moval of the Boc moiety in **3** furnished a species which assumed the parallel sheet arrangement in the solid state. We note parenthetically that, in peptide **2**, H-bonding between the phenolic hydroxyl and the N-terminus of a neighboring strand causes deviation from the ideal β-strand conformation at the C-terminus. Our mimic **3**, lacking the phenolic hydroxyl, shows no such deviation.

The importance of β-pleated sheets in peptides and proteins is well established. Martin,[13a] Clardy and Schreiber,[13b] and Simon and Bartlett[13c] have recently described novel molecules which can adopt extended or sheetlike structures. None of these however share our objectives to mimic native β-strands and sheets with regard to side-chain orientations and interstrand H-bond donating capabilities. We believe that the design and synthesis of **3** open up a new approach to novel, nonpeptidal mimics of β-pleated strands and sheets.[14] Efforts to determine the solution structures of **3** and related compounds and to design pyrrolinone-based inhibitors of human renin and the HIV1 protease will be reported in due course.

Acknowledgments. We acknowledge support of this investigation by Bachem, Inc. (Torrance, CA), the National Institutes of Health (Institute of General Medical Sciences) through grant GM-41821, Merck Research Laboratories, and Sterling Winthrop Inc. In addition, we thank Dr. George Furst, and Mr. John M. Dykins of the University of Pennsylvania Spectroscopic Service Centers for assistance in securing and interpreting high-field NMR and mass spectra, respectively.

Supplementary Material Available: Listings of complete spectral data for **3** and **10-18** and tables of experimental details, positional parameters, and thermal parameters for the X-ray analyses of **3** and **18** (28 pages). Ordering information is given on any current masthead page.

(13) (a) Martin, S. F.; Austin, R. E.; Oalmann, C. J.; Baker, W. R.; Condon, S. L.; deLara, E.; Rosenberg, S. H.; Spina, K. P.; Stien, H. H.; Cohen, J.; Kleinert, H. D. *J. Med. Chem.* **1992**, *35*, 1710. (b) Hagihara, M.; Anthony, N. J.; Stout, T. J.; Clardy, J.; Schreiber, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 6568. (c) Simon, R. J.; Kania, R. S.; Zuckerman, R. N.; Huebner, V. D.; Jewell, D. A.; Banville, S.; Ng, S.; Wang, L.; Rosenberg, S.; Marlowe, C. K.; Spellmeyer, D. C.; Tan, R.; Frankel, A. D.; Santi, D. V.; Cohen, F. E.; Bartlett, P. A. *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 9367.

(14) For example, see: Halverson, K. J.; Sucholeiki, I.; Ashburn, T. T.; Lansbury, P. T., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 6701. Zhang, Z.-Y.; Poorman, R. A.; Maggiora, L. L.; Heinrikson, R. L.; Kézdy, F. J. *J. Biol. Chem.* **1991**, *266*, 15591.

Electrophilic Activation of the Horner-Wadsworth-Emmons-Wittig Reaction: Highly Selective Synthesis of Dissymmetric Olefins

Scott E. Denmark* and Chien-Tien Chen

Roger Adams Laboratory, Department of Chemistry
University of Illinois, Urbana, Illinois 61801

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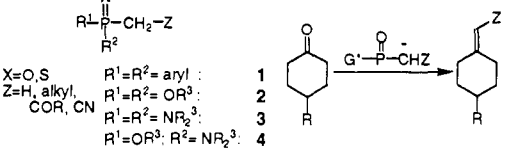
The carbonyl olefination reaction employing phosphoryl-stabilized carbanions (Horner-Wadsworth-Emmons (HWE)) reaction[1] is now a well-established and useful alternative to the Wittig olefination.[2] The HWE reaction of anions derived from phosphine oxides (**1**), phosphonates (**2**), phosphonamides (**3**), and their thiono counterparts (X = S) have well-documented advantages in many situations. One class of reagents, the (intrinsically chiral) phosphonamidates (**4**), has rarely been employed. As part of our general program of the structure[3] and utility[4] of auxiliary-based, chiral P=O stabilized anions, we have examined the potential of scalemic phosphonamidates for the synthesis of dissymmetric alkylidenes, Scheme I. The syntheses of chiral

(1) (a) Walker, B. J. In *Organophosphorus Reagents in Organic Synthesis*; Cadogan, J. I. G., Ed.; Academic Press: New York, 1979; Chapter 3. (b) Wadsworth, W. S., Jr. *Org. React.* **1977**, *25*, 73. (c) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (d) Kelly, S. E. In *Comprehensive Organic Synthesis, Additions to C-X π Bonds, Part 1*; Schreiber, S. L., Ed.; Pergamon Press: Oxford, 1991; Vol. 1; Chapter 3.1.

