkl, G.; Troetsch-Schaller, I.; Hoelzl, W. *Tetrahedron Lett.* **1988**, *29*, 785. (f) Bossio, R.; Marcaccini, S.; Pepino, R. *Tetrahedron Lett.* **1986**, *27*, 4643. (g) Hoffman, R. W.; Barth, W. *Chem. Ber.* **1985**, *118*, 634. (h) Wipf, P.; Heimgartner, H. *Chimia* **1984**, *38*, 357.

[5] For more recent citations on the spectroscopy of nitrile ylides, see: (a) Orton, E.; Collins, S. T.; Pimentel, G. C. *J. Phys. Chem.* **1986**, *90*, 6139. (b) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928. (c) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Am. Chem. Soc.* **1985**, *107*, 7204. (d) Wentrup, C.; Fischer, S.; Berstermann, H. M.; Kuzaj, M.; Luerssen, H.; Burger, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 85. (e) Turro, N. J.; Cha, Y.; Gould, I. R.; Padwa, A.; Gasdaska, J. R.; Tomas, M. *J. Org. Chem.* **1985**, *50*, 4415.

[6] (a) Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 6397. (b) Caramella, P.; Gandour, R. W.; Hall, J. A.; Deville, C. G.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 385.

Scheme II

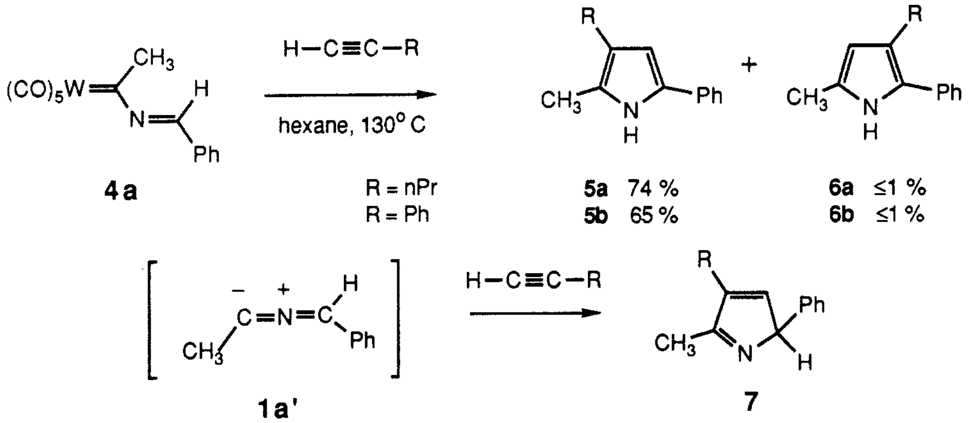
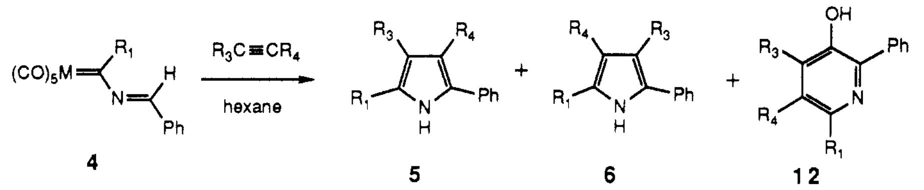


Table I. Reactions of Chromium and Tungsten Complexes 4 with Alkynes[a]

