°C/0.02 Torr) provided cyclopropane **69** (0.243 g, 70%) as a 1:1 mixture of cis/trans isomers (degree of deuteration according to ^{1}H NMR >90%).

Methylation of Cyclopropane 11. Cyclopropane **11** (0.348 g, 2.00 mmol, trans:cis = 1:1) was added at −78 °C to a solution of LDA (3.00 mmol) in 6 mL of tetrahydrofuran. After 2 h methyl iodide (0.31 mL, 5.00 mmol) was added and the mixture was warmed to room temperature within 16 h. Extractive workup and distillation (100–130 °C/0.02 Torr) provided 0.176 g (47%) of *trans*-2-methoxy-1-methyl-2-phenylcyclopropyl cyanide (**41**; according to ^{1}H NMR trans:cis > 95:5). ^{13}C NMR ($CDCl_3$): *trans*-**41**, δ 135.0, 128.6, 127.1, 127.0 (s, 3 d, Ph), 121.6 (s, CN), 70.0 (s, C-2), 55.3 (q, OMe), 23.8 (t, C-3), 19.2 (s, C-1), 15.9 (q, Me). For further analytical data see experiment **1** + **40**.

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Thermal Reactions of Acyloxy and Alkoxy Carbene Complexes with Imines: Metathesis, Acetate Rearrangements, and a New Route to Imino Carbene Complexes via Peterson Type Eliminations

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The first examples of the reactions of imines ($R^3N{=}CHR^2$; R^3 = CH_3, R^2 = Ph, *p*-MePh) with acetoxy Fischer carbene complexes ($(CO)_5M{=}C(OAc)R^1$; M = Cr, W, R^1 = Ph) are described. The reaction of the chromium complex gives exclusively the *O*-acyl imidate **14** (MeN=C(OAc)Ph), which is the first example of a metathesis of an imine and a carbene complex. The tungsten complex gives a product that results from an unprecedented insertion of the imine into the carbene carbon–heteroatom bond along with the *O*-acyl imidate **14** as a minor product. This new insertion product was characterized by spectroscopic methods and by X-ray diffraction and determined to be the animal carbene complex **13b**. Crystal data for **13b**: space group $P\bar{1}$, Z = 2, a = 8.269 (3) Å, b = 10.766 (5) Å, c = 13.851 (7) Å, α = 68.83 (5)°, β = 75.97 (6)°, γ = 81.39 (4)°, R = 0.046, and R_w = 0.050 for the 2267 reflections with $F_o \geq 5\sigma(F_o)$. It was determined that this insertion product is the result of an acetate transfer rather than a hydride transfer and that a likely intermediate in the mechanism is the zwitterion that results from initial addition of the imine nitrogen to the carbene carbon. The reaction of the acetoxy carbene complexes $(CO)_5M{=}C(OAc)R^1$ (M = Cr, W, R^1 = Ph, Me, tBu) with *N*-trimethylsilyl imines $Me_3SiN{=}CHR^2$ provides a new method for the synthesis of imino carbene complexes $(CO)_5M{=}C(R^1)N{=}CHR^2$ in a process that involves a Peterson type elimination. In a related reaction, it was found that imino complexes could also be accessed from the reaction of alkoxy carbene complexes $(CO)_5M{=}C(OMe)R^1$ (M = Cr, W, R^1 = Ph, Me, tBu) with *N*-trimethylsilyl imines.

The reaction of Fischer carbene complexes[1] with alkenes to produce cyclopropanes[2,3] has been of longstanding mechanistic interest and more recently of interest in applications to organic synthesis.[4] The corresponding thermal reaction of Fischer carbene complexes with imines to produce aziridines of the type **4** is unknown. The thermal reactions that have been reported led to aminolyses,[5] condensations,[6] or formal [2 + 2] cycloadditions.[7] For example, the reaction of the methyl complex **5** with the *N*-methyl imine of benzaldehyde gives the α,β-unsaturated carbene complex **7**, which is the result of a base-induced condensation and elimination between the relatively acidic complex **5** and the imine.[6] The reaction of **5** with imines less basic than **6** leads only to extensive decomposition of the carbene complex. The photoinduced reaction of Fischer carbene complexes with imines pro-

(1) For recent reviews on the chemistry of Fischer carbene complexes, see: (a) Brown, E. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. (b) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (d) Casey, C. P. *React. Intermed.* **1985**, *3*. (e) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (f) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1. (g) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, England, 1990; Vol. 5.

(2) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 3966.

(3) For reviews, see: (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (b) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.

(4) For a listing of recent citations, see footnote 4 in: Murray, C. K.; Yang, D. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660.

(5) (a) Knauss, L.; Fischer, E. O. *J. Organomet. Chem.* **1971**, *31*, C68. (b) Knauss, L.; Fischer, E. O. *Chem. Ber.* **1970**, *103*, 3744.

(6) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680.

(7) (a) Barrett, A. G. M.; Brock, C. P.; Sturgess, M. A. *Organometallics* **1985**, *4*, 1903. (b) Barrett, A. G. M.; Mortier, J.; Sabat, M.; Sturgess, M. A. *Organometallics* **1988**, *7*, 2553.

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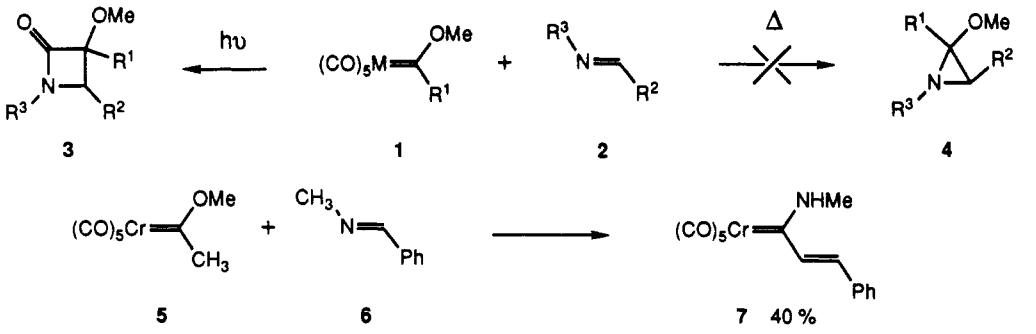
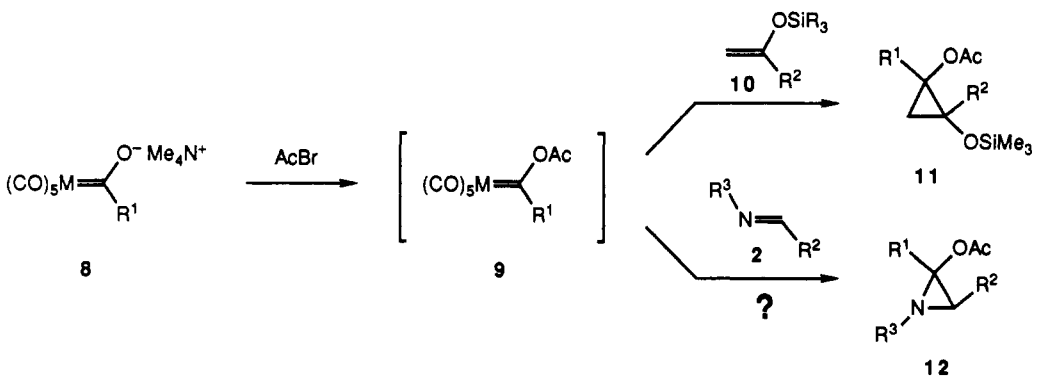
Scheme I



Scheme II



duces β-lactams and has been developed by Hegedus into one of the more synthetically important reactions of Fischer carbene complexes.[6,8,9]

In a recent study we have found that acyloxy complexes of the type **9** will cyclopropanate enol ethers with much greater rates and under conditions that are significantly less severe than are necessary for the same cyclopropanation with an alkoxy carbene complex.[4] This is apparently due to the greater electrophilicity of the carbene carbon of an acyloxy complex compared to that of an alkoxy complex. The expectation was that acyloxy complexes would also be more reactive toward imines, and the question was whether the anticipated greater reactivity would result in the realization of the first aziridine synthesis from the reaction of a Fischer carbene complex and an imine. We report here our initial studies on the reactions of acyloxy complexes with imines and the application of the unexpected results of these reactions to the development of a new method for the preparation of imino carbene complexes.

Acetoxy carbene complexes are not generally stable in solution at room temperature, although it has been shown that they can be generated and isolated cleanly at low temperatures (≤−20 °C).[12a,b] Initially, we chose to examine the reactions of the acetoxy complexes **9a,b**. The chromium and tungsten tetramethylammonium acylates **8a,b** were treated with acetyl bromide in methylene chloride at −20 °C to generate the acyloxy complexes **9a,b**, and each in turn was reacted with the *N*-methyl imine of benzaldehyde. The reaction of the chromium complex gave the *O*-acyl imidate **14**, and this represents the first example of a metathesis reaction of a Fischer carbene complex and an imine, although *O*-alkyl imidates have been seen from the metathesis reactions with azo[10] and nitroso[11] compounds. The reaction of the tungsten complex gave as the major product the *N*-aminal carbene complex **13b**, which is the result of an unprecedented formal insertion of the imine into the heteroatom–carbene carbon bond. The presence of the aminal functionality in complex **13** was confirmed by base hydrolysis to give the (methylamino)carbene complex **15b** as a 3.0:1 mixture of *E* and *Z* isomers. It has long been established that the barrier to rotation about the nitrogen–carbene carbon bond in amino carbene complexes is quite high (≥25 kcal) and that the rotamers can be isolated and cannot be interconverted thermally.[1,12c]