(2) (a) Gosney, I.; Rowley, A. G. In *Organophosphorus Reagents in Organic Synthesis*; Cadogan, J. I. G., Ed.; Academic Press: New York, 1979; Chapter 2. (b) References 1c,d.

Scheme I



Scheme II

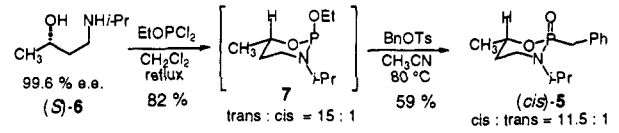
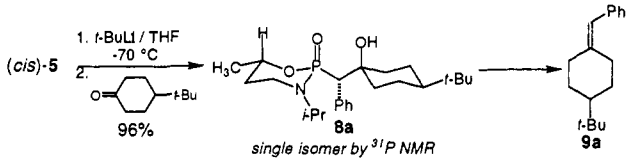


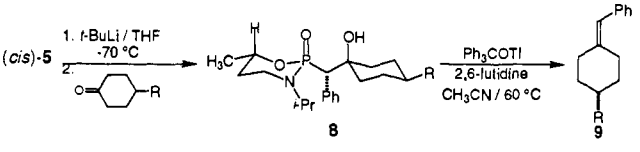
Table I. Optimization of Electrophile-Activated Olefination of **8a**



reagent (equiv)	base[a] (equiv)	temp, °C (time, h)	solvent	yield,[b] %	ee,[c] % (config)
	A (1.5)	-78 → 65 (24)	THF	72	11 (*R*)
	A (1.5)	-78 (0.25)	THF	8[d]	3 (*R*)
MeOTf (5)	B (5)	rt[f] (13)	CH_2Cl_2	27[e]	>99 (*S*)
Et_3OBF_4 (1)	B (2)	rt (6)	CH_2Cl_2	46[e]	>99 (*S*)
Ph_3CClO_4 (1.6)	B (2)	rt (1.25)	CH_2Cl_2	59[e]	>99 (*S*)
Ph_3CClO_4 (1.6)	B (2)	60 (3)	CH_3CN	60	>99 (*S*)
Ph_3CBF_4 (1.6)	B (2)	60 (1.75)	CH_3CN	69	>99 (*S*)
Ph_3COTf (1.6)	B (2)	60 (2.5)	CH_3CN	68-80	>99 (*S*)
Ph_3COTf (2.3)	B (2)	rt (22)	HCO_2Me	61	nd[g]
Ph_3COTf (2.1)	B (2)	rt (28)	CH_3NO_2	51	nd

[a] A: KHMDS. B: 2,6-Lutidine. [b] Yield of isolated, purified product. [c] Footnote 16. [d] (*cis*)-**5** was recovered in 77% yield. [e] Starting material remained. [f] Room temperature. [g] Not determined.

Table II. Asymmetric Olefination of 4-Substituted Cyclohexanones



R	product	de	yield,[a] %	product	ee,[b] %	ee,[b] % (config)
$C(CH_3)_3$	**8a**	>98[c]	96	**9a**	68	>99 (*S*)
CH_3	**8b**	88[c]	99	**9b**	73	86 (*S*)
C_6H_5	**8c**	98[d]	94	**9c**	76	>99 (*S*)
$CO_2C(CH_3)_3$	**8d**	98[d]	98	**9d**	77	95 (*S*)

[a] Yield of isolated, purified product. [b] Footnote 16. [c] ^{31}P NMR analysis. [d] HPLC analysis.

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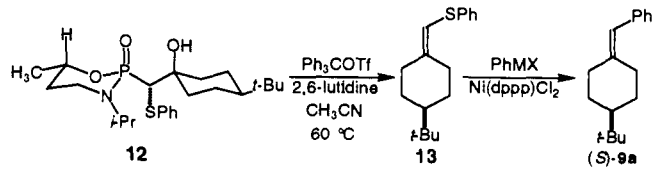
Table III. Nickel-Catalyzed Coupling of **13**



