J. Am. Chem. Soc. 1990, 112, 6729-6731

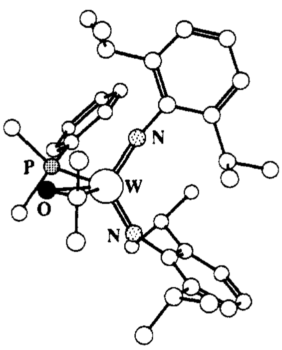


Figure 1. A view of the structure of W(NAr)$_2$(PMe$_2$Ph)(η^2-OCMe$_2$): N-W-C = 108.8 (3)° and 110.8 (3)°, P-W-N = 100.6 (2)° and 106.8 (2)°, P-W-C = 113.7 (3)°, N-W-N = 116.0 (3)°, W-O = 2.025 (5) Å, W-C = 2.118 (9) Å, W-N = 1.785 (6) and 1.776 (7) Å, W-P = 2.509 (2) Å, C-O = 1.39 (1) Å.

al-nitrogen π bonds (four).[7] The W(NAr)$_2$ fragment therefore could be regarded as isolobal and isoelectronic with the HfCp$_2$ fragment, and W(NAr)$_2$(PMe$_2$Ph)$_2$ therefore is analogous to TiCp$_2$(PMe$_3$)$_2$,[8] a view that is useful in explaining the orientation of the acetone ligand in **2a** and π-bound ligands in analogous complexes. Of course an imido ligand is much more "flexible" than a Cp ligand in terms of π bonding,[9] a fact that allows W(NAr)$_2$L$_2$L$'$ complexes to form readily. Although W(NAr)$_2$L$_2$L$'$ complexes could be considered 20e species with an occupied π^* orbital, we can expect the N-W-N angle to be relatively large in order to reduce the overall W-N bond order and minimize the destabilizing effect of that configuration. This analysis is consistent with a recent crystal structure of Os(NAr)$_2$I$_2$(PMe$_2$Ph) in which N-Os-N = 155°.[10]

On the basis of the results presented here, we can speculate that other pseudotetrahedral complexes containing the bent 14e M(NAr)$_2$ core will show certain "metallocene-like" structural preferences, but yet will react readily with donor ligands to yield five-coordinate species or substituted pseudotetrahedral bis(imido) products. Preliminary results for complexes based on the $[\mathrm{Re}(\mathrm{NAr})_2]^+$[11] and $[\mathrm{Os}(\mathrm{NAr})_2]^{2+}$[10] cores confirm that this is often the case. We hope to be able to explore the chemistry of a wide variety of such d^2 bis(imido) complexes, in particular chemistry that bears on the potential utility of the d^2/d^0 redox couple.

Acknowledgment. We thank the National Institutes of Health (Grant GM 31978) and the National Science Foundation (CHE 88-22508) for research support, the U.S. Department of Energy, Division of University and Industry Programs, for funds to purchase the X-ray diffractometer (Grant DE-FG05-86ER75292), Dr. W. M. Davis for collecting the data set for **2a**, and Dr. W. E. Crowe for helpful discussions. J.T.A. thanks the Deutscher Akademischer Austauschdienst for a NATO Postdoctoral Fellowship.

Supplementary Material Available: Experimental details, a description of the X-ray study, a labeled ORTEP drawing, and tables of final positional parameters and final thermal parameters for **2a** (15 pages); table of final observed and calculated structure factors for **2a** (31 pages). Ordering information is given on any current masthead page.

---

(7) If the N/W/N plane is defined to be the *xz* plane, then the b$_1$ combination of in-plane p orbitals on the two nitrogen atoms overlaps poorly with the b$_1$ orbital on the metal (d$_{xz}$) as the N-W-N angle decreases from 180°. If this interaction *is* counted as a π bond, then four are formed. Only three π bonds can form in a trans, square-planar W(NR)$_2$L$_2$ species.[2]

(8) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 394.

(9) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(10) Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Davis, W. M.; Schofield, M. H., unpublished results.

(11) Weinstock, I. A. Ph.D. Thesis, MIT, 1990.