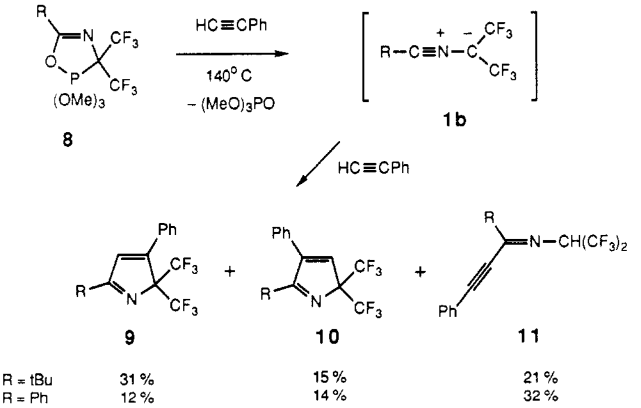


entry no.	complex	M	R_1	R_3	R_4	product series	yield, % 5	6	12
1	**4a**	W	CH_3	nPr	H	**a**	74	≤1	
2	**4a**	W	CH_3	Ph	H	**b**	65	≤1	
3	**4b**	W	Ph	nPr	H	**c**	76		
4	**4c**	Cr	CH_3	nPr	H	**a**	40	9	51
5	**4c**	Cr	CH_3	Ph	H	**b**	20	25	18
6	**4d**	Cr	Ph	nPr	H	**c**	64		28
7	**4e**	Cr	tBu	nPr	H	**d**	94	≤1	5
8	**4c**	Cr	CH_3	OEt	nPr	**e**	73	≤1	
9	**4c**	Cr	CH_3	Et	$CO(CH_3)$	**f**	95	≤1	
10	**4b**	W	Ph	Et	Et	**g**	86		

[a] All reactions were carried out at 0.014 M in 4 in hexane under argon with 3 equiv of alkyne at 80 °C for ~24 h. Workup involves removal of solvent and direct loading onto a silica gel column.

mally at C-1 (i.e. 1') unless R_2 and R_3 are strongly electron withdrawing substituents (i.e. CF_3 in **1b** in Scheme III). To date nitrile ylides by and large have not found their way into synthetic applications,[2,7] although a few synthetic equivalents to nitrile ylides have been developed recently.[8] We report here that imino carbene complexes of the group 6 metals can serve as synthons for nitrile ylides and do so over a much broader range of dipolarophiles than do either nitrile ylides or their synthetic equivalents.[9-11]

Scheme III



Recently we reported that imino carbene complexes of chromium of the type **4** will react with acetylenes to give pyrroles and 3-hydroxypyridines[9,10] (Scheme II). Subsequently we have found, as indicated by the data in Table I, that the regioselectivity is dependent on the nature of the alkyne and furthermore that tungsten imino complexes give higher chemoselectivity for pyrroles over 3-hydroxypyridines and also give higher regioselectivity for a specific

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(7) For more recent citations, see: (a) Tian, W. S.; Livinghouse, T. *J. Chem. Soc., Chem. Commun.* **1989**, 819. (b) Groundwater, P. W.; Struthers-Semple, C.; Sharp, J. T. *J. Chem. Soc., Chem. Commun.* **1987**, 1367. (c) Groundwater, P. W.; Sharp, J. T. *Tetrahedron Lett.* **1987**, *28*, 2069. (d) Hickey, D. M. B.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1119.

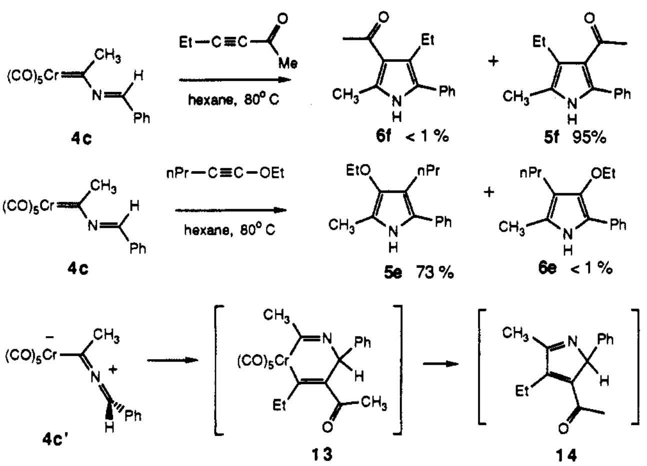
(8) (a) Burker, K.; Neuhauser, H.; Eggersdorfer, M. *Synthesis* **1987**, *10*, 924. (b) Padwa, A.; Gasdaska, J. R.; Hoffmanns, G.; Rebello, H. *J. Org. Chem.* **1987**, *52*, 1027. (c) Tsuge, O.; Kanemasa, S.; Yamada, T.; Matsuda, K. *J. Org. Chem.* **1987**, *52*, 2523. (d) Tsuge, O.; Ueno, K.; Kanemasa, S.; Yorozu, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1809. (e) Padwa, A.; Gasdaska, J. R.; Tomas, M.; Turro, N. J.; Cha, Y.; Gould, I. R., *J. Am. Chem. Soc.*, **1986**, *108*, 6739. (f) Tsuge, O.; Kanemasa, S.; Yamada, T.; Matsuda, K. *Heterocycles* **1985**, *23*, 2489. (g) Tsuge, O.; Kanemasa, S.; Matsuda, K. *Chem. Lett.* **1985**, 1411. (h) Tsuge, O.; Kanemasa, S.; Matsuda, K. *J. Org. Chem.* **1986**, *51*, 1997.