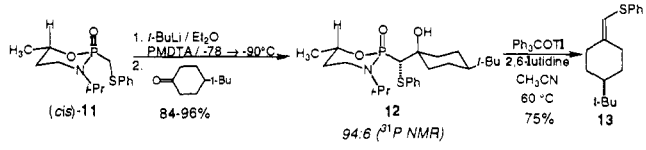
de(**12**),[a] %	solvent	cat.[b]	reagent	yield,[c] %	ee(**10a**),[d] % (config)	specificity,[e] %
89	THF	A	PhMgBr	51	71 (*S*)	80
80	Et_2O	A	PhMgBr	76	67 (*S*)	84
90	Et_2O	A	$Ph_2Zn{\cdot}MgBr_2$	84	68 (*S*)	76
82	Et_2O	B	PhMgBr	70	77 (*S*)	94
87	Et_2O	B	PhMgBr	80	82 (*S*)	94

[a] ^{31}P NMR analysis. [b] A: Commercial. B: Analytically pure. [c] Yield of isolated, purified product. [d] Footnote 16. [e] Footnote 18.

allenes and chiral olefins employing scalemic phosphoranes,[5] phosphonates,[6] thionophosphonates,[7] phosphonamides,[8] phosphine oxides,[9] and phosphinothioic amides[10] have been described. By far the most selective, direct transformations employ the chiral phosphondiamides[8] and menthyl phosphonoacetates[6] with enantioselectivities of up to 90%. Further, Gais has reported high selectivities for the elimination–coupling process with chiral sulfoximines.[11] In this communication we disclose an alkylidenation reaction for the highly selective synthesis of dissymmetric olefins (86–100% ee) that employs a novel electrophilic activation of the HWE process.[12]

On the basis of our studies on asymmetric alkylation of chiral phosphonamidate anions,[4b,f] the *N*-isopropyl-(2*S*,6*S*)-1,3,2-oxazaphosphorinane *cis*-**5**[13] was chosen as the test nucleophile. The synthesis of **5** involved a modification of our previously described route, Scheme II. By employing the Arbuzov reaction with benzyl tosylate, we can take advantage of the highly selective formation of phosphite *trans*-**7** to increase the proportion of the desired cis isomer[14] (pure cis, 59%), Scheme II.

Scheme III



Reaction of Li^+*cis*-**5**$^-$ (*t*-BuLi/THF/−78 °C) with 4-*tert*-butylcyclohexanone afforded a single adduct, **8a**[13] (^{31}P, HPLC analysis), in 96% yield, Table I. The isolation of **8a** was not unexpected since (1) there are no activating groups on the carbanion, (2) the phosphorus is in a six-membered ring, and (3) a lithium counterion was used. Attempts to decompose **8a** to the alkene were initially discouraging. Low-temperature formation of the potassium alkoxide followed by heating to reflux (THF) produced the alkene **9a**[15] with poor selectivity. A control experiment at −78 °C revealed that the low selectivity resulted from a facile fragmentation of K^+**8a**$^-$ that returned *cis*-**5** in 72% yield along with 8% of nearly racemic **9a**. The ready reversibility of HWE reactions is well documented[15] and not surprising in this case given the congestion around the β-hydroxy phosphonamidate.

To avoid unfavorable partitioning of a β-alkoxy phosphonamidate, we attempted to form the requisite oxaphosphetane by activating the phosphorus moiety under weakly basic conditions. Orienting experiments with MeOTf and Meerwein's salt in the presence of 2,6-lutidine (or 2,6-di-*tert*-butylpyridine) at room temperature afforded (*S*)-**9a** in enantiomerically pure form.[16] Byproducts associated with reaction at the hydroxyl function could be suppressed by using various trityl salts. Of the three different trityl salts examined (ClO_4^-, BF_4^-, OTf^-), the BF_4^- and the OTf^- gave the best results. None of the salts gave clean, complete reaction in dichloromethane solution. However, after extensive optimization, we found that brief warming (60 °C to dissolve **8a**) of the reaction mixtures in acetonitrile[17] gave the most reproducible results and highest enantiomeric excesses. Room temperature reactions in solvents of similar dielectric constants gave poorer results.

Using this optimized protocol, the reaction was shown to be applicable to a variety of 4-substituted cyclohexanones, Table II. In all cases the adducts **8b–d**[13] were formed in high yield (94–99%) with excellent diastereoselectivity (88–100% de). The trityl

(3) (a) Denmark, S. E.; Dorow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 864. (b) Denmark, S. E.; Cramer, C. J. *J. Org. Chem.* **1990**, *55*, 1806. (c) Denmark, S. E.; Miller, P. C.; Wilson, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 1468.