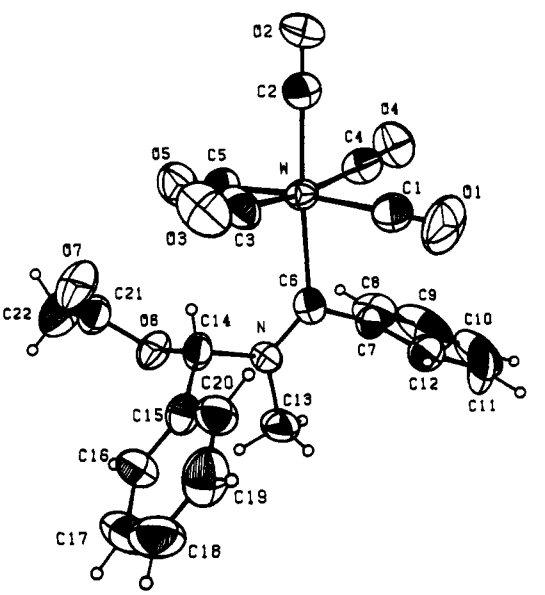
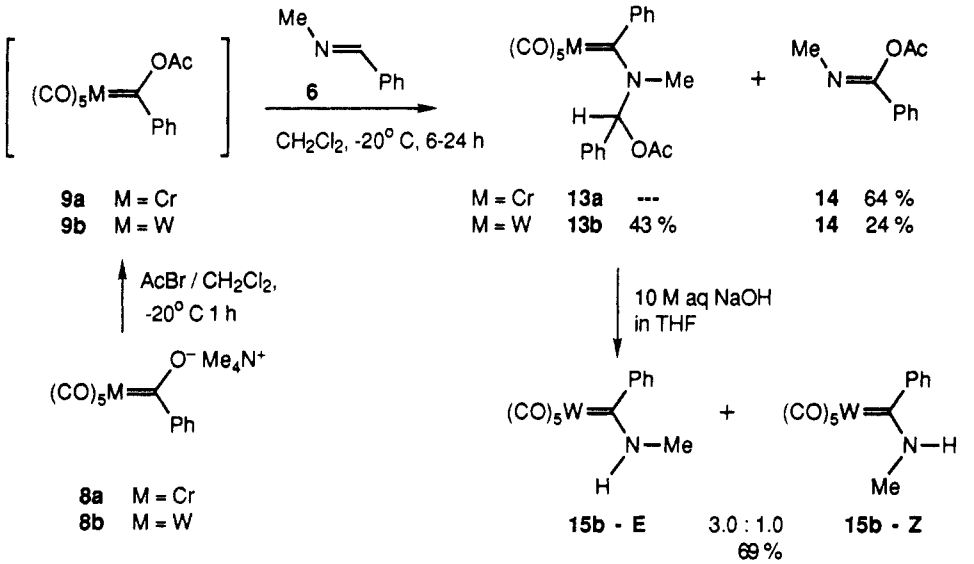


Figure 1. ORTEP drawing of compound **13b**.

(8) McGuire, M. A.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 5538.
(9) For a list of citations in this area, see: Hegedus, L. S.; D'Andrea, S. *J. Org. Chem.* **1988**, *53*, 3113.
(10) (a) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700. (b) Hegedus, L. S.; Lundmark, B. R. *J. Am. Chem. Soc.* **1989**, *111*, 9194. (c) Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263. (d) Hegedus, L. S.; Kramer, A.; Yiju, C. *Organometallics* **1985**, *4*, 1747.
(11) (a) Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, 3665. (b) Herndon, J. W.; McCullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83.
(12) (a) Connor, J. A.; Jones, E. M. *J. Chem. Soc. A* **1971**, 3368. (b) Fischer, E. O.; Selmayr, T.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 2947. (c) Fischer, E. O.; Moser, E. *J. Organomet. Chem.* **1968**, *13*, 387.

Scheme III



The *E* and *Z* isomers of **15b** have been previously reported, separated, and characterized.[13] The assignment of the isomers of **15b** was made on the basis of the chemical shifts of the *N*-methyl groups, which were δ 2.91 ppm for the *E* isomer and δ 3.64 ppm for the *Z* isomer, both of which correlated very well with the published values.[13]

The initial assignment of the stereochemistry of the aminal complex **13b** was also made on the basis of the chemical shift of the *N*-methyl group, which was observed at δ 2.73 ppm and which is closer to the chemical shift of the *N*-methyl group in the *E* isomer of **15b**. As will be discussed below, the stereochemistry of **13b** has mechanistic implications, and thus a confirmation of the stereochemical assignment of **13b** was undertaken by X-ray diffraction. The details of this analysis are presented in the Experimental Section, and an ORTEP drawing taken from these data is presented in Figure 1. Clearly the aminal carbon in complex **13b** is syn to the metal, and as a consequence of this large group being syn to the metal, there is some distortion in the carbon monoxide ligand that is closest to the aminal substituent of the nitrogen.

Three possible mechanisms that can account for the formation of the metathesis product **14** and imine insertion product **13b** are presented in Scheme IV. The interaction of the acyloxy carbene complex **9** with the imine **6** could lead to either the formation of the zwitterionic species **17**[14] or the azametallacyclobutane intermediate **16**. The metathesis product can be derived only from the azametallacycle **16** in a process that should also produce the nonstabilized benzylidene complex **20**. It has been demonstrated that the benzylidene complex **20** would not be stable under the reaction conditions.[15a] Complex **20** has been shown to thermally decompose at 25 °C to give *cis*- and *trans*-stilbene, and we have detected these products in the ^{1}H NMR spectrum of the crude reaction mixtures that contain the imidate **14**.[15b,c] The insertion product **13** could be envisioned to arise from either the zwitterionic intermediate **17** or the azametallacyclic intermediate **16**. In addition, there are two possible pathways to the insertion product **13** from the zwitterionic intermediate **17**, and these are indicated in Scheme IV. A concerted [3,3]-sigmatropic rearrangement[16] could result in the direct formation of **13** from the zwitterionic intermediate **17**, or alternatively, formation of **13** could be the result of a two-step process in which the first step involves a 1,2-migration of the acetate group from the carbene carbon to the metal to generate the azomethine ylide intermediate **18**. Although this type of 1,2-migration of acetate from the carbene carbon to the metal has not been reported, similar migrations have been observed for other heteroatom substituents.[17] The syn relationship of the aminal substituent and the metal in complex **13b** is the only possible stereochemical outcome from the mechanism involving the azomethine intermediate **18**. This syn relationship in **13b** could be accounted for in the [3,3]-sigmatropic mechanism by either the boat or chair transition states **21** or **22**. Notice, however, that in both the boat and chair transition states the tungsten pentacarbonyl group must occupy an axial position to account for the observed stereochemistry in **13b**. The boat transition state **21** may be preferred to the chair transition state **22** due to the anticipated long-range diaxial interactions of the methyl and hydrogen in **22** with the tungsten pentacarbonyl group. At this point, a distinction between the [3,3]-sigmatropic and azomethine mechanisms cannot be made.

(13) (a) Fischer, E. O.; Schmid, K. R.; Kalbfus, W.; Kreiter, C. G. *Chem. Ber.* **1973**, *106*, 3893. (b) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1981**, *114*, 1853. (c) Guy, J. T., Jr.; Bennett, D. W. *Transition Met. Chem.* **1984**, *9*, 43.

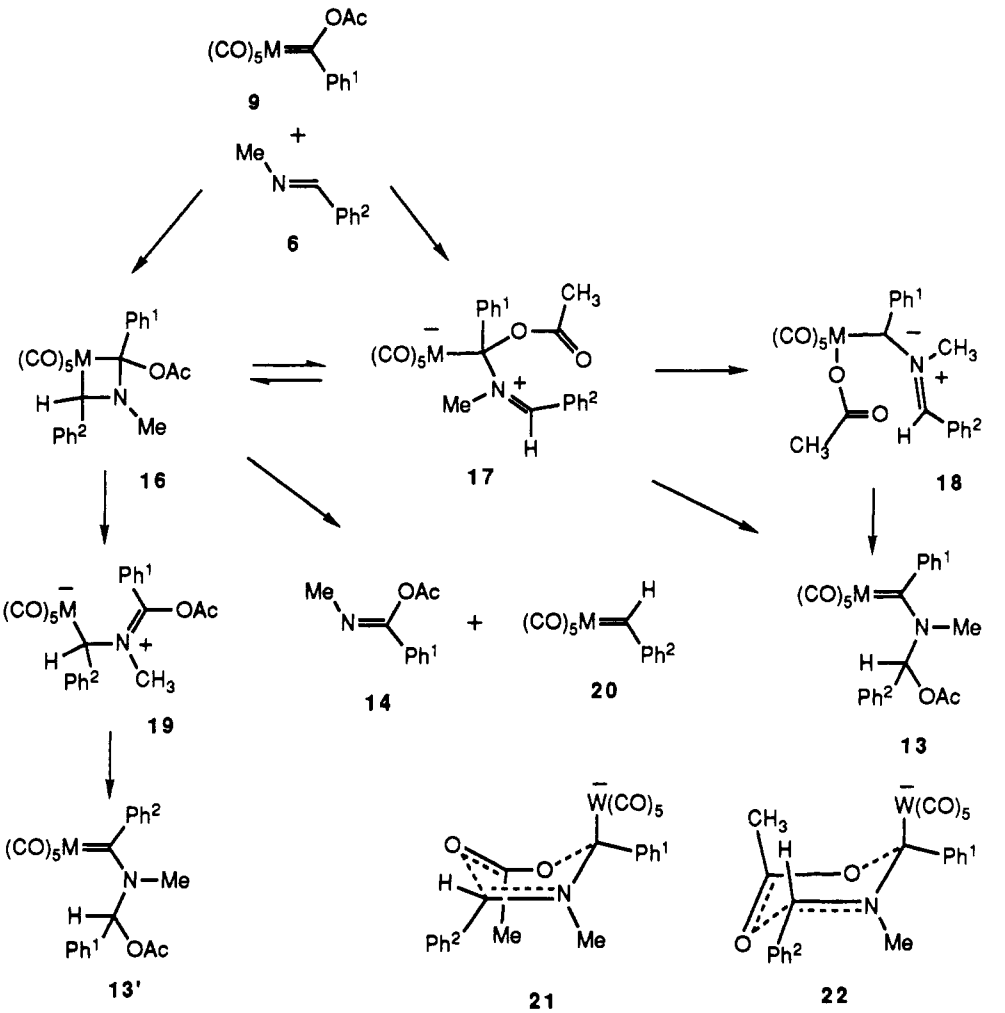
(14) For zwitterionic intermediates in other reactions of carbene complexes, see ref 10 and: (a) Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653. (b) Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G.; Fischer, H. *Chem. Ber.* **1973**, *106*, 1262. (c) Fischer, H.; Märkl, R. *Chem. Ber.* **1985**, *118*, 3683. (d) Brookhart, M.; Kegley, S. E. *Organometallics* **1984**, *3*, 650. (e) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908. (f) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

(15) (a) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282. (b) Fischer, H.; Schmid, J.; Märkl, R. *J. Chem. Soc., Chem. Commun.* **1985**, 572. (c) Fischer, H.; Seuner, S.; Ackermann, K. *J. Chem. Soc., Chem. Commun.* **1984**, 684.