Tin-Directed Baeyer-Villiger and Beckmann Fragmentations

Roger P. Bakale, Mark A. Scialdone, and Carl R. Johnson*

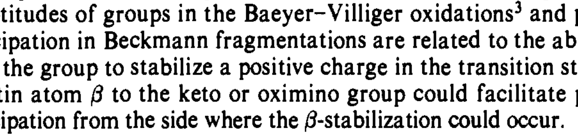
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

Received May 15, 1990

The synthetic usefulness of carbon-carbon bond fragmentations of cyclic systems to give acyclic systems is limited by the degree of regiochemical control. Functionality that can exert control through transition-state stabilization is needed to achieve selectivity. We were interested in utilizing the β-effect[1] of tin[2] to direct carbon-carbon bond fragmentations that were both efficient and compatible with multiple functionalities. Since the migratory aptitudes of groups in the Baeyer-Villiger oxidations[3] and participation in Beckmann fragmentations are related to the ability of the group to stabilize a positive charge in the transition state, a tin atom β to the keto or oximino group could facilitate participation from the side where the β-stabilization could occur. The β-trimethylsilyl group has been demonstrated to exert regiochemical control in Baeyer-Villiger oxidations[4] and to favor Beckmann fragmentations over normal Beckmann rearrangements of oximes.[5,6] These directive effects of the silyl group are not completely pervasive, and in favorable cases, the "normal" products are observed.[4-6] Tin has been used to direct lead tetraacetate mediated oxidative fragmentations of β-stannyl oximes (to provide alkenes and nitrile oxides)[7] and β-stannyl carboxylic acids (to provide alkenes and carbon dioxide).[8]

The requisite β-tributylstannyl ketones were prepared by either conjugate addition of Bu$_3$SnM (M = Li, Cu, etc.) to α,β-unsaturated ketones[9] or alkylation of the ketone or imine enolates with ICH$_2$SnBu$_3$.[10] The β-tributylstannyl oximes were prepared by treatment of the β-tributylstannyl ketones with hydroxylamine. Both syn and anti oximes (with respect to tin) were obtained except where the ketone had α-substitution which directed the oxime formation exclusively anti.

Treatment of β-tributylstannyl ketones with 3-chloroperoxybenzoic acid (mCPBA) resulted in a tin-directed oxidative fragmentation to give carboxylic acids (eq 1). It can be seen that the β-tributylstannyl group is the dominant group for controlling the regiochemical selectivity in these oxidations (Table I).[11] The



(1)

---

(1) The term β-effect refers to the ability of tin (and related atoms) to stabilize cationic character at a β position presumably by electron delocalization from the C-Sn σ-bond into the empty β p orbital. For a recent discussion of such effects, see: Lambert, J. B.; Wang, G.-t.; Teramura, D. H. *J. Org. Chem.* **1988**, *53*, 5422-5428.

(2) For recent reviews on organotin chemistry, see: Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987. Sato, T. *Synthesis* **1990**, 259-270.

(3) Hassall, C. H. *Org. React.* (*N.Y.*) **1957**, *9*, 73-106.

(4) (a) Hudrlik, P. F.; Hudrlik, A. M.; Nagendrappa, G.; Yimenu, T.; Zellers, E. T.; Chin, E. *J. Am. Chem. Soc.* **1980**, *102*, 6894. (b) See also: Asaoke, M.; Takenouchi, K.; Takei, H. *Tetrahedron Lett.* **1988**, *29*, 325.

(5) (a) Nishiyama, H.; Sakuta, K.; Osaka, N.; Itoh, K. *Tetrahedron Lett.* **1983**, *24*, 4021. (b) Nishiyama, H.; Sakuta, K.; Osaka, N.; Arai, H.; Matsumoto, M.; Itoh, K. *Tetrahedron* **1988**, *44*, 2413.

(6) Hudrlik, P. F.; Waugh, M. A.; Hudrlik, A. M. *J. Organomet. Chem.* **1984**, *271*, 69.

(7) Nishiyama, H.; Arai, H.; Ohki, T.; Iton, K. *J. Am. Chem. Soc.* **1985**, *107*, 5310.

(8) Nishiyama, H.; Matsumoto, M.; Arai, H.; Sakaguchi, H.; Itoh, K. *Tetrahedron Lett.* **1986**, *27*, 1599.

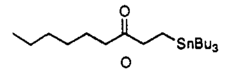
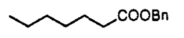
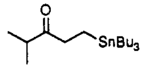
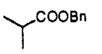
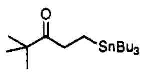
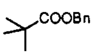
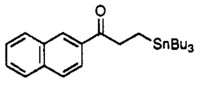
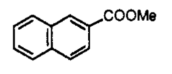
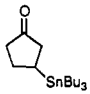
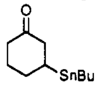
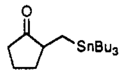
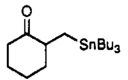
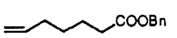
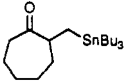
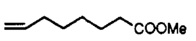
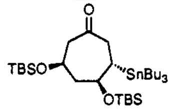
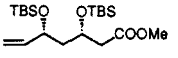
(9) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836. Piers, E.; Morton, H. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1033. Lipshutz, B. H; Ellsworth, E. E.; Dimock, S. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, *30*, 2065.

