Chromium-53 Nuclear Magnetic Resonance Studies of Pentacarbonylchromium–Carbene Complexes[†]

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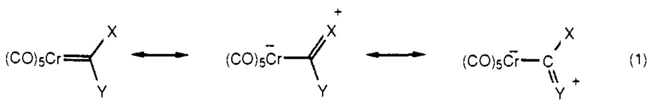
Abstract: The ^{53}Cr NMR spectra of 46 chromium–carbene complexes were recorded, and chemical shift and line width data are reported, along with associated infrared, UV–visible, and ^{13}C NMR spectroscopic data. The ^{53}Cr chemical shifts correlated very well with the donor–acceptor properties of the carbene ligand and were quite sensitive to steric influences on efficiency of π-overlap of the heteroatom with the carbene carbon. There was no correlation of $\delta(^{53}\text{Cr})$ with reactivity toward imines to form β-lactams, but line width appeared to be related to reactivity. Preliminary attempts to utilize ^{53}Cr NMR data to direct synthetic utilization of chromium–carbene complexes are reported.

Heteroatom-stabilized "Fischer" chromium carbene complexes[1] (e.g., **1–46**) were first prepared about 20 years ago by the reaction of organolithium reagents with chromium hexacarbonyl, followed by O-alkylation of the resulting acylate complex.[2] This procedure, by necessity, produces alkoxycarbene complexes, and it remains the most commonly used approach to these complexes, although a complementary procedure involving the reaction of chromium pentacarbonyl dianion with acid halides has recently been developed.[3] Methoxy *alkyl*carbene complexes have been further elaborated by aldol-condensation reactions at the α-position,[4] while vinylcarbene complexes undergo facile cycloaddition chemistry (Diels–Alder),[5] broadening the range of alkoxycarbene complexes available. Aminocarbene complexes are usually prepared by exchange processes involving displacement of alkoxy groups from alkoxycarbenes, although this route is limited to sterically unhindered amines.[6] A more versatile procedure involving the reaction of chromium pentacarbonyl dianion with dialkylamides and trimethylsilyl chloride has recently been developed.[7]

The motivation for much of the recent research into syntheses of functionalized carbene complexes is their increased use as reagents in organic synthesis.[8] Thermal reactions of (alkoxy)(aryl) or vinyl carbene complexes with alkynes have been used to synthesize hydroquinone,[9] heteroaromatic,[10] and cyclic ketone[11] derivatives. Similar thermal reactions of (amino)(aryl) carbenes produced indenones or amino indenes.[12] Thermal reactions of methoxycarbene complexes with isonitriles produced cyclic bis imines,[13] while reaction with allenes produced carbocycles.[14] Photolytic reaction of methoxy[15] and amino[16] carbene complexes with imines produced β-lactams and with nucleophiles produced α-amino acid derivatives.[17]

The application of chromium carbene complexes to organic synthesis is quite a recent phenomenon, and the bulk of previous research concerning chromium carbene complexes focussed on the use of crystallographic and spectroscopic techniques to elucidate the structural, electronic, physical, and chemical nature of the carbene ligand itself and to probe the extent of interactions of the carbene ligand with the chromium pentacarbonyl fragment. In chromium carbene complexes, the three groups attached to the sp^2-hybridized carbene carbon—the metal, the heteroatom, X, and the other group, Y—are all potentially engaged in π-bonding with the carbene carbon. Depending on the relative π-donor abilities of these groups, the appropriate description of the bonding lies somewhere between the three extremes shown in eq 1.



(1)

I (Cr π-donor) II (X-π-donor) III (Y-π-donor)

By correlating X-ray crystallographic bond lengths with bond orders in closely related systems, it was shown that carbenes for which X was a thio or oxy functional group (X = SR, OR, OTMS, OH) had the shortest $\text{Cr–C}_{\text{carbene}}$ bond lengths, indicating substantial π-donation (back-bonding) from the metal to the carbene carbon (structure I). Replacement of X by an amino group, which is a much better π-donor, lengthens the $\text{Cr–C}_{\text{carbene}}$ bond substantially and shortens the C–X bond (structure II). As the X group becomes a better donor, the carbene carbon becomes a weaker π-acceptor of the metal's electron density, resulting in increased π-back-bonding from the metal to the CO groups, and

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[†] Dedicated to E. J. Corey on the occasion of his 60th birthday.