(4) (a) Denmark, S. E.; Rajendra, G.; Marlin, J. E. *Tetrahedron Lett.* **1989**, *30*, 2469. (b) Denmark, S. E.; Dorow, R. L. *J. Org. Chem.* **1990**, *55*, 5926. (c) Denmark, S. E.; Marlin, J. E. *J. Org. Chem.* **1991**, *56*, 1003. (d) Denmark, S. E.; Stadler, H.; Dorow, R. L.; Kim, J.-H. *J. Org. Chem.* **1991**, *56*, 5063. (e) Denmark, S. E.; Chatani, N.; Pansare, S. V. *Tetrahedron* **1992**, *48*, 2191. (f) Chen, C.-T.; Denmark, S. E. Manuscript in preparation.

(5) (a) Tömösközi, I.; Bestmann, H. J. *Tetrahedron Lett.* **1964**, 1293. (b) Bestmann, H. J.; Lienert, J. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 763. (c) Bestmann, H. J.; Heid, E.; Ryschka, W.; Lienert, J. *Justus Liebigs Ann. Chem.* **1974**, 1684. (d) Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 5699. (e) Bestmann, H. J.; Tömösközi, I. *Tetrahedron* **1968**, *24*, 3299. (f) For asymmetric catalysis in the Wittig reaction, see also: Bestmann, H. J.; Lienert, J. *Chem.-Ztg.* **1970**, *94*, 487.

(6) (a) Tömösközi, I.; Janzsö, G. *Chem. Ind.* (*London*) **1962**, 2085. (b) Gais, H.-J.; Schmiedl, G.; Ball, W. A.; Bund, J.; Hellmann, G.; Erdelmeier, I. *Tetrahedron Lett.* **1988**, *29*, 1773. (c) Rehwinkel, H.; Skupsch, J.; Vorbrüggen, H. *Tetrahedron Lett.* **1988**, *29*, 1775. (d) See also: Toda, F.; Akai, H. *J. Org. Chem.* **1990**, *55*, 3446.

(7) Takahashi, T.; Matsui, M.; Maeno, N.; Koizumi, T. *Heterocycles* **1990**, *30*, 353.

(8) (a) Hanessian, S.; Delorme, D.; Beaudoin, S.; Leblanc, Y. *J. Am. Chem. Soc.* **1984**, *106*, 5754. (b) Hanessian, S.; Delorme, D.; Beaudoin, S.; Leblanc, Y. *Chem. Scr.* **1985**, *25*, 5.

(9) (a) Polniaszek, R. P.; Foster, A. L. *J. Org. Chem.* **1991**, *56*, 3137. (b) Harmat, N. J. S.; Warren, S. *Tetrahedron Lett.* **1990**, *31*, 2743.

(10) Johnson, C. R.; Elliott, R. C.; Meanwell, N. A. *Tetrahedron Lett.* **1982**, *23*, 5005.

(11) (a) Gais, H.-J.; Erdelmeier, I.; Lindner, H. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 935. (b) Gais, H.-J.; Erdelmeier, I. *J. Am. Chem. Soc.* **1989**, *111*, 1125. (c) Gais, H.-J.; Bülow, G. *Tetrahedron Lett.* **1992**, *33*, 461, 465.

(12) The electrophilic activation of the HWE reaction has been implemented previously by Corey[12a] and Johnson[12b] using Ag(I) or CH_3I to activate *thiono*phosphonamides and phosphino*thioic* amides, respectively. Moreover, the thermal decomposition of β-hydroxy phosphonamides is proposed to occur via a zwitterionic intermediate.[12c] (a) Corey, E. J.; Kwiatkowski, G. T. *J. Am. Chem. Soc.* **1966**, *88*, 5654. (b) Johnson, C. R.; Elliott, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 7041. (c) Corey, E. J.; Kwaitkowski, G. T. *J. Am. Chem. Soc.* **1968**, *90*, 6816.

(13) All new compounds have been fully characterized. See supplementary material for experimental and spectroscopic details.

(14) The trans isomer showed uniformly lower selectivity in all reactions.

(15) (a) Bottin-Strzalko, T.; Seyden-Penne, J. *Bull. Soc. Chim. Fr.* **1984**, Part II, 161. (b) Buss, A. D.; Warren, S.; Leake, J. S.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2215.