(10) Seyferth, D.; Andrews, S. B. *J. Organomet. Chem.* **1971**, *30*, 151-166.

(11) New compounds were fully characterized spectroscopically and by microanalysis and/or HRMS.

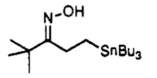
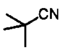
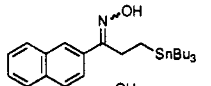
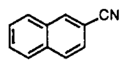
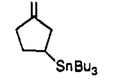
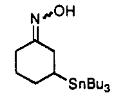
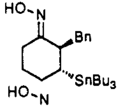
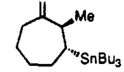
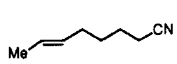
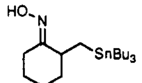
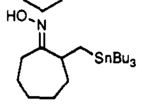
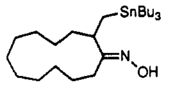
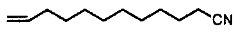
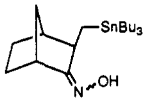
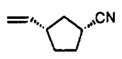
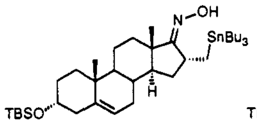
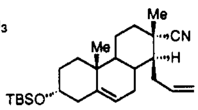
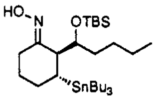
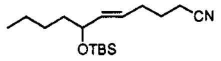
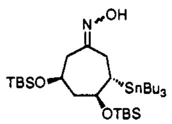
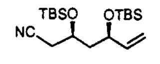
0002-7863/90/1512-6729$02.50/0 © 1990 American Chemical Society

Table I. Tin-Directed Baeyer–Villiger Oxidation of β-Tributylstannyl Ketones

β-Tributylstannyl Ketone	Conditions[a]	Isolated Product[b]	Yield (%)
	B		85
	B		74
	B		93
	C		76
	A		87
	A		89
	A		57
	A		95
	B		76
	A	 TBS = *t*-butyldimethylsilyl	59

[a] Reaction conditions: (A) The β-tributylstannyl ketone in CH_2Cl_2 (ca. 0.1 M) was treated with mCPBA (2 equiv) in the presence bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl) sulfide (radical inhibitor) at 25 °C. (B) Same as A with a reaction temperature between 55 and 60 °C. (C) Same as A except dichloroethane as solvent with a reaction temperature of 85 °C. [b] Product isolation: Methyl esters were prepared by esterification with diazomethane in ether; benzyl esters were prepared by esterification with benzyl bromide and DBU in benzene.

Table II. Tin-Directed Beckmann Fragmentations of β-Tributylstannyl Oximes[a]

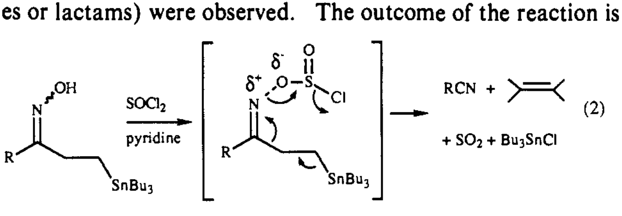
β-Tributylstannyl Oxime	Nitrile	Yield (%)
		93
		90
		97
		99
		99
		93
		89
		85
		99
		92
		86
		95
		67

[a] Reaction conditions: The β-tributylstannyl oxime in CH_2Cl_2 (ca. 0.2 M) was treated with pyridine (4 eqiv) and $SOCl_2$ (2 equiv) at 0 °C for 0.5–2.0 h followed by aqueous workup.

β-tributylstannyl group is superior to the β-trimethylsilyl group, which is intermediate between secondary and tertiary alkyl groups in directing Baeyer–Villiger oxidations.[4a] The cases of the *tert*-butyl and naphthyl ketones are particularly dramatic in that participation of the primary β-stannylethyl group occurs to the complete exclusion of migration of the tertiary or aryl substituent.[12] This is a complete reversal of the "normal" regiochemistry of a Baeyer–Villiger oxidation.

Stannyl esters or lactones were never observed as intermediates in these reactions. A 2-(tributylstannyl)ethyl ester, prepared independently, was shown to survive under the reaction conditions. β-(Tributylstannyl)cycloalkanones with α-substitution did not react under the conditions examined.