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shortening of the trans Cr–CO bond length is predicted and observed.[18] The problem with X-ray data is that the changes in bond lengths are very small and often less than the accuracy limits of the measurement. Hence only gross changes in structure can be detected, and less subtle effects cannot accurately be assessed.

Infrared spectroscopy has also been used to assess the π-interactions between the carbene carbon and its associated groups. The ν_{CO} of the carbonyl group trans to the carbene ligand responds to the degree of π-back-donation from the metal to the carbene carbon. As X and Y become better donors, the carbene carbon accepts less electron density from the metal, resulting in increased π-back-bonding from the metal to the trans carbonyl group. This leads to a shift to longer wavelength (lower force constant) for the trans carbonyl group. For example, the $\nu_{CO_{trans}}$ for aminocarbenes are somewhat lower (10–20 cm^{-1}) than those of methoxycarbenes, consonant with more π-donation to the carbene carbon by nitrogen than by oxygen.[18] This was also observed, to a smaller degree, for a series of substituted (aryl)(methoxy) and (aryl)(amino) chromium carbene complexes.[19] For aryl substituents having negative Hammett σ-constants (Me, MeO, Me_2N) an almost linear relationship between the trans CO force constant and the σ-constant was observed. A much smaller effect for electron-withdrawing groups (positive σ-constants) was observed, and the magnitude of the differences in both cases was quite small.

Chromium carbene complexes are characterized by a long-wavelength absorption band in the electronic spectrum assignable to a π–π^* transition. This band shifts to longer wavelength with changes in the heteroatom in the order N < O < S,[20] and these carbenes range in color from pale yellow to deep red. π-Unsaturation in the alkyl group also results in shifts to longer wavelength (CH_3 < Ar < C≡C—Ph). The electronic spectra of tungsten and chromium carbene complexes are quite similar and consist of three or four discernible absorptions. Assignments have been made for tungsten carbene complexes,[21] while those for the corresponding chromium carbene complexes (this work) were assigned by analogy. In order of increasing energy they are as follows: spin forbidden metal-to-ligand charge transfer (MLCT); spin allowed MLCT; ${}^1A_1$–${}^1B_2$ ligand field transition (LF); and spin allowed ligand-to-metal charge transfer (LMCT). Although the allowed MLCT band is characteristic, its position cannot be directly correlated with π-acceptor properties of the carbene ligand,[22] and consequently, electronic spectroscopy has not been extensively used to probe the donor–acceptor capabilities of the carbene ligand.

In contrast to the above spectroscopic techniques, for which only small differences are noted even between extreme cases, the carbon-13 NMR chemical shift of the carbene carbon in these complexes spans a range of over 200 ppm. Thus it is not surprising that attempts to use ${}^{13}C$ NMR spectroscopy to investigate the electronic environment of the carbene carbon were made very early in the history of chromium carbene complexes.[23,24] However, the conclusions drawn from these studies were flawed by a failure to consider that, in contrast to the ${}^1H$ NMR chemical shift, the observed ${}^{13}C$ chemical shift is the sum of *local* and *nonlocal* contributions of a *diamagnetic* shielding term as well as a *paramagnetic* shielding term.[25] Since the nonlocal contributions depend, in a nonuniform way, on the three substituents on the carbene carbon, X, Y, and Cr, direct correlation $\delta({}^{13}C)$ with the degree of shielding or deshielding experienced by the carbene carbon is difficult. Simple correlations of ${}^{13}C$ chemical shifts with the degree of "shielding" or "deshielding" the carbene carbon experiences due to its three substituents are unwarranted.