(16) (a) The enantiomeric purity of **9a–d**[13] was established by conversion to the corresponding epoxides **10a–d**[13] and analysis by chiral capillary GC and HPLC. (b) The absolute configurations of **9a**,[5b] **9b**,[5b,c,16c] and **9d**[5c] were established by polarimetry; that of **9c** was assigned by analogy. (c) Brewster, J. H.; Privett, J. E. *J. Am. Chem. Soc.* **1966**, *88*, 1419.

(17) The utility of acetonitrile as a solvent for reactions of trityl cations has been discussed: Freedman, H. H. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1973; Vol. IV; Chapter 28.

triflate-induced olefination also proceeded smoothly (68–77% yield) to afford the dissymmetric olefins **9b–d**[13] with essentially complete stereospecificity.[18,19]

Attempts to generalize this process to substituents other than phenyl (e.g., CH_3, Cl, $SnBu_3$) were not successful. However, we have now discovered that the phenylthio group in *cis*-**11**[13] is compatible with both stages of the olefination process (Scheme III). Moreover, this group can be readily replaced with high stereospecificity to allow general introduction of other organic groups. Considerable optimization of the first stage led to the use of PMDTA[20] in Et_2O at −90 °C to maximize the diastereoselectivity of addition. Trityl triflate-activated olefination of **12** cleanly afforded the (phenylthio)methylidene **13**. To establish the overall stereochemical course, the phenylthio group was displaced in a nickel-catalyzed coupling with PhMgBr.[21,22] This reaction proceeds readily at room temperature to afford **9a** in good yield. The coupling reaction is extremely sensitive to the purity of **13** and the Ni(dppp)Cl_2 catalyst. As shown in Table III, *the coupling proceeded with retention of configuration and 94% stereospecificity* using analytically pure catalyst. The use of Ph_2Zn[11b] increased the yield but afforded **9a** in lower ee.[23]

We can infer the stereostructure of **8a–d** by assuming a syncycloelimination to the olefins **9a–d**. Since the olefins are all of *S* configuration, this reduces to a structure for **8** that arises from exclusive equatorial attack by the *pro-R* face of the anions.[24] This pathway is consistent with other reactions of *cis*-**5**[4f] and with the extreme equatorial selectivity expected for bulky nucleophiles.[25] The electrophilic activation of the HWE process is believed to proceed via the *O*-trityl phosphonium ion[26] which captures the β-hydroxyl group prior to proton loss. Mechanistic studies are underway to establish the nature of these intermediates and the rate of their formation and breakdown.

In summary, we have documented a general procedure for the preparation of dissymmetric alkylidenes with high enantioselectivity. The mildness and high stereospecificity of the olefination reaction augur well for its application in synthesis.

Acknowledgment. We are grateful to the National Institutes of Health (GM 45532) for generous support of this research. C.-T.C. thanks the University of Illinois for a Graduate Fellowship.

Supplementary Material Available: Preparation and full spectroscopic characterization of *cis*-**5**, **8a–d**, **9a–d**, **10a–d**, *cis*-**11**, **12**, and **13** (16 pages). Ordering information is given on any current masthead page.

(18) Stereospecificity is defined as 100[ee(9)]/[de(8)].
(19) The amino alcohol (*S*)-6 can be recovered after HCl digestion and ion-exchange chromatography. The recoveries are low on a small scale due to water solubility and volatility.
(20) PMDTA: *Penta*methyl*di*ethylene*tri*amine. Standard conditions (*t*-BuLi/−78 °C) in THF, Et_2O, and DME gave **12** as a ~3:1 mixture of isomers. However, with 2 equiv of PMDTA the selectivity increased in the order THF (3.9:1), toluene (8.7:1), Et_2O (11.1:1) at −78 °C.
(21) (a) Wenkert, E.; Ferreira, T. W. *J. Chem. Soc., Chem. Commun.* **1982**, 840. (b) Okamura, H.; Miura, M.; Takei, H. *Tetrahedron Lett.* **1979**, 43. (c) Naso, F. *Pure Appl. Chem.* **1988**, *60*, 79. (d) Fiandanese, V. *Pure Appl. Chem.* **1990**, *62*, 1987. (e) Luh, T.-Y.; Ni, Z.-J. *Synthesis* **1990**, 89. (f) Luh, T.-Y. *Acc. Chem. Res.* **1991**, *24*, 257.
(22) This reaction is analogous to the catalyzed coupling of bromoalkylidenes to form dissymmetric olefins. (a) Walborsky, H. M.; Banks, R. B. *J. Org. Chem.* **1981**, *46*, 5074. (b) Walborsky, H. M.; Banks, R. B.; Banks, M. L. A.; Duraisamy, M. *Organometallics* **1982**, *1*, 667.
(23) We have demonstrated that (c-C_6H_{11})$_2$Zn coupled cleanly to afford the alkylidenes in 84% yield and 88% specificity. Further extensions are in progress.
(24) These anions are sp^2 hybridized with no C–Li contact. Dorow, R. L. Ph.D. Thesis, University of Illinois, Urbana, 1989.
(25) Ashby, E. C.; Laemmle, J. T. *Chem. Rev.* **1975**, *75*, 521.
(26) Related organotrialkoxyphosphonium ions have been prepared and identified by Frost. Avila, L. Z.; Bishop, P. A.; Frost, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 2242.