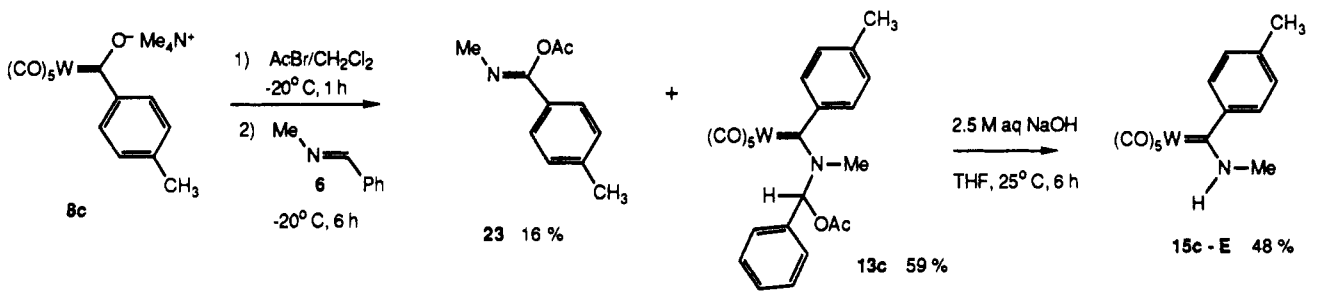
(16) For other possible [3,3]-sigmatropic rearrangements involving carbene complexes, see: (a) Casey, C. P.; Shusterman, A. J. *Organometallics* **1985**, *4*, 736. (b) Aumann, R.; Kuckert, E.; Heinen, H. *Chem. Ber.* **1987**, *120*, 1293. (c) Barrett, A. G. M.; Carpenter, N. E. *Organometallics* **1987**, *6*, 2249. (d) Herndon, J. W.; McCullen, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 6854.

(17) (a) Fischer, H.; Motsch, A.; Märkl, R.; Ackermann, K. *Organometallics* **1985**, *4*, 726. (b) Fischer, E. O.; Himmelreich, D.; Cai, R.; Fischer, H.; Schubert, U.; Zimmer-Basser, B. *Chem. Ber.* **1981**, *114*, 3209. (c) Fischer, H.; Fischer, E. O.; Himmelreich, D.; Cai, R.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1981**, *114*, 3220. (d) Fischer, H.; Fischer, E. O.; Cai, R. *Chem. Ber.* **1982**, *115*, 2702. (e) Fischer, H.; Fischer, E. O.; Cai, R.; Himmelreich, D. *Chem. Ber.* **1983**, *116*, 1009. (f) Fischer, H. *J. Organomet. Chem.* **1980**, *195*, 55. (g) Fischer, H.; Fischer, E. O. *J. Mol. Catal.* **1985**, *28*, 85. (h) The thermal decomposition of acetoxy complexes may involve an initial 1,2-migration of acetate to the metal center: Wulff, W. D.; McCallum, J. S.; Kunng, F. A. *J. Am. Chem. Soc.* **1988**, *110*, 7419.

Scheme IV



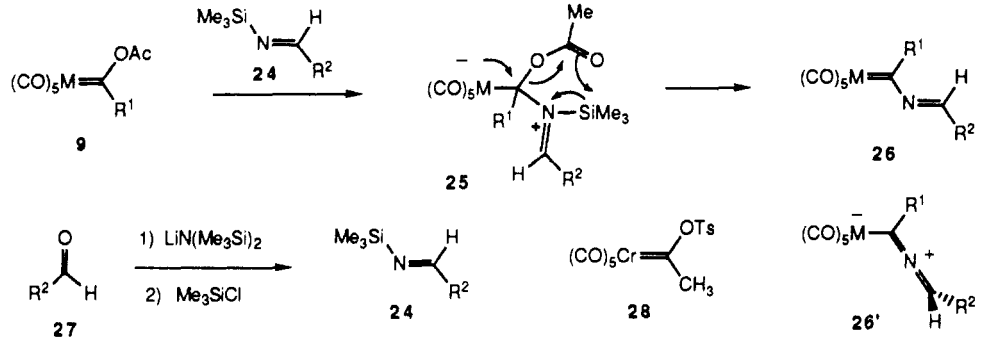
Scheme V



It is also possible that the imine insertion product could arise from a mechanism that involves the azametallacyclobutane intermediate **16**. Ring opening of the metallacycle would produce the zwitterion **19**, and then a 1,3-hydride shift would lead to the imine insertion product. A fundamental difference between this mechanism and the others is that it involves a hydride migration rather than an acetate migration. This mechanism must be considered, since zwitterionic intermediates corresponding to **19** have been detected and isolated from the reactions of Fischer carbene complexes and azo compounds.[10]

A distinction can be made between the mechanisms involving hydride migration versus those that involve acetate migration, since as indicated in Scheme IV the phenyl groups in the carbene complex **9** and in the imine **6** will be differentiated by these mechanisms. As illustrated in Scheme IV, the acetate migration mechanisms will lead to the formation of **13**, whereas the hydride migration mechanism will lead to **13′**. Thus, to distinguish between these two mechanisms the *p*-methylphenyl-substituted metal acylate **8c** was prepared and treated with acetyl bromide to generate the corresponding acetoxy complex **9c**. The solution of this acetoxy complex was reacted directly with the phenyl-substituted imine **6**, and as expected, this reaction produced both the metathesis product and the imine insertion product. The imine insertion product **13c** was obtained as a single regioisomer, and as was the case with **13b**, **13c** was produced as a single stereoisomer, which was assigned as the *Z* isomer shown in Scheme V on the basis of the chemical shift of δ 2.74 ppm for the *N*-methyl group. The location of the *p*-methylphenyl group in **13c** was determined to be on the carbene carbon when base hydrolysis of the aminal function gave the (aminomethyl)-*p*-methylbenzylidene complex **15c**. Complex **15c** was found to be ~95% stereoisomerically pure and was assigned as the *E* isomer on the basis

Scheme VI

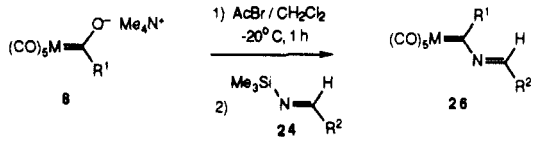


of its *N*-methyl shift of δ 2.90 ppm. That the hydrolysis of **13c** is more stereoselective than that of **13b** may be attributed to the fact that stronger base was used for **13b** and caused isomerization of **15b**. Clearly the formation of imine insertion product **13c** could not have occurred according to the hydride shift mechanism shown in Scheme IV that involves the zwitterionic intermediate **19**. Since the reaction of the (acyloxy)chromium complex did not produce any of the imine insertion product, it is evident that the formation of the zwitterionic intermediate **17** is more prevalent for tungsten than for chromium, and this is consistent with related observations contrasting the chemistry of chromium and tungsten carbene complexes.[14a]

The conclusion from the above studies that the formation of the imine insertion product **13** most likely involves the intermediacy of a switterionic intermediate of the type **17** (Scheme IV) led to the conception of a new synthetic approach to the synthesis of imino complexes of the type **26** that is outlined in Scheme VI. Imino complexes of the type **26** have proven useful in the synthesis of pyrroles and 3-hydroxypyridines[18] and have been demonstrated to be especially advantageous as synthons for nitrile ylides in [3 + 2] cycloadditions.[19] This new approach to these complexes involves the reaction of acetoxy complexes with silyl imines of the type **24**. Assuming that the mechanism of this reaction would be similar to that for the reaction of **9** with the *N*-methyl imine **6**, it would be expected that the zwitterionic intermediate **25** would be generated in this reaction. This zwitterionic intermediate has an additional pathway open to it for acetate transfer. In addition to acetate transfer to the iminium carbon, it is also possible that acetate transfer could occur to the *N*-silyl group, which would lead to the loss of trimethylsilyl acetate and the formation of the imino carbene complex **26**. As will be discussed below, the transfer of acetate to the silyl group with formation of the imino complex **26** was found to be the only detected outcome of these reactions.