Transition-metal NMR spectroscopy[26] provides a potentially much more informative technique for the investigation of organometallic compounds, since the chemical shift ranges for most transition-metal nuclei are large and the chemical shift is sensitive to even minor structural changes. Since virtually all synthetically important reactions of chromium carbene complexes involve reaction at the chromium metal center itself, a spectroscopic technique which provides *direct* information about that metal center should provide valuable insight into the relation between complex structure and chemical reactivity. For this reason, a systematic study of the ${}^{53}Cr$ NMR spectra of a wide range of chromium carbene complexes was undertaken.

To date, only a few ${}^{53}Cr$ solution NMR measurements have been achieved, and these have concentrated on highly symmetric systems such as $CrO_4^{2-}/Cr_2O_7^{2-}$, CrO_2XY (X, Y = Cl, F),[27] and $Cr(CO)_6$.[28] There are several technical problems involved in the routine measurement of the ${}^{53}Cr$ resonance. Chromium 53 has a small magnetic moment which results in a low Larmor frequency (20.3 MHz at 8.4 T) and a low sensitivity. It has a spin I of ${}^3/_2$ and a relatively large quadrupole moment which leads to short nuclear relaxation times T_1 and T_2 (particularly if the local symmetry of the complex is low), the latter resulting in large experimental line widths. The low natural isotope abundance (9.55% ${}^{53}Cr$) combined with the small overall receptivity (0.489, ${}^{13}C$ = 1) results in low sensitivity.[27-29] The measurement is further complicated by difficulties encountered in designing a probe which does not arc while the observation pulses are applied and provides fast recovery from intense radio frequency pulses without sacrificing the necessary sensitivity. These technical problems have, in part, been overcome.

Two kinds of information are available from ${}^{53}Cr$ NMR measurements, the chemical shift, $\delta({}^{53}Cr)$, and the line width, $\Delta\nu_{1/2}$. The chemical shift provides information concerning the electronic environment of the metal, but since the chemical shift is a function of the energy state (d–d separation) of the chromium atom in a complex (see below), conclusions about donor–acceptor properties of various carbene ligands should be based on both $\delta({}^{53}Cr)$ and the energies of the ligand field transitions (from electronic spectroscopy). In contrast, line-width measurements provide direct information concerning the degree of symmetry of the electric field at the nucleus (electron distribution about the metal).

The chemical shift of the ${}^{53}Cr$ depends on the overall shielding of the nucleus, and it is a sum of the local and nonlocal contributions of both the diamagnetic (σ_{dia}) and paramagnetic (σ_{para}) shielding terms (eq 2).[29] The nonlocal contributions (i.e., those from other nuclei present in the molecule) are negligibly small if the metal atom is not directly bonded to another heavy atom.

$$\delta\,{}^{53}Cr \sim \sigma_i = \sigma_{dia} + \sigma_{para}$$

$$\text{where} \quad \sigma_{para} = \left[-K\,\Delta E^{-1}\langle r^{-3}\rangle_{3d}\,\bar{C}_d^{\,2}\right] \qquad (2)$$

The σ_{dia} term reflects the electron density in the immediate vicinity

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of the ^{53}Cr nucleus and has the opposite sign of σ_{para}. Since σ_{dia} is dominated by the core electrons, the value is almost constant for a given nucleus. Thus, for ^{53}Cr, the shielding differences are dominated by the paramagnetic shielding constant σ_{para}, which is a function of several factors (eq 2). In the average energy approximation, ΔE is a weighted average of the symmetry allowed d–d transitions between energy levels that have the same symmetry properties as the angular momentum operator $\hat{L}$. For d^6 complexes having C_{2v} symmetry (e.g., dimethoxymethylenepentacarbonylchromium) these correspond to the $^1A_1 \rightarrow {}^1A_2$, $^1A_1 \rightarrow {}^1B_1$, and $^1A_1 \rightarrow {}^1B_2$ transitions.[30] Since, in chromium (and other) carbene complexes some of these transitions are masked by strong ligand-to-metal charge-transfer bands (LMCT), ΔE is often assumed to be the wavelength of the d–d transition with the lowest energy.[31] The term $\langle r \rangle$ is the average distance to the valence d electrons from the ^{53}Cr nucleus, while $\bar{C}_d^2$ represents the mean value of the product of the LCAO coefficients of the ground and excited states taking part in the transition. These three terms are not easily independently quantified. The factor $\langle r^{-3}\rangle_{nd}\bar{C}_d^2$ is especially sensitive to variations in the total ligand field strength, and correlations of this factor with nephelauxetic ratios, electronegativity values, infrared spectroscopic force constants, and ligand substituent constants have been made.[26]