Amine Carbonyls of Zerovalent Titanium, Zirconium, and Hafnium. Structural Characterization of (1,4,7-Trimethyl-1,4,7-triazacyclononane)tetracarbonyltitanium(0)[1]

John E. Ellis,*[,†] Anthony J. DiMaio,[†] Arnold L. Rheingold,[‡] and Brian S. Haggerty[‡]

Department of Chemistry
University of Minnesota
Minneapolis, Minnesota 55455
Department of Chemistry
University of Delaware
Newark, Delaware 19716

Received October 5, 1992

Zerovalent metal carbonyl chemistry of the group 4 elements has remained very poorly explored in the past largely due to the unavailability of suitable precursors; e.g., binary carbonyls of titanium are exceedingly unstable, and those of zirconium and hafnium are unknown.[2] For this reason, (dmpe)Ti$(CO)_5$[3] was recently introduced as a useful synthetic equivalent of the unknown Ti$(CO)_7$ since the dmpe group was found to be easily displaced by Lewis bases under an atmosphere of CO to provide new zerovalent titanium carbonyls.[4] We now report that related zirconium and hafnium complexes of the formula (trmpe)M$(CO)_4$[3,5] also contain a labile phosphine group and thereby function as the first available synthetic equivalents of the unknown heptacarbonyls of these elements. In this communication the use of these labile phosphine carbonyls in the synthesis of the initial examples of amine carbonyls of the group 4 elements is described.[6] Amine carbonyls constitute an important class of coordination compounds and have been reported previously for virtually all later transition metals.[7] While acyclic amines such as $R_2NCH_2CH_2NR_2$ or $RN(CH_2CH_2NR_2)_2$, R = H, Me do not appear to form isolable group 4 carbonyl complexes under a variety of conditions,[8] the macrocyclic triamines tacn and Me_3tacn[3] react as shown in eqs 1 and 2 to provide the desired species, where L designates tacn or Me_3tacn and the bold numbers identify the products. Previously, Wieghardt and co-workers established that these amines form unusually robust carbonyl derivatives of the later transition metals.[9]

$$\text{(trmpe)M(CO)}_4 + \text{L} \xrightarrow[\text{DME}]{-25\ ^\circ\text{C}} \text{LM(CO)}_4 + \text{trmpe} \quad (1)$$

1, M = Zr, L = tacn; **2**, Me_3tacn; **3**, M = Hf, L = tacn

$$\text{(dmpe)Ti(CO)}_5 + \text{L} \xrightarrow[\text{THF}]{20\ ^\circ\text{C}} \text{LTi(CO)}_4 + \text{CO} + \text{dmpe} \quad (2)$$

4, L = tacn, **5**, Me_3tacn

In a typical synthesis, a solution of (trmpe)Zr$(CO)_4$ (0.100 g, 0.22 mmol) and excess tacn (0.113 g, 0.88 mmol) in 45 mL of DME[3] was stirred under CO (1 atm) for 12 h at −25 °C. During this time a red precipitate formed, which was collected and crystallized from cold (−25 °C) CH_3CN/Et_2O to provide 0.060 g (82% yield) of **1**. By very similar procedures a 40% yield of **2** was obtained, while 70–80% yields of **3–5** were isolated. All products were air sensitive, thermally stable, red to dark red microcrystalline materials of satisfactory purity.[10] Interactions of (trmpe)Hf$(CO)_4$ and Me_3tacn failed to provide tractable products.

Infrared spectra of the tacn products **1**, **3**, and **4** showed carbonyl absorptions[11] at surprisingly low energies and were very similar to those of the corresponding anionic species $[(C_5Me_5)M(CO)_4]^-$.[12] Thus, the secondary amine, tacn, and $[C_5Me_5]^-$

[†] University of Minnesota.
[‡] University of Delaware.

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