The synthesis of a number of imino complexes could be achieved in moderate to good yield, and these results are summarized in Table I. The silyl imines are generated from the corresponding aldehyde **27** and bis(trimethylsilyl)lithium amide according to the procedure developed by Colvin et al. and Cainelli and Panunzio et al.[20] The silyl imine **24a** was prepared as described in the literature in THF solvent, and then solvent was removed at 0 °C and replaced by methylene chloride. If the silyl imine **24a** is added to the acetoxy complex as a THF solution, significantly reduced yields of the imino complexes are obtained. The preparation of imino complex **26a** failed when the silyl imine **24a** was generated in hexane and then added to a methylene chloride solution of the acetoxy complex **9a**. The *N*-silyl imine of acetaldehyde (**24b**) was generated and used in THF, since attempted removal of THF from this solution at 0 °C on a vacuum line resulted in substantial loss of the silyl imine. The solutions of the silyl imines were added to a solution of acetoxy complexes at low temperatures (−20 to −40 °C), and the dark purple solution turned to the light orange of the imino complexes at that temperature in 1–12 h. As had been observed previously, the imino carbene complexes are quite stable and can be purified on silica gel in the presence of air.[21] It should be pointed out that the reaction parameters indicated in Table I are not necessarily optimized with regard to temperatures, reaction times, or equivalents of *N*-silyl imine.

Table I. Preparation of Imino Complexes from Acyloxy Complexes



Metal Acylate			Silyl Imine		Equiv Imine	Time (h)	Temp °C	Imino Complex	
	M	R^1		R^2					% Yield
8a	Cr	Ph	**24a**	Ph	5.0	2	-20	**26a**	64
8a	Cr	Ph	**24b**	Me	4.5	1	-30	**26b**	43
8d	Cr	Me	**24a**	Ph	1.5	4	-40	**26c**	44
8e	Cr	tBu	**24a**	Ph	5.0	12	-35	**26d**	26
8b	W	Ph	**24a**	Ph	1.0	12	-20	**26e**	60[a]
8b	W	Ph	**24b**	Me	3.0	8	-40	**26f**	36

[a] Acetyl chloride.

The ^{13}C NMR chemical shifts of the carbene carbon of the imino complexes (δ 180–190 ppm) are significantly upfield from those of the carbene carbon of alkoxy complexes (δ 320–360 ppm) and even from those of amino complexes (δ 260–300).[21] The solid-state structure of an imino complex has been determined[21c] and is most consistent with the resonance structure **26'** (Scheme VI), in which the C–N–C angle is nearly linear; this compound thus has an axis of chirality. It has been demonstrated for an *O*-alkyl imidate complex that the epimerization about this axis of chirality is sufficiently slow to permit separation of diastereomers.[22]

(18) (a) Dragisich, V.; Murray, C. K.; Warner, B. P.; Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 1251. (b) Aumann, R.; Heinen, H. *J. Organomet. Chem.* **1990**, *389*, C1.

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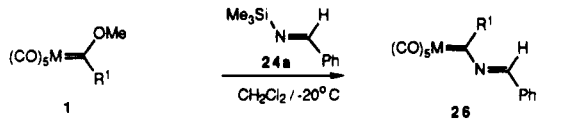
(22) (a) Yang, D. C.; Dragisich, V.; Wulff, W. D.; Huffman, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 307. (b) Wulff, W. D.; Dragisich, V.; Huffman, J. C.; Kaelser, R. W.; Yang, D. C. *Organometallics* **1989**, *8*, 2196.

(23) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.

Table II. Preparation of Imino Complexes from Alkoxy Complexes



Metal Acylate	M	R^1	Time	Imine equiv	Imino Complex	% Yield
1a	Cr	Ph	16 h	1.2	26a	73
1b	Cr	Me	1 h	1.8	26c	68
1c	Cr	tBu	24 h [a]	1.5	26d	30 (60) [b]
1d	W	Me	30 min [c]	1.2	26g	16 (25) [b]

[a] Also 72 h at 25 °C. [b] Yield based on unrecovered starting material. [c] −20 to 0 °C, 30 min; 25 °C, 30 min.

It was quite interesting to note that the imino complex **26c** could be prepared from an acetoxy carbene complex that has acidic hydrogens on the carbon α to the carbene carbon (R^1 = Me). This reaction was first attempted with some hesitation, since it had been reported previously that the tosyloxy complex **28** (Scheme VI) will react with imine **6** to give exclusively products that result from initial deprotonation of the methyl group.[7]

Given the established potential of imino carbene complexes in organic synthesis,[18,19] this new procedure for the preparation of imino complexes from the Peterson type elimination of trimethylsilyl acetate from the reaction of *N*-trimethylsilyl imines and acetoxy carbene complexes should have significant utility, since it gives superior yields compared to existing procedures.[21] Nonetheless, this procedure has the operational drawback that it requires the in situ generation of two reactive species, the silyl imine **24** and the acetoxy complex **9**. It was therefore gratifying to find that this same general procedure for the preparation of the imino complexes **26** could be extended to the reaction of silyl imines and methoxy carbene complexes **1**, where the elements of trimethylmethoxysilane are lost in the Peterson type elimination. This procedure has the intrinsic advantage that the only reactive species that need be generated in situ is the *N*-silyl imine. The alkoxy complexes are stable to air and water and can be handled and manipulated with standard laboratory techniques without any special precautions. The alkoxy complexes can be stored for periods of years in a bottle flushed with nitrogen and kept in a standard laboratory freezer. This procedure has the additional advantage that the yields of imino carbene complexes are generally higher. For example, the imino complex **26c** can be prepared in 44% yield from the acyloxy complex and in 68% yield from the methoxy complex. The reactions listed in Table II have not been optimized with respect to the reaction parameters. We are currently attempting to optimize the conditions for these reactions and to develop other syntheses of imino carbene complexes based on the Peterson elimination reactions.[31]

Summary

The thermal reaction of acetoxy Fischer carbene complexes with imines did not produce aziridines for either chromium or tungsten. The chromium acetoxy complexes were found to react with imines to give *O*-acyl imidates, which is the first example of a metathesis reaction of a carbene complex and an imine. Perhaps the chromium complexes would give aziridines if metathesis could be prevented by keeping the metal center saturated.[14e] The reaction of acetoxy tungsten carbene complexes with imines gave an unprecedented product that resulted from the formal insertion of the imine into the carbene carbon–heteroatom bond. It was shown that this insertion occurs with the migration of the acetoxy group to the imine carbon and occurs with a stereoselectivity that is consistent with a mechanism that involves either a 1,2-migration of acetate from the zwitterionic intermediate **17** to the metal center or a direct [3,3]-sigmatropic rearrangement of the zwitterionic intermediate **17**. The intermediacy of the zwitterionic intermediates in these reactions suggested the new route for the synthesis of imino carbene complexes that was developed and that involves the reaction of acetoxy carbene complexes with *N*-silyl imines. The need for the development of a new synthesis of imino carbene complexes arose from the increasing importance of these complexes in heterocyclic synthesis and the fact that existing procedures are relatively inefficient. This synthesis of imino carbene complexes can also be extended to the reaction of alkoxy carbene complexes with *N*-silyl imines and is the more attractive procedure in terms of convenience and efficiency.

Experimental Section

All reagents were obtained from commercial suppliers and used as received unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl immediately prior to use. Anhydrous diethyl ether was obtained from containers opened within 48 h of use or freshly distilled from benzophenone ketyl. Benzene was stored over activated 4-Å molecular sieves for at least 48 h before use or freshly distilled from benzophenone ketyl. Methylene chloride was distilled over calcium hydride under a nitrogen atmosphere. Any other solvents were stored over a 4-Å sieves for at least 48 h before use. Benzoyl chloride, acetyl chloride, and acetic anhydride were distilled prior to use. Triethylamine was refluxed over calcium hydride then distilled prior to use. All reactions were carried out under an argon or nitrogen atmosphere. Reactions that required heat or were run over a longer period of time were carried out in a Pressure Flask, which is a single-necked flask equipped with a threaded high-vacuum stopcock that has previously been described.[24] Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

Reaction of the *N*-Methyl Imine of Benzaldehyde (6) with Phenyl Acetoxy Chromium Carbene Complex (9a). A slurry of the tetramethylammonium metal acylate **8a**[23] (425 mg, 1.14 mmol) and methylene chloride (1.9 mL) was degassed by the freeze–thaw method (−196 to 0 °C, three cycles) and cooled to −20 °C. Upon slow addition (over 5 min) of 1 equiv of acetyl bromide the bright yellow slurry turned dark purple. This mixture was stirred for 1 h at −20 °C, and then 3 equiv of degassed imine **6** (0.42 mL) were added via syringe pump over approximately 2 h followed by stirring for an additional 24 h. The reaction mixture was warmed to room temperature and diluted first with methylene chloride (50–100 mL) and then with hexane to precipitate out salts. The brown/purple mixture was filtered through Celite and concentrated, and the resulting brown oil was chromatographed

(24) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9.

(25) Complexes **1b,d** were prepared according to Fischer's original procedure.[26]

(26) (a) Fischer, E. O.; Maasbol, A. *Chem. Ber.* **1967**, *100*, 2445. (b) Fischer, E. O.; Schubert, U.; Kleine, W.; Fischer, H. *Inorg. Synth.* **1979**, *19*, 164. (c) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M. *Org. Synth.* **1987**, *65*, 140.

(27) Complex **1a** was prepared by a slight alteration[30] of Casey's modification[28] of Fischer's original procedure.[26]

(28) Casey, C. P.; Cyr, C. R.; Boggs, R. A. *Synth. React. Inorg. Met.-Org. Chem.* **1973**, *3*, 249.

(29) Hafner, A.; Hegedus, L. S.; deWeck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413.

(30) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813.

(31) For a related synthesis of alkenyl carbene complexes, see: Macomber, D. W.; Madukar, P.; Rogers, R. D. *Organometallics* **1989**, *8*, 1275.

on silica gel with a 1:1:4 mixture of ether/methylene chloride/hexane as eluent to give 130 mg (0.73 mmol, 64%) of **14** (R_f 0.16) as a white solid: mp 38 °C. Spectral data for **14**: ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 3.20 (s, 3 H), 7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.78 (q, J = 130.2 Hz), 34.24 (q, J = 141.1 Hz), 128.32 (d, J = 162.1 Hz), 128.65 (d, J = 162.85 Hz), 132.24 (d, J = 161.73 Hz), 135.1 (s), 174.03 (s); IR (neat) 3140 w, 3092 w, 1687 s, 1662 s, 1449 m, 1370 s, 1322 s, 1285 s, 1203 m, 1040 s, 1018 s, 724 m, 704 s cm^{-1}; mass spectrum m/e (% relative intensity) 177 M^+ (33), 105 (100), 77 (48), 51 (20). Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67,78; H, 6.27; N, 7.90. Found: C, 67.64; H, 6.30; N, 7.77.