(9) Dragisich, V.; Murray, C. K.; Warner, B. P.; Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 1251.

(10) (a) For a related reaction of *O*-acyl imidate complexes, see ref 9 and: Aumann, R.; Heinen, H.; Krüger, C.; Betz, P. *Chem. Ber.* **1990**, *123*, 599. (b) While this paper was in review, two reports appeared by Aumann describing the reactions of imino complexes with alkynes: Aumann, R.; Heinen, H. *J. Organomet. Chem.* **1990**, *389*, C1. Aumann, R.; Heinen, H. *J. Organomet. Chem.* **1990**, *391*, C7.

(11) For references to metallo nitrile ylides, see: (a) Fehlhammer, W. P.; Voelkl, A.; Plaia, U.; Beck, G. *Chem. Ber.* **1987**, *120*, 2031. (b) Fehlhammer, W. P.; Achatz, D.; Plaia, U.; Voelkl, A. *Z. Naturforsch., B: Chem. Sci.* **1987**, *42*, 720.

Scheme IV

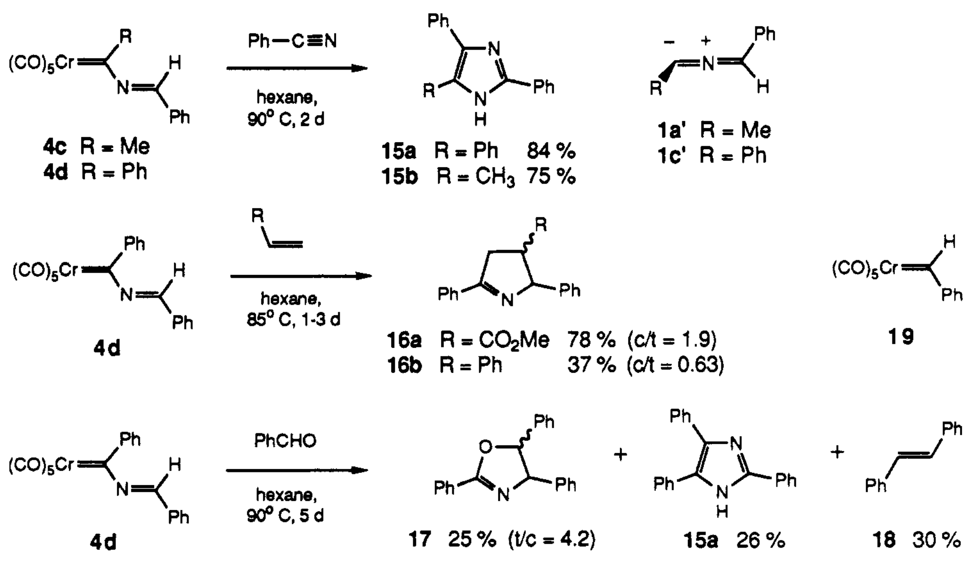


pyrrole isomer in reactions with unsymmetrical alkynes. The reaction of the tungsten complex **4a** with 1-pentyne gives the pyrrole **5a** in 74% yield in a greater than 65:1 selectivity over the regioisomer **6a**.[12] This is to be compared with the same reaction of the corresponding chromium complex **4c** (Table I, entry 4), which gives a 4:1 mixture of the pyrroles along with an equal amount of the 3-hydroxypyridine **12a**. Tungsten complexes are also selective for pyrroles over 3-hydroxypyridines for internal alkynes (entry 10, Table I). Although nitrile ylides will react with electron-poor alkynes to give pyrroles, there are no known examples of nitrile ylides (or synthetic equivalents) producing cycloadducts with alkylacetylenes.[2] The tungsten complex **4a** thus serves as a synthon for the nitrile ylide **1a′** in the preparation of the pyrrole **5a**. Cycloadditions with arylacetylenes have only been observed with highly reactive nitrile ylides and generate low yields of cycloadducts.[2,13] In the only known regioselectivity study, it was found that the bis(trifluoromethyl)-substituted nitrile ylides **1b** will react with phenylacetylene to give nearly equal amounts of the two regioisomers **9** and **10** in addition to the product **11** resulting from deprotonation of the alkyne[13] (Scheme III). In contrast, the tungsten complex **4a** reacts with phenylacetylene to give a single isomeric pyrrole (**5b**). As is also the case with 1-pentyne, the nitrile ylide **1a′** (Scheme II) would not be expected to react with phenylacetylene, but in its stead the tungsten complex **4a** can be employed to give pyrroles derived from alkyl- or arylalkynes with high regioselectivity.[14]