β-Tributylstannyl oximes upon treatment with thionyl chloride/pyridine fragmented (eq 2) to give nitriles in good yields (Table II);[11] no normal Beckmann rearrangement products (amides or lactams) were observed. The outcome of the reaction is



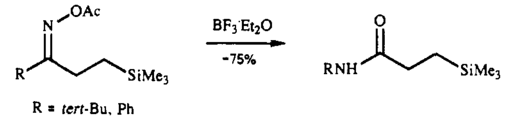
insensitive to the stereochemistry of the oxime although differences in the kinetics of the two oximes were sometimes observed. As with the tin-directed Baeyer–Villiger reaction, the β-tributylstannyl group is a powerful directing influence, overcoming even the high propensity of anti aryl and *tert*-alkyl groups to migrate in a normal Beckmann rearrangement process.[13] These Beckmann fragmentations are especially clean and facile; tin-containing byproducts remaining after aqueous workup are highly polar and remain near the origin upon simple chromatography on silica gel.

The ease of installation of tributylstannyl groups β to keto groups through alkylation or conjugate addition chemistry and the pervasive effects of these groups in circumventing normal

---

[12] For example, in the case of *tert*-butyl 2-(trimethylsilyl)ethyl ketone, migration of the *tert*-butyl group dominated by 2:1 (ref 4a).

[13] This is in direct contrast to similar reactions (ref 5b) with β-silyl oxime derivatives containing anti *tert*-alkyl or phenyl groups:



R = *tert*-Bu, Ph

pathways in the reactions of concern are noteworthy. The Beckmann fragmentations, in particular, occur rapidly under mild conditions and proceed in high yields; these factors attest to the utility of the process in synthetic chemistry.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-8922955).

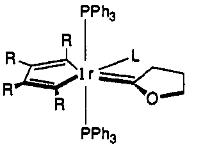
Carbene Ligand Insertion into a Metallacycle Ring: A Metallacyclopentadiene to Metallacyclobutene Conversion

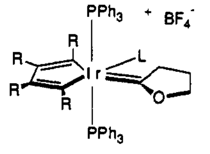
Joseph M. O'Connor,* Lin Pu, Susan Woolard, and Raj K. Chadha

Department of Chemistry (D-006)
University of California at San Diego
La Jolla, California 92093

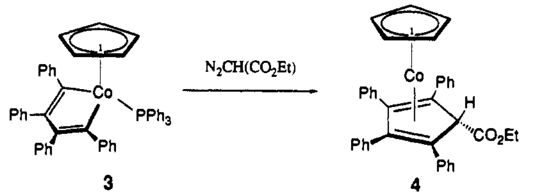
Received May 14, 1990

In an effort to couple the reactivity patterns of metal carbene and metallacycle complexes, we recently prepared the first examples of isolable, mononuclear metallacycle–carbene complexes, **1**-L (L = Cl, F; R = CO_2CH_3) and **2**-L (L = CO, H_2O; R = CO_2CH_3).[1] One specific goal in the synthesis of these complexes was to observe an unprecendented carbene ligand insertion into the metallacycle ring of a characterized metallacycle–carbene complex.[2] A reductive elimination from the resultant metallacyclohexadiene product would lead to a five-membered carbocycle. Indeed, we recently observed the reaction of cobalt metallacycles (e.g., **3**) with ethyl diazoacetate to give cyclopentadiene products (e.g., **4**).[3] This reaction may involve metallacycle–carbene intermediates. Intramolecular migratory coupling reactions of carbene and (sp^3) carbon ligands are precedented:[4] however, we are aware of only one mononuclear case that appears to involve a vinyl ligand–carbene ligand coupling.[5] In light of the ready accessibility of both carbene and metallacycle complexes, the development of metallacycle–carbene coupling reactions would represent significant new carbon–carbon bond formation methodology. Herein we report a novel metallacyclopentadiene to metallacyclobutene conversion,[6] which proceeds via carbene ligand insertion into the carbon–metal bond of a metallacycle.