Reaction of the *N*-Methyl Imine of Benzaldehyde (6) with Phenyl Acetoxy Tungsten Carbene Complex (9b). A mixture of the metal acylate **8b**[23] (599 mg, 1.15 mmol) and methylene chloride (2.3 mL) was degassed by the freeze–thaw method (−196 to 0 °C, three cycles) and cooled to −20 °C. Upon slow addition (over 5 min) of 1 equiv of acetyl bromide and bright yellow slurry turned dark purple. This mixture was stirred for 1 h at −20 °C, and then 1 equiv of degassed imine **6** (0.14 mL) was added via syringe pump over approximately 1 h. The reaction mixture turned bright orange-yellow after 1 h, but stirring was continued for 6 h. The workup and purification of this reaction mixture was the same as that above for the reaction of complex **9a**, except that a 1:1:10 solvent mixture was used as eluent. In addition to the imidate **14** (R_f 0.38; 33 mg, 0.28 mmol, 24%), a second fraction (R_f 0.13) was isolated and identified as the yellow crystalline organometallic complex **13b** (294 mg, 0.50 mmol, 43%); mp 112–115 °C dec. Spectra data for **13b**: ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 2.73 (s, 3 H), 6.79 (t, 2 H, J = 8.58 Hz), 7.14 (t, 1 H, J = 7.49 Hz), 7.22 (s, 2 H), 7.37–7.48 (m, 7 H), 8.34 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.77 (q, J = 130.0 Hz), 37.53 (q, J = 142.0 Hz), 93.93 (d, J = 164.3 Hz), 118.72 (d, J = 158.9 Hz), 125.51 (d, J = 158.0 Hz), 126.5 (d, J = 159.5 Hz), 128.6 (d, J = 159.0 Hz), 129.2 (d, J = 161.0 Hz), 129.7 (d, J = 159.6 Hz), 133.37 (s), 153.57 (s), 168.4 (s), 197.7 (s), 203.7 (s), 266.9 (s); IR (neat) 3060 w, 3030 w, 2966 w, 2064 w, 1976 s, 1920 s, 1762 m, 1496 m, 1451 m, 1441 m, 1400 m, 1373 m, 1215 m, 1074 m, 1025 m, 744 m, 704 m, 652 m cm^{-1}; mass spectrum m/e (% relative intensity) 563 (10), 533 (10), 505 (25), 481 (25), 449 (100), 178 (35), 147 (20), 119 (100), 91 (40), 77 (62). Anal. Calcd for $C_{22}H_{17}NO_7W$: C, 44.69; H, 2.90; N, 2.37. Found: C, 44.89; H, 2.92; N, 2.38.

The animal complex **13b** by ^{1}H NMR spectroscopy was a single diastereomer, which was assigned as *E* on the basis of the chemical shift of the *N*-methyl group (δ 2.73 ppm) and ultimately by X-ray diffraction analysis. Analysis of the ^{1}H NMR spectrum of the reaction mixture prior to purification reveals that the minimum ratio of *E*:*Z* isomers is 91:9 on the basis of the presence of unidentified singlets in the region expected for the absorption of the *N*-methyl group for the *Z* isomer (δ ~3.4–3.7 ppm). In the ^{1}H NMR spectrum of the purified **13b** the minimum ratio of *E*:*Z* is 170:1.

X-ray Data Collection, Structure Determination, and Refinement for 13b. A yellow single crystal of **13b** was mounted on a pin and transferred to the goniometer. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. Successful refinement of the structure was carried out in the centric space group $P\bar{1}$. A summary of data collection parameters is given in Table III.

The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The methyl hydrogen atoms are included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, B = 5.5 Å^2). Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.046 and R_w = 0.050. The final values of the positional parameters are given in Table IV, and the bond distances and angles are given in Table V. The

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(33) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72, 99, 149 (present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands).

(34) Sheldrick, G. M. SHELXS. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: London, 1985; pp 175–189.

Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	**13b**
color/shape	yellow/parllelepiped
fw	591.23
space group	$P\bar{1}$
temp, °C	22
cell constants	
a, Å	8.269 (3)
b, Å	10.766 (5)
c, Å	13.851 (7)
α, deg	68.83 (5)
β, deg	75.97 (6)
γ, deg	81.39 (4)
cell vol, Å^3	1113
formula units/unit cell	2
D_{calc}, g cm^{-3}	1.76
μ_{calc}, cm^{-1}	54.6
diffractometer/scan	Enraf-Nonius CAD-4/ω–2θ
range of rel transmissn factors, %	94/100
radiation (graphite monochromator)	MoKα (λ = 0.710 73 Å)
max cryst dimens, mm	0.10 × 0.15 × 0.20
scan width, deg	0.80 + 0.35 tan θ
std rflns	300, 030, 003
decay of standards, %	±1
no. of reflns measd	3901
2θ range, deg	2 ≤ 2θ ≤ 50
range of h,k,l	+9,±12,±16
no. of reflns obsd [$F_o \geq 5\sigma(F_o)$][b]	2267
computer programs[c]	SHELX[32]
structure soln	SHELXS[34]
no. of params varied	286
weights	$[\sigma(F_o) + 0.0001F_o^2]^{-1}$
GOF	0.66
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.046
R_w	0.050
largest feature final diff map, e Å^{-3}	0.7

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections, $\theta > 15°$. [b] Corrections: Lorentz-polarization and absorption (empirical, ψ scan). [c] Neutral scattering factors and anomalous dispersion corrections from ref 33.

Table IV. Final Fractional Coordinates for 13b

atom	x/a	y/b	z/c	B(eqv),[a] Å^2
W	0.98307 (8)	0.81080 (6)	0.8012 (5)	2.32
O(1)	1.073 (2)	0.789 (1)	1.047 (1)	6.45
O(2)	0.621 (1)	0.717 (1)	0.945 (1)	5.62
O(3)	1.079	0.501 (1)	0.882 (1)	5.14
O(4)	0.801 (1)	1.094 (1)	0.8215 (9)	4.51
O(5)	0.933 (1)	0.851 (1)	0.6005 (9)	4.87
O(6)	1.356 (1)	0.7773 (9)	0.5571 (7)	3.17
O(7)	1.224 (1)	0.593 (1)	0.5858 (9)	4.69
N	1.365 (1)	0.8494 (9)	0.6927 (8)	2.10
C(1)	1.039 (2)	0.794 (2)	0.973 (1)	3.58
C(2)	0.753 (2)	0.751 (2)	0.903 (1)	3.68
C(3)	1.052 (2)	0.612 (2)	0.860 (1)	3.94
C(4)	0.875 (2)	0.996 (1)	0.821 (1)	3.30
C(5)	0.948 (2)	0.831 (1)	0.688 (1)	3.02
C(6)	1.237 (2)	0.892 (1)	0.753 (1)	2.57
C(7)	1.261 (2)	1.018 (1)	0.765 (1)	2.88
C(8)	1.214 (2)	1.141 (1)	0.700 (1)	4.21
C(9)	1.240 (3)	1.359 (2)	0.706 (2)	6.38
C(10)	1.311 (3)	1.249 (2)	0.791 (2)	8.02
C(11)	1.365 (3)	1.132 (2)	0.857 (2)	6.97
C(12)	1.337 (2)	1.011 (2)	0.847 (1)	4.49
C(13)	1.523 (2)	0.918 (1)	0.646 (1)	3.51
C(14)	1.363 (2)	0.729 (1)	0.666 (1)	2.86
C(15)	1.518 (2)	0.634 (1)	0.691 (1)	2.95
C(16)	1.645 (2)	0.620 (2)	0.611 (1)	3.59
C(17)	1.789 (2)	0.536 (2)	0.638 (2)	4.84
C(18)	1.792 (2)	0.466 (2)	0.740 (2)	5.43
C(19)	1.660 (2)	0.480 (2)	0.821 (2)	5.16
C(20)	1.523 (2)	0.564 (2)	0.794 (1)	3.64
C(21)	1.278 (2)	0.697 (2)	0.526 (1)	3.43
C(22)	1.261 (3)	0.765 (2)	0.414 (1)	5.00

[a] B(eqv) = $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table V. Bond Distances (Å) and Angles (deg) for 13b