Nuclei with a spin quantum number $I > {}^1/_2$ (^{53}Cr $I = {}^3/_2$) couple with an electronic field gradient. The magnitude of this coupling is proportional to the nuclear quadrupole moment Q. This interaction provides a process for nuclear relaxation that can be several orders of magnitude more efficient than other common types of relaxation processes. For isotropic solutions in the extreme narrowing limit ($\omega_0\tau_c \ll 1$) the longitudinal and transverse relaxation rates $1/T_{1q}$ and $1/T_{2q}$ are equal and are related to the line width $\Delta\nu_{1/2}$ as shown in eq 3.[32] For a given nucleus, I and Q are constant and the line width depends only on the correlation time for molecular tumbling, τ_c, and on the square of the electric

$$T_{1q}^{-1} = T_{2q}^{-1} = 3\pi^2 \cdot \frac{2I+3}{I^2(2I+1)} \left(\frac{e^2Qq}{h}\right)^2 \tau_c = \pi\Delta\nu_{1/2} \qquad (3)$$

field gradient, $(q)^2$. Line widths are very temperature sensitive since τ_c is proportional to the viscosity of the sample and inversly proportional to the temperature. The electric field gradient depends on the degree of symmetry of the electron distribution about the nucleus. A uniform spherical electronic environment about the nucleus produces zero electric field gradient and hence sharp lines. As this spherical electronic environment is distorted (i.e., polarized) by differences in ligand donor–acceptor properties, the line width increases accordingly. Hence line widths are related to the degree of symmetry (or distortion) of the electronic environment directly about the nucleus. (The term (e^2Qq/h) in eq 3 corresponds to the quadrupole coupling constant that can be measured by using solid-state nuclear quadrupole resonance (NQR) techniques.)

Results and Discussion

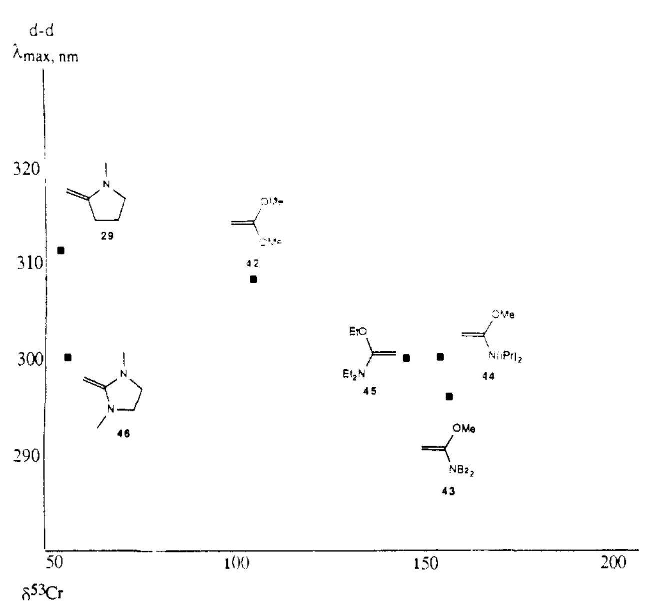

Figure 1. Class I carbene complexes.