High-yield cycloadditions are encountered in the reactions of nitrile ylides with electron-poor acetylenes; however, low regioselectivities are observed for internal unsymmetrical alkynes.[2] As indicated in the reaction of complex **4c** with 3-hexyn-2-one, even chromium imino complexes can serve as highly valuable synthons for nitrile ylides in reactions of this type (Scheme IV). It is also to be noticed that while the pyrrole **5f** is selectively produced from 3-hexyn-2-one, the regioselectivity is reversed for 1-ethoxy-1-pentyne, giving only the pyrrole **5e**.[12] The regioselectivity of these two reactions can be correlated with the resonance structure **4c′**, and in the case of 3-hexyn-2-one the intermediacy of the metallacycle **13** would be expected on the basis of polarity matching.[9] This type of reversal in regioselectivity has not been observed before in nitrile ylides since electron-rich alkynes such as alkoxyacetylenes or ynamines are not known to react with nitrile ylides. The closest example is the reaction of enol ethers with the bis(trifluoromethyl) nitrile ylides **1b**.[17] In this case the regiochemistry is the same as for electron-poor olefins due to the fact that **1b** reacts as the nitrile ylide species **1** (Scheme I) rather than the azoniaallenide species **1′** as is the case for most nitrile ylides. Pyrrole formation from the reaction of carbene complex **4c** with 1-ethoxy-1-pentyne gives the same regioisomer (**5e**) as would be expected from the same reaction of the free nitrile ylide **1a′** if the reaction in fact were possible.

Our initial studies concerning the extension of the cycloadditions of imino carbene complexes to π-systems other than alkynes are summarized in Scheme V. Nitrile ylides are known to undergo cycloaddition with carbon–nitrogen triple bonds; however, there are no examples of aryl- or alkyl-substituted nitrile ylides undergoing dipolar cycloadditions with either acetonitrile or benzonitrile.[2] It was therefore pleasing to find that the imidazoles **15a** and **15b** could be obtained in high yield and as a single isomer (for **15b**) from the cycloaddition between benzonitrile and the chromium imino carbene complexes **4d** and **4c**, which in this case function as surrogates for the impotent nitrile ylides **1a′** and **1c′**. The reaction of **4d** with styrene occurs with the same regio- and stereoselectivity and with the same overall yield as has been reported for the nitrile ylide **1c′**.[18,19a] Likewise the reaction of **4d** with methyl acrylate is similar to the known reaction of the nitrile ylide **1c′** with the exception that it is not as cis selective, giving a 1.9:1.0 mixture of cis:trans isomers.[8d,20,21] The reaction of **4d** with benzaldehyde is rather curious in two aspects: first, it gives

Scheme V



the opposite regioisomeric oxazoline **17**[22] as has been found for the nitrile ylide **1c′**,[19a,23] and second, the imidazole **15a** was also isolated from this reaction. The formation of imidazole **15a** may be the result of the initial extrusion of benzonitrile from complex **4d** to give the benzylidene complex **19** and then the subsequent reaction of benzonitrile with **4d**. This type of extrusion has been observed in related complexes,[24] and in support of this process occurring in this reaction is the isolation of *trans*-stilbene, a known thermal decomposition product of complex **19**.[26] This extrusion process was only noticed in the reaction with benzaldehyde, and this may be related to the fact tht it was the slowest of all the reactions described in this work.

The regiochemical outcome of the reaction of complex **4c** with benzaldehyde was unexpected and is not consistent with the regiochemistry of all of the other reactions described in this work. Current investigations are designed to determine if the regiochemistry is actually reversed in this case or whether the initial Δ^3-oxazoline is isomerized via a double-bond migration to the observed Δ^2-oxazoline **17**. Further studies will be directed to optimization and development of greater stereoselectivity in the reactions of imino carbene complexes with alkenes and carbonyl compounds, particularly with regard to the reactions of tungsten complexes, which were found to be superior to those of chromium as nitrile ylide synthons in reactions with alkynes.