1, L = Cl, F R = CO_2CH_3 **2**, L = CO, OH_2



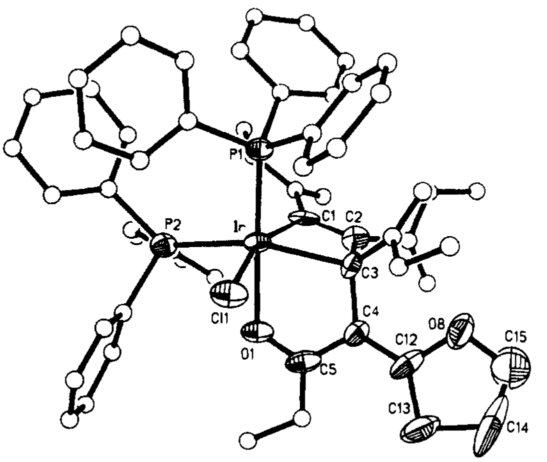
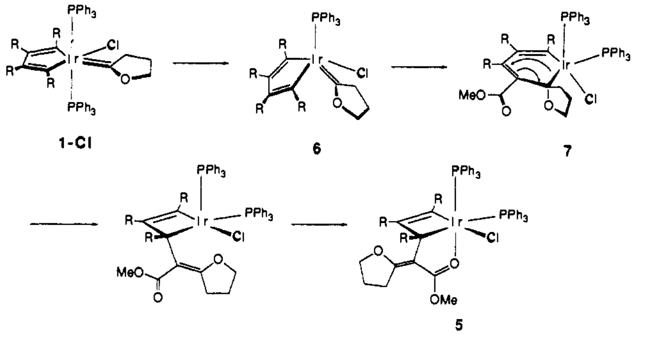


Figure 1.

Scheme I



When a chloroform-d_1 solution of the neutral metallacycle–carbene **1**-Cl (0.13 M) is heated at 72 °C, the ^1H NMR resonances due to **1**-Cl are gradually and quantitatively replaced by a new set of resonances, which arise from formation of iridiacyclobutene **5**.[7] In the ^1H NMR spectrum of **5**, four singlets (3 H each) are observed at δ 2.36, 2.55, 3.30, and 3.62, which are assigned to the hydrogens of four unique carboxymethyl groups. ^1H NMR resonances at δ 2.04 (m, 2 H), 3.10 (m, 2 H), and 4.24 (m, 2 H) are consistent with an intact oxacyclopentylidene ring; however, in the $^{13}C\{^1H\}$ NMR spectrum of **5**, the farthest downfield resonance is at 187 ppm. Thus the carbene ligand in **1**-Cl is no longer present in **5**. A broad doublet at 18.22 (J = 67.6 Hz) ppm in the $^{13}C\{^1H\}$ NMR spectrum is consistent with an sp^3 carbon trans to a PPh_3 ligand. In the $^{31}P\{^1H\}$ NMR spectrum two doublets are observed at δ −10.9 (J = 10 Hz) and −23.9 (J = 10 Hz), indicative of nonequivalent cis PPh_3 ligands. The spectroscopic data are thus consistent with either an iridiacyclohexadiene structure or the actual iridiacyclobutene structure.

In order to unambiguously determine the structure of complex **5** a single-crystal X-ray diffraction study was performed (Figure 1).[8] The X-ray results indicate that a remarkable transformation

---

[1] O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 7578. O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.*, in press.

[2] Metallacycle–carbene intermediates have been proposed for the thermal decomposition of nickelacyclohexane complexes and for metallacycle rearrangements in olefin metathesis reactions: Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7418. Biefeld, C. G.; Eick, H. A.; Grubbs, R. H. *Inorg. Chem.* **1973**, *12*, 2166.

[3] O'Connor, J. M.; Pu, L.; Uhrhammer, R.; Johnson, J. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 1889. O'Connor, J. M.; Johnson, J. A. *Synlett* **1989**, 57.

[4] (a) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43. (b) Threlkel, R. S.; Bercaw, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (c) Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3026, and references therein. (d) Thorn, D. L. *Organometallics* **1986**, *5*, 1897, and references therein. (e) McCrindle, R.; Arsenault, G. J.; Farwaha, R.; Hampden-Smith, M. J.; McAlees, A. J. *J. Chem. Soc., Chem. Commun.* **1986**, 943. (f) Roder, K.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 686, and references therein. (g) Davey, C. E.; Osborn, V. A.; Winter, M. J.; Woodward, S. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1989; p 159. (h) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 464. (i) Wang, C.; Lang, M. G.; Sheridan, J. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 3236.

[5] O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 4129. See also: Maitlis, P. M.; Bailey, N. A.; Adams, H.; Martinez, J. M. *J. Chem. Soc., Chem. Commun.* **1989**, 286.

[6] McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451.

[7] Complete spectroscopic and analytical data for **5**, **2**-H_2O, and **1**-F are provided as supplementary material. Complex **2**-H_2O was prepared by treatment of **1**-Cl with $AgBF_4$ in wet CH_2Cl_2, and **1**-F was prepared by treatment of **2**-H_2O with KF in methylene chloride solution.

0002-7863/90/1512-6731$02.50/0 © 1990 American Chemical Society