The ^{53}Cr NMR spectra of 46 different chromium carbene complexes and four isonitrile complexes were measured in acetone solvent and are reported in Table I, along with other pertinent spectroscopic data. The ^{53}Cr chemical shifts span a range of over 300 ppm downfield from Cr(CO)$_6$, which was used as an external standard. The line widths (peak width at half height) range from 2–3 Hz for the very symmetrical Cr(CO)$_6$ standard to over 3500 Hz. Both parameters potentially contain valuable information about the electronic (and therefore chemical) nature of the carbene ligand relative to the Cr(CO)$_5$ fragment common to all of these complexes. The chemical shift is particularly informative. However, since ΔE (from UV–visible spectra) has a strong influence on δ(^{53}Cr) (see eq 2) direct comparisons of chemical shift values amongst chromium carbene complexes are best restricted to complexes having similar ΔE's. Equation 2 simplifies to equation 4. With ΔE constant, the chemical shift value allows the direct comparison of the effects of changes in the carbene

$$\delta\,{}^{53}\mathrm{Cr} \approx \frac{1}{\Delta E} R, \quad R = \langle r^{-3} \rangle_{3d} \bar{C}_d^2 \qquad (4)$$

ligand *as a whole* on R, which, in turn, is strongly dependent on the charge density at the metal. Thus for carbene complexes having similar ΔE values, changes in δ(^{53}Cr) reflect changes in the donor–acceptor properties of the carbene ligand itself, since the Cr(CO)$_5$ fragment is common to all complexes in Table I. *Note also that chemical shift comparisons are only valid for complexes of the same type and symmetry*!

When viewed in this manner, three classes of carbene complexes emerge: those having $\Delta E \cong 305$ nm (Class I); those having $\Delta E \cong 320$ nm (Class II); and those having $\Delta E \cong 335$ nm (Class III). The δ(^{53}Cr) values for members of each class of complex are presented graphically in Figures 1–3. These data not only confirm the gross trends noted by other spectroscopic techniques (e.g., *N*-carbenes are generally better donors, hence more shielded, than *O*-carbenes) but also contain considerably more detailed information concerning the net electronic interaction of the carbene ligand with the chromium metal center and the dependence of this interaction on subtle structural features of the carbene ligand. A comparison of the chemical shift ranges for the three classes of carbene complexes confirms the inverse dependence of δ(^{53}Cr) on ΔE (eq 4); Class I complexes, which have the largest ΔE (shortest wavelength $\lambda_{\max}$), appear in the δ(^{53}Cr) 50–150 ppm range, Class II complexes, with intermediate ΔE values, in the 80–215 ppm range, and Class III, with the smallest ΔE values, in the 150–300 ppm range. Most informative is comparison of δ(^{53}Cr) values within a class.

Class I complexes (Figure 1) are the most strongly shielded, as might be expected for carbenes that contain two donor heteroatoms. Two nitrogens (**46**) are more shielding (better π-donors) than two oxygens (**42**), as expected. However, cyclic *mono*-aminocarbene complex **29** has almost the *identical* chemical shift as bis aminocarbene complex **46** and is at least 30 ppm *upfield* from all acyclic monoaminocarbenes. This is almost certainly due to efficient π-overlap of the nitrogen lone pair with the empty

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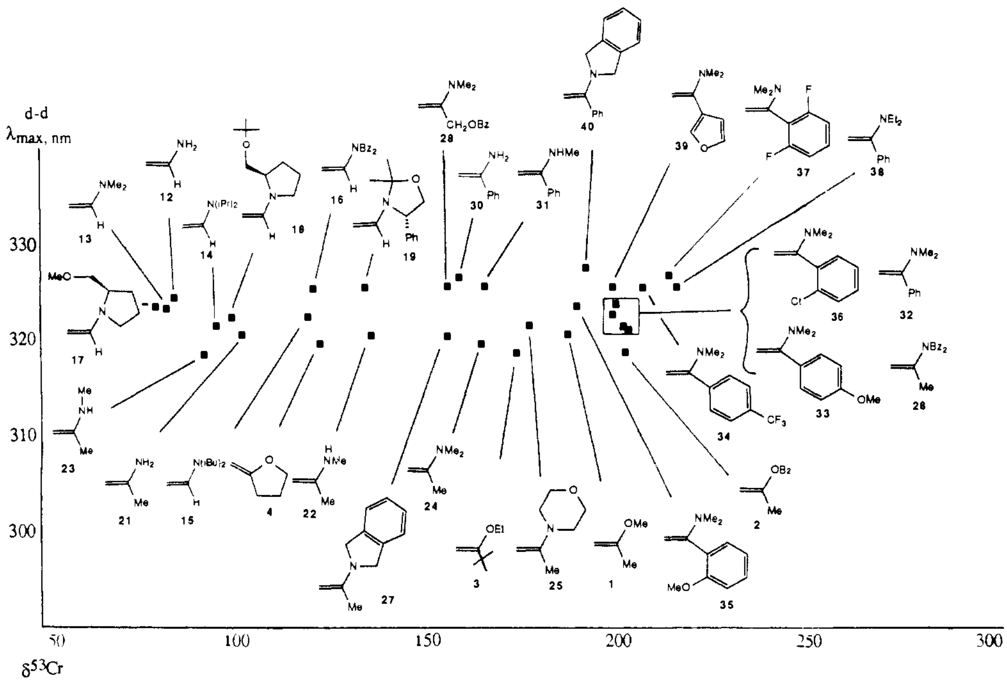


Figure 2. Class II carbene complexes.

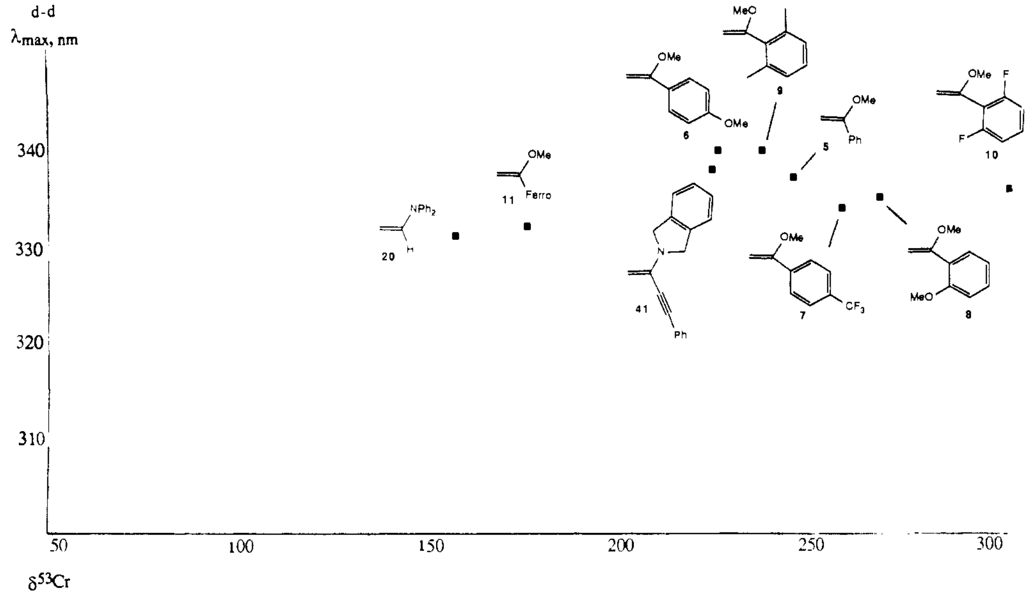


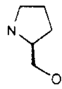
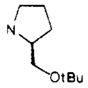
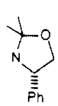
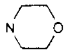
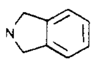
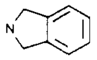
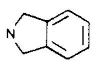
Figure 3. Class III carbene complexes.

carbene carbon p-orbital, enforced by the rigidity of the five-membered ring. The fact that **29** and **46** have virtually identical chemical shifts indicates that the second nitrogen in **46** has little effect on the electron density around the metal and implies that a single nitrogen rigidly held in position for efficient π-overlap provides the maximum electron density acceptable by the metal. Similar effects are seen with cyclic monoalkoxycarbene **4** (δ 123) and dialkoxycarbene **42** (δ 109). The ^{53}Cr NMR signals of the other bis-heteroatom carbene complexes **43–45** appear almost 100 ppm downfield from **46** and **29** and 40–50 ppm downfield from dimethoxycarbene