	Distances		
W-C(1)	2.08 (2)	W-C(2)	2.01 (2)
W-C(3)	2.05 (2)	W-C(4)	2.03 (1)
W-C(5)	1.99 (2)	W-C(6)	2.25 (1)
O(1)-C(1)	1.11 (2)	O(2)-C(2)	1.15 (2)
O(3)-C(3)	1.12 (2)	O(4)-C(4)	1.14 (2)
O(5)-C(5)	1.19 (2)	O(6)-C(14)	1.42 (2)
O(6)-C(21)	1.38 (2)	O(7)-C(21)	1.19 (2)
N-C(6)	1.32 (2)	N-C(13)	1.49 (1)
N-C(14)	1.47 (2)	C(6)-C(7)	1.48 (2)
C(7)-C(8)	1.36 (2)	C(7)-C(12)	1.41 (2)
C(8)-C(9)	1.35 (2)	C(9)-C(10)	1.40 (3)
C(10)-C(11)	1.35 (3)	C(11)-C(12)	1.41 (2)
C(14)-C(15)	1.54 (2)	C(15)-C(16)	1.36 (2)
C(15)-C(20)	1.36 (2)	C(16)-C(17)	1.42 (2)
C(17)-C(18)	1.35 (2)	C(18)-C(19)	1.39 (2)
C(19)-C(20)	1.38 (2)	C(21)-C(22)	1.49 (2)
	Angles		
C(1)-W-C(2)	91.4 (6)	C(1)-W-C(3)	89.0 (6)
C(2)-W-C(3)	85.4 (6)	C(1)-W-C(4)	88.1 (6)
C(2)-W-C(4)	84.4 (6)	C(3)-W-C(4)	169.3 (6)
C(1)-W-C(5)	175.3 (6)	C(2)-W-C(5)	93.3 (6)
C(3)-W-C(5)	91.4 (6)	C(4)-W-C(5)	92.4 (6)
C(1)-W-C(6)	86.4 (5)	C(2)-W-C(6)	175.6 (6)
C(3)-W-C(6)	98.4 (6)	C(4)-W-C(6)	91.6 (5)
C(5)-W-C(6)	88.9 (5)	C(14)-O(6)-C(21)	115 (1)
C(6)-N-C(13)	123 (1)	C(6)-N-C(14)	123 (1)
C(13)-N-C(14)	114 (1)	W-C(1)-O(1)	178 (1)
W-C(2)-O(2)	179.7 (9)	W-C(3)-O(3)	175 (1)
W-C(4)-O(4)	173 (1)	W-C(5)-O(5)	176 (1)
W-C(6)-N	130.5 (9)	W-C(6)-C(7)	115.8 (9)
N-C(6)-C(7)	114 (1)	C(6)-C(7)-C(8)	124 (1)
C(6)-C(7)-C(12)	118 (1)	C(8)-C(7)-C(12)	118 (1)
C(7)-C(8)-C(9)	126 (2)	C(8)-C(9)-C(10)	115 (2)
C(9)-C(10)-C(11)	123 (2)	C(10)-C(11)-C(12)	119 (2)
C(7)-C(12)-C(11)	118 (2)	O(6)-C(14)-N	105 (1)
O(6)-C(14)-C(15)	114 (1)	N-C(14)-C(15)	111 (1)
C(14)-C(15)-C(16)	120 (1)	C(14)-C(15)-C(20)	118 (1)
C(16)-C(15)-C(20)	112 (1)	C(15)-C(16)-C(17)	118 (2)
C(16)-C(17)-C(18)	120 (2)	C(17)-C(18)-C(19)	121 (2)
C(18)-C(19)-C(20)	119 (2)	C(15)-C(20)-C(19)	120 (2)
O(6)-C(21)-O(7)	123 (1)	O(6)-C(21)-C(22)	110 (1)
O(7)-C(21)-C(22)	127 (1)		

thermal parameters, least-squares planes, final fractional coordinates for hydrogen, and observed and calculated structure factors can be found in the supplementary material.

Base Hydrolysis of 13b to the Amino Complex 15b. The tungsten complex **13b** (44 mg, 0.074 mmol) was dissolved in THF (2.5 mL), and 1.0 mL of 10 M aqueous NaOH was slowly added. After it was stirred for 2 h at room temperature, the mixture was neutralized and worked up by extracting with ether (3 × 20 mL). The ether extracts were washed with brine, dried over $MgSO_4$, filtered through Celite, and concentrated to a yellow oil. The crude reaction mixture was chromatographed on silica gel with a 1:1:10 mixture of ether/methylene chloride/hexane, and two fractions were collected. The first fraction (9.8 mg, 0.027 mmol) was identified by ^1H NMR spectroscopy as the *E* isomer of the amino complex **15b**, and the second fraction (9.0 mg, 0.024 mmol) was found to be a 1:1 mixture of the *E* and *Z* isomers of **15b**. The total yield of **15b** was 69% (0.051 mmol). The recorded ^1H NMR spectra for **15b-*E*** and **15b-*Z*** match very closely those that have been previously reported.[13] Spectral data: **15b-*E***, ^1H NMR δ 2.91 (d, 3 H, J = 5.1 Hz), 6.82 (d, 2 H, J = 8.0 Hz), 7.20 (t, 1 H, J = 7.5 Hz), 7.40 (t, 2 H, J = 7.8 Hz), 8.92 (broad, 1 H); **15b-*Z***, ^1H NMR (from *E* and *Z* mixture) δ 3.64 (d, 3 H, J = 5.1 Hz), 7.03 (d, 3 H, J = 8.0 Hz), 7.27 (t, 1 H), 7.36 (t, 2 H, J = 7.9 Hz), 8.55 (broad, 1 H).

Synthesis of the (*p*-Methylbenzoyl)pentacarbonyltungsten Tetramethylammonium Salt 8c. A solution of 4-bromotoluene (1.75 g, 10.23 mol) in THF (54.0 mL) was cooled to −78 °C, and 2 equiv of *n*-butyllithium was slowly added. This mixture was stirred for 1.5 h at −78 °C; then it was transferred via cannula to a slurry of $W(CO)_6$ in ether at 0 °C. The resulting red/orange solution was warmed to room temperature and stirred for 2 h. The solvent was removed, and the residue was dissolved in water that was deoxygenated by purging with nitrogen for 15 min. This orange/yellow solution was filtered through Celite, and then 10 mL of a saturated solution of tetrabutylammonium bromide was added. Immediately a brown/orange precipitate fell out of solution. The wet salt was dried overnight on a vacuum line and then crystallized from methylene chloride to give 2.63 g (5.09 mmol, 49.8%) of **8c** as an orange solid. Spectral data for **8c**: ^1H NMR ($CDCl_3$) δ 2.27 (s, 3 H), 3.42 (s, 12 H), 7.09 (d, 2 H, 7.78 Hz), 7.45 (d, 2 H, J = 8.03 Hz); ^{13}C NMR ($CDCl_3$) δ 20.88, 55.64, 126.81, 128.29, 138.11, 154.64, 204.43, 206.00, 208.32.

Reaction of the *N*-Methyl Imine of Benzaldehyde (6) with the *p*-Methylphenyl Acetoxy Tungsten Carbene Complex 9c. This reaction was carried out with the procedure described for tungsten complex **9b** by starting with the salt **8c** (599 mg, 1.15 mmol), 2.3 mL of methylene chloride, 0.078 mL (1.05 mmol) of acetyl bromide, and 1 equiv of the imine **6** (0.143 mL, 1.16 mmol). The products were isolated by chromatography on silica gel with a 1:1:13 mixture of ether/methylene chloride/hexane as eluent. The first to elute was the imidate **23** (R_f 0.55; 72 mg, 0.165 mmol, 16%). Spectral data for **23**: ^1H NMR ($CDCl_3$) δ 2.29 (s, 3 H), 2.42 (s, 3 H), 3.21 (s, 3 H), 7.27 (d, 2 H, J = 8.02 Hz), 7.53 (d, J = 8.13 Hz); ^{13}C NMR ($CDCl_3$) δ 21.59, 25.73, 34.47, 128.72, 129.39, 132.19, 143.29, 173.50, 174.20; IR (neat) 2900 w, 1690 s, 1662 m, 1610 w, 1370 w, 1320 s, 1286 s, 1035 m, 1014 m cm^{-1}; mass spectrum *m/e* (% relative intensity) 191 M (8), 163 (10), 119 (100), 91 (30), 65 (10); calcd for $C_{11}H_{13}O_2N$ *m/e* 191.0946, measured *m/e* 191.0947.

The imine insertion product **13c** (R_f 0.26; 304 mg, 0.62 mmol, 59%) eluted second. Spectral data for **13c**: ^1H NMR ($CDCl_3$) δ 2.35 (s, 3 H), 2.38 (s, 3 H), 2.74 (s, 3 H), 6.73 (t, 2 H, J = 9.9 Hz), 7.22 (m, 2 H), 7.49 (m, 5 H), 8.38 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 20.79 (q, J = 130.34 Hz), 21.05 (q, J = 126.82 Hz), 37.46 (q, J = 141.07 Hz), 94.02 (d, J = 161.84 Hz), 118.62 (d, J = 158.4 Hz), 125.49 (d, J = 158.4 Hz), 129.08 (d, J = 161.83 Hz), 129.15 (d, J = 162.03 Hz), 129.64 (d, J = 161.95 Hz), 133.42 (s), 136.10 (s), 151.02 (s), 168.32 (s), 197.73 (s), 203.82 (s), 267.67 (s); IR (neat) 2900 w, 2064 s, 1977 s, 1919 s, 1770 m, 1753 m, 1507 w, 1495 m, 1400 w, 1211 m, 1026 m cm^{-1}. Anal. Calcd for $C_{23}H_{19}NO_7W$: C, 45.64; H, 3.16; N, 2.31. Found: C, 45.60; H, 3.21; N, 2.46.

The aminal complex **13c** by ^1H NMR spectroscopy was a single diastereomer, which was assigned as *E* on the basis of the chemical shift of the *N*-methyl group (δ 2.74 ppm). Analysis of the ^1H NMR spectrum of the reaction mixture prior to purification reveals that the minimum ratio of *E*:*Z* isomers is 87:13 on the basis of the presence of unidentified singlets in the region expected for the absorption of the *N*-methyl group for the *Z* isomer (δ ~3.4–3.7 ppm). In the ^1H NMR spectrum of the purified **13c** the minimum ratio of *E*:*Z* is 100:1.

Base Hydrolysis of 13c to the Amino Complex 15c. The procedure for the hydrolysis of **13c** was similar to that described for tungsten complex **13b**. Tungsten complex **13c** (160 mg, 0.26 mmol) was dissolved in THF (5 mL), and 1.0 mL of 2.5 M aqueous NaOH was added slowly. After it was stirred for 2 h at room temperature, the mixture was neutralized and worked up. The product was purified by chromatography on silica gel with a 1:1:10 mixture of ether/methylene chloride/hexane as eluent to give 57.3 mg (0.125 mmol, 48%) of **15c** as a single isomer. Spectral data for **15c**: ^1H NMR ($CDCl_3$) δ 2.37 (s, 3 H), 2.90 (d, 3 H, J = 6.11 Hz), 6.72 (d, 2 H, J = 7.95 Hz), 7.19 (d, 2 H, J = 7.77 Hz), 8.90 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.12 (q, J = 126.5 Hz), 37.36 (q, J = 141.06 Hz), 119.79 (d, J = 165.31 Hz), 129.09 (d, J = 158.48 Hz), 137.02 (s), 147.12 (s), 203.81 (s), 262.92 (s); IR (neat) 2900 w, 2064 s, 1979 s, 1919 s, 1770 m, 1753 m, 1507 w, 1495 m, 1400 w, 1211 m, 1026 m cm^{-1}; mass spectrum *m/e* (% relative intensity) 457 M (27), 429 (28), 373 (100), 345 (50), 315 (62), 288 (33), 157 (40), 119 (45), 91 (32); calcd for $C_{14}H_{11}NO_5{}^{182}W$ *m/e* 455.0120, measured *m/e* 455.0122; calcd for $C_{14}H_1NO_5{}^{184}W$ *m/e* 457.0150, measured *m/e* 457.0161; calcd for $C_{14}H_1NO_5{}^{186}W$ *m/e* 459.0182, measured *m/e* 459.0185.

The amino complex **15c** by ^1H NMR spectroscopy was a single diastereomer, which was assigned as *E* on the basis of the chemical shift of the *N*-methyl group (δ 2.90 ppm). Analysis of the ^1H NMR spectrum of the reaction mixture prior to purification reveals that the minimum ratio of *E*:*Z* isomers is 100:1 on the basis of the presence of unidentified singlets in the region expected for the absorption of the *N*-methyl group for the *Z* isomer (δ ~3.4–3.7

ppm). In the ^1H NMR spectrum of the purified **15c** the minimum ratio of *E*:*Z* is 95:5.

Generation of the *N*-Trimethylsilyl Imine of Benzaldehyde (24a). Benzaldehyde (0.58 mL, 5.7 mmol) was dissolved in THF (11.4 mL, 0.5 M solution) and cooled to −40 °C. Lithium bis(trimethylsilyl)amide (5.7 mL of a 1 M solution in THF) was added slowly, and then the mixture was stirred for 45 min. Trimethylsilyl chloride (1 equiv) was added to quench the reaction, and the solvent was removed carefully on a rotary evaporator and then on a vacuum line. The remaining yellow oil was dissolved in cold (0 °C) methylene chloride to obtain an approximately 1 M solution of the silyl imine. This solution was deoxygenated by the freeze–thaw process (−196 to 0 °C, three cycles) and was used directly in reactions with alkoxy and acetoxy carbene complexes.

Generation of the *N*-Trimethylsilyl Imine of Acetaldehyde (24b). Acetaldehyde was condensed with use of liquid N_2 into a small graduated tube to a measured volume and then dissolved carefully in cold THF (0 °C) to obtain a solution of the desired molarity (2.21 M). The acetaldehyde solution (2.3 mL, 5.0 mmol) was then added to more cold THF (3 mL at −40 °C) in a reaction flask. Lithium bis(trimethylsilyl)amide (5.0 mL of a 1 M solution in THF) was added slowly, and then the mixture was stirred for 45 min at −40 °C. Trimethylsilyl chloride (1 equiv) was added to quench the reaction, and after 10 min the solution was concentrated to ~2–3 mL on a vacuum line at −40 °C and then used directly in reactions with alkoxy and acetoxy carbene complexes.

Preparation of Pentacarbonyl[phenyl[(phenylmethylene)amino]methylene]chromium (26a) from Acetoxy Complex 9a. A slurry of tetramethylammonium chromium acylate **8a**[23] (425 mg, 1.14 mmol) and methylene chloride (1.9 mL) was deoxygenated by the freeze–thaw method (−196 to 0 °C, three cycles) and cooled to −20 °C. Upon slow addition (over 5 min) of 1 equiv of acetyl bromide the yellow slurry turned very dark purple. This mixture was stirred for 1 h at −20 °C, and then approximately 5 equiv of a deoxygenated 1 M solution of silyl imine **24a** (see preparation above) in methylene chloride was added via cannula. The reaction mixture turned light red and cloudy and was stirred for 2 h at −20 °C. The reaction mixture was warmed to room temperature and diluted with methylene chloride (50–100 mL) and then with an equal volume of hexane to precipitate out salts. The crude mixture was filtered through Celite and concentrated, and the resulting orange/red oil was chromatographed on silica gel with a 1:1:10 mixture of methylene chloride/ether/hexane. The imino complex **26a** (282 mg, 0.73 mmol, 64%) was isolated (R_f 0.21) as an orange/red oil that solidified very quickly upon complete removal of solvent: mp 73–74 °C (lit.[21c] mp 74 °C). Spectral data for **26a**: ^1H NMR (CD_2Cl_2) δ 7.42–7.50 (m, 5 H), 7.51–7.59 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 111.97, 126.94, 127.87, 128.35, 128.88, 129.71, 130.92, 132.48, 139.18, 209.58, 217.22, 223.61; IR (neat) 2056 s, 1977 s, 1921 s, 659 s cm^{-1}; mass spectrum *m/e* (% relative intensity) 385 M^+ (0.4), 357 (0.3), 329 (0.9), 273 (4), 245 (18), 193 (15), 165 (5), 142 (10), 105 (18), 103 (32), 58 (100), 52 (16); calcd for $C_{19}H_{11}CrNO_5$ *m/e* 385.0042, measured *m/e* 385.0041.

Preparation of Pentacarbonyl[phenyl(ethylideneamino)methylene]chromium (26b) from Acetoxy Complex 9a. The preparation of **26b** was carried out on a 1.13-mmol scale for the metal acylate **8a**[23] according to the procedure described above for complex **26a** with the reaction parameters indicated in Table I. Several organometallic products were observed by TLC, but only the imino complex **26b** survived chromatography on silica gel in the presence of air. The imino complex **26b** (R_f 0.22) was obtained in 43% yield (158 mg, 0.49 mmol) as an orange/red solid: mp 56.5–58 °C (lit.[21b] mp 58 °C). Spectral data for **26b**: ^1H NMR ($CDCl_3$) δ 2.17 (d, 3 H, *J* = 5.6 Hz), 6.75 (q, 1 H, *J* = 5.6 Hz), 7.43 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.50 (q, *J* = 131 Hz), 110.37 (d, *J* = 179 Hz), 126.36 (d, *J* = 161 Hz), 128.74 (d, *J* = 161 Hz), 130.51 (d, *J* = 161 Hz), 139.72 (s), 203.81 (s), 217.42 (s), 223.65 (s); IR ($CHCl_3$) 2056 s, 1974 m, 1918 s, 1444 w, 1148 w, 840 w, 691 w, 640 w cm^{-1}; mass spectrum *m/e* (% relative intensity) 323 M^+ (5), 295 (5), 239 (10), 211 (24), 183 (70), 155 (66), 103 (27), 52 (100); calcd for $C_{14}H_9CrNO_5$ *m/e* 322.9885, measured *m/e* 322.9877.

Preparation of [Methyl[(phenylmethylene)amino]methylene]pentacarbonylchromium (26c) from Acetoxy Complex 9d. The preparation of **26c** was carried out on a 1.63-mmol scale for the metal acylate **8d**[23] according to the procedure described above for complex **26a** with the reaction parameters indicated in Table I. Several organometallic products were observed by TLC, but only the imino complex **26c** survived chromatography on silica gel in the presence of air. The imino complex **26c** (R_f 0.28) was obtained in 44% yield (225 mg, 0.697 mmol) as an orange/red solid: mp 90.5 °C (lit.[21c] mp 87 °C, lit.[21a] mp 93 °C). Spectral data for **26c**: ^1H NMR (CD_2Cl_2) δ 2.66 (d, 3 H, *J* = 2.3 Hz), 7.21 (q, 1 H, *J* = 2.3 Hz), 7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 34.13 (q, *J* = 132 Hz), 110.44 (d, *J* = 179 Hz), 128.05 (d, *J* = 160 Hz), 128.31 (s), 129.56 (d, *J* = 163 Hz), 132.19 (d, *J* = 163 Hz), 208.33 (s), 217.19 (s), 223.34 (s); IR ($CHCl_3$) 2922 m, 2857 m, 2056 s, 1975 m, 1933 s, 1602 m, 1111 m cm^{-1}; mass spectrum *m/e* (relative intensity) 323 M^+ (16), 239 (12), 211 (22), 183 (100), 142 (98), 89 (50). Anal. Calcd for $C_{14}H_9CrNO_5$: C, 52.03; H, 2.91; N, 4.33; Cr, 16.09. Found: C, 52.10; H, 2.86; N, 4.40; Cr, 16.21.

Preparation of [*tert*-Butyl[(phenylmethylene)amino]methylene]pentacarbonylchromium (26d) from Acetoxy Complex 9e. To a slurry of chromium hexacarbonyl (10.3 g, 47.0 mmol) in 100 mL of ether was added tBuLi (28 mL, 47.6 mmol) at 25 °C and the solution stirred for 5 h. The ether was removed by a rotary evaporator that was vented with nitrogen and then the remaining solid dissolved in water (100 mL) that was deoxygenated by purging with nitrogen and cooled to 0 °C; then an excess of tetramethylammonium bromide was added as a saturated deoxygenated aqueous solution. The reaction mixture was kept under nitrogen flow at all times. The solution was stirred for 2 h and quickly filtered to give tetramethylammonium [*tert*-butyl(oxido)methylene]pentacarbonylchromate (^1H NMR ($CDCl_3$) δ 1.27 (s, 9 H), 3.42 (bs, 12 H)) as a red-brown solid (7.12 g, 20.3 mmol, 43%), which was placed under vacuum to dry.

A slurry of the above salt (2.12 g, 6.04 mmol) and methylene chloride (14 mL) was deoxygenated by the freeze–thaw method (−196 to 0 °C, three cycles), cooled to −70 °C, and treated with acetyl bromide (0.45 mL, 6.09 mmol). This mixture was stirred for 5 h at −70 °C, and 5 equiv of silyl imine **24a** (prepared as a solution described above) was added via cannula. The reaction mixture was warmed to −35 °C and allowed to react overnight. The reaction mixture was filtered through Celite and concentrated. The remaining oil was chromatographed with a 1:1:20 mixture of ether/methylene chloride/hexane to give the imino complex **26d** (569 mg, 1.56 mmol, 26%) as an orange solid: mp 65–67 °C. Spectral data for **26d**: ^1H NMR ($CDCl_3$) δ 1.32 (s, 9 H), 7.06 (s, 1 H), 7.42 (m, 2 H), 7.47 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 28.96 (q, J_{C-H} = 127 Hz), 46.30 (s), 108.78 (d, J_{C-H} = 185 Hz), 127.49 (d, J_{C-H} = 159 Hz), 128.39 (s), 129.62 (d, J_{C-H} = 160 Hz), 131.96 (d, J_{C-H} = 162 Hz), 210.79 (s), 217.75 (s), 223.18 (s); IR (neat) 2968 w, 2053 s, 1973 m, 1909 s, 1463 w, 1365 w, 1073 w, 749 w, 688 w, 656 s cm^{-1}; mass spectrum *m/e* (% relative intensity) 365 M^+ (5), 377 (4), 309 (5), 281 (5), 253 (15), 225 (100), 208 (3), 180 (2), 169 (7), 158 (8), 142 (39), 135 (2), 117 (16), 105 (2), 89 (5), 79 (3), 75 (1), 68 (4), 64 (2). Anal. Calcd for $C_{17}H_{15}CrNO_5$: C, 55.89; H, 4.14; N, 3.83. Found: C, 56.23; H, 4.20; N, 3.77.

Preparation of Pentacarbonyl[phenyl[(phenylmethylene)amino]methylene]tungsten (26e) from Acetoxy Complex 9b. The preparation of **26e** was carried out on a 0.79-mmol scale from the metal acylate **8b**[23] according to the procedure described above for complex **26a** with the reaction parameters indicated in Table I. A single organometallic product was observed by TLC and purified by chromatography on Florisil in the presence of air. The imino complex **26e** (R_f 0.22) was obtained in 60% yield (245 mg, 0.47 mmol) as an orange/red solid: mp 70–72 °C. Spectral data for **26c**: ^1H NMR ($CDCl_3$) δ 7.38 (s, 1 H), 7.42 (m, 3 H), 7.50 (m, 5 H), 7.54 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 113.41, 127.23, 128.56, 128.80, 128.99, 131.61, 132.57, 138.92, 192.78, 198.50, 202.93; IR (neat) 3003 w, 2354 w, 2063 s, 1974 m, 1910 s, 1445 m, 1200 m, 1176 m, 1130 m, 834 m, 764 m, 749 m, 687 m, 653 m cm^{-1}; mass spectrum *m/e* (% relative intensity) 517 M^+ (23, ^{184}W), 489 (15), 461 (23), 433 (15), 405 (50), 377 (95), 350 (100), 322 (25), 272 (35), 246 (18), 174 (23), 103 (30), 89 (30). Anal. Calcd for $C_{19}H_{11}NO_5W$: C, 44.13; H, 2.14; N, 2.71. Found: C, 43.97; H, 2.18; N, 2.66.

Preparation of Pentacarbonyl[phenyl(ethylideneamino)methylene]tungsten (26f) from Acetoxy Complex 9b.

The preparation of **26f** was carried out on a 1.3-mmol scale from the metal acylate **8b**[23] according to the procedure described above for complex **26a** with the reaction parameters indicated in Table I. A single organometallic product was observed by TLC and purified by chromatography on Florisil in the presence of air. The imino complex **26e** (R_f 0.22) was obtained in 36% yield (212 mg, 0.47 mmol) as an orange/yellow solid: mp 87-88 °C. Spectral data for **26c**: ^{1}H NMR ($CDCl_3$) δ 2.20 (d, 3 H, J = 5.61 Hz), 6.70 (q, 1 H, J = 5.61 Hz), 7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.53 (q, J = 131.2 Hz), 112.00 (d, J = 184.51 Hz), 128.23 (d, J = 159.65 Hz), 128.84 (d, J = 165.66 Hz), 131.24 (d, J = 161.69 Hz), 139.33 (s), 186.35 (s), 198.71 (s), 203.31 (s); IR (neat) 2952 m, 2924 s, 2854 m, 2063 w, 1970 w, 1927 s, 1458 w, 1377 w, 699 w cm^{-1}; mass spectrum m/e (% relative intensity) 455 M$^+$ (45, ^{184}W), 427 (15), 399 (15), 371 (36), 343 (36), 343 (84), 317 (100), 286 (65), 272 (41), 258 (25), 156 (25), 84 (35). Anal. Calcd for $C_{14}H_9NO_5W$: C, 36.95; H, 1.99; N, 3.08. Found: C, 36.86; H, 1.95; N, 3.00.

General Procedure for the Reaction of the Methoxy Complexes 1 with *N*-Silyl Imines: Preparation of Pentacarbonyl[methyl[(phenylmethylene)amino]methylene]tungsten (26g). A solution of the silyl imine **24a** (9.35 mmol) in methylene chloride prepared as described above was quickly transferred by syringe to a solution of the methyl methoxy tungsten complex **1d**[25] (2.92 g, 7.62 mmol) in methylene chloride (15 mL) at -20 °C. The solution was warmed to 0 °C slowly over 30 min and then to room temperature for 30 min. The solution was quenched with saturated $NaHCO_3$ and separated. The organic layer was washed with brine (1×), dried over $MgSO_4$, and concentrated. The remaining oil was chromatographed in 1:4 benzene/hexane to give the starting complex (1.07 g, 2.81 mmol, 37%) as a yellow solid and the imino complex **26g** (538 mg, 1.18 mmol, 16%) as an orange-yellow solid: mp 91-92 °C. Spectral data for **26g**: ^{1}H NMR ($CDCl_3$) δ 2.80 (d, 3 H, J = 2.3 Hz), 7.11 (q, 1 H, J = 2.2 Hz), 7.48 (m, 2 H), 7.54 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 35.91 (q, J_{C-H} = 132 Hz), 111.14 (d, J_{C-H} = 185 Hz), 127.51 (s), 128.12 (d, J_{C-H} = 160 Hz), 129.51 (d, J_{C-H} = 164 Hz), 132.15 (d, J_{C-H} = 162 Hz), 189.29 (s), 198.30 (s), 203.34 (s); IR (neat) 3069 w, 3041 w, 2968 m, 2920 m, 2351 w, 2063 s, 1972 sh, 1906 s, 1599 w, 1497 w, 1467 m, 1427 w, 1409 m, 1350 w, 1316 w, 1229 m, 1193 w, 1173 m, 1070 m, 1002 w, 926 m, 866 m, 823 w, 750 s, 688 s cm^{-1}; mass spectrum m/e (% relative intensity) 455 M$^+$ (10, ^{184}W), 427 (9), 399 (9), 371 (17), 343 (33), 330 (11), 315 (75), 302 (11), 286 (37), 272 (36), 260 (16), 247 (11), 233 (21), 222 (10), 210 (11), 191 (9), 178 (50), 156 (21), 143 (15), 130 (51), 115 (74), 103 (97), 90 (100), 77 (84), 69 (9); calcd for $C_{14}H_9NO_5W$ m/e 454.9991, measd m/e 454.9997.

It was subsequently found that it is not necessary to deoxygenate the reaction mixture by the freeze-thaw method but rather this can be done in a flask flushed with argon. This reaction can produce varying amounts of an unidentified polar, red compound whose formation can be suppressed if the reaction is quenched with 1.0 M aqueous HCl. The imino complexes **26a,c,d** were prepared from the methoxy complexes **1a**,[27] **1b**,[25] and **1c**[29] according to the above procedure with the reaction times and equivalents of *N*-silyl imine indicated in Table II. The spectral data for imino complexes **26a,c,d** are presented above.

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Supplementary Material Available: Listings of thermal parameters, least-squares planes, and final fractional coordinates for hydrogen atoms (3 pages); a listing of the observed and calculated structure factors for the X-ray diffraction analysis of compound **13b** (5 pages). Ordering information is given on any current masthead page.

C-Glycoside Synthesis by Palladium-Catalyzed Iodoaglycon–Glycal Coupling

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Efficient coupling of iodo derivatives of anthracycline aglycons with furanoid and pyranoid glycals has been achieved with use of stoichiometric portions of the reactants in the presence of catalytic amounts of palladium(II) acetate and a tertiary amine in dimethylformamide solution at room temperature. This procedure, which occurs regio- and stereospecifically, is an effective route to aryl *C*-glycosides. Demonstration of the efficacy of this palladium-mediated coupling reaction was illustrated by its use in a one-pot four-step sequence that produced the anthracycline *C*-glycoside 4-[2′-deoxy-3′,5′-diacetyl-β-D-*ribo*(=*arabino*)-furanosyl]-8-ethyl-1-methoxybenzo[*d*]naphtho[1,2-*b*]pyran-6-one in 94% isolated yield.

An efficient route to *C*-glycosides[1] developed in our laboratory[2-5] involves, as a key step, palladium-mediated coupling of a 1,2-unsaturated carbohydrate (glycal) with a suitable derivative of an aromatic or heterocyclic aglycon in a regio- and stereospecific[6,7] manner. This reaction utilizes aryl mercurials[3-5] or arylstannanes[2] as aglycon precursors and requires stoichiometric palladium to form the reactive arylpalladium reagent.[6,8] The study of factors that affect the palladium-mediated coupling of enol ethers with aryl halides has led to the development of a glycal-aglycon coupling reaction requiring only catalytic palla-

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