Imino carbene complexes are easily prepared,[9,10,25] and their stability to air and water makes them useful isolable synthetic equivalents to nitrile ylides for a variety of 1,3-dipolarophiles. As demonstrated in cycloadditions with alkynes, imino carbene complexes are superior to nitrile ylides or their synthetic equivalents in the synthesis of pyrroles since the scope of acetylenic 1,3-dipolarophiles can be extended to electronically neutral as well as to electron-rich systems.

Acknowledgment. This work was supported by a grant from the National Institutes of Health (Grant No. PHS-GM 33589). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Cancer Research Center (Grant No. CA-14599).

Supplementary Material Available: Spectral data for all new compounds (14 pages). Ordering information is given on any current masthead page.

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(12) The regiochemistry of the pyrroles was determined by NOE experiments that were performed on both **5** and **6** for each series (see the supplementary material). The regiochemistry of pyrrole **5e** is the same as that observed for an ynamine with an *O*-acyl imidate complex.[10a] The regiochemistry of pyrrole **5f** was confirmed by X-ray diffraction, and details will be presented in a full account of this work.

(13) Burger, K.; Roth, W. D.; Neumayr, K. *Chem. Ber.* **1984**, *109*, 1984.

(14) The assignment of the regiochemistry of the pyrroles **5b** and **6b** made by NOE was also consistent with the spectral and physical data that have been reported for **5b**[15] and **6b**.[16]

(15) (a) Barton, D. H. R.; Motherwell, W. B.; Simon, E. S.; Zard, S. Z. *J. Chem. Soc., Perkin Trans. 1* **1986**, 2243. (b) Chiu, P. K.; Sammes, M. P. *Tetrahedron* **1988**, *44*, 3531.

(16) (a) Guy, R. W.; Jones, R. A. *Aust. J. Chem.* **1966**, *19*, 1871. (b) Yoshida, N.; Tomita, K.; Wachi, K.; Tanaka, K.; Iizuka, Y. *Yakugaku Zasshi* **1973**, *93*, 584.

(17) Burger, K.; Roth, W. D.; Einhellig, K.; Hatselmann, L. *Chem. Ber.* **1975**, *108*, 2737.

(18) The regio- and stereochemistry of **16b** was assigned on the basis of the spectral data that have been reported previously for both the cis and trans isomers.[19]

(19) (a) Padwa, A.; Smolanoff, J.; Wetmore, S. J. *J. Org. Chem.* **1973**, *38*, 1333. (b) Hunter, D. H.; Steiner, R. P. *Can. J. Chem.* **1975**, *53*, 355.

(20) The regio- and stereochemistry of **16a** was assigned on the basis of the spectral data that have been reported previously for both the cis and trans isomers.[8d,21]

(21) Padwa, A.; Dharan, M.; Smolanoff, J.; Wetmore, S. J. *J. Am. Chem. Soc.* **1973**, *95*, 1945.

(22) The spectral data for **17** match those that were previously reported: (a) Mall, T.; Stamm, H. *Chem. Ber.* **1988**, *121*, 1353. (b) Ardabilichi, N.; Fitton, A. O.; Frost, J. R.; Oppong-Boachie, F. K.; Hadi, A. H. b. A.; Sharif, A. b. M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 539.

(23) Giezendanner, H.; Heimgartner, H.; Jackson, B.; Winkler, T.; Hansen, H. J.; Schmid, J. *Helv. Chim. Acta* **1973**, *56*, 2611.

(24) Wulff, W. D.; Dragisich, V.; Huffman, J. C.; Kaesler, R. W.; Yang, D. C. *Organometallics* **1989**, *8*, 2196.

(25) Murray, C. K.; Warner, B. P.; Dragisich, V.; Wulff, W. D.; Rogers, R. D. *Organometallics*, in press.

(26) (a) Fischer, H.; Schmid, J.; Märkl, R. *J. Chem. Soc., Chem. Commun.* **1985**, 572. (b) Fischer, H.; Seuner, S.; Ackermann, K. *J. Chem. Soc., Chem. Commun.* **1984**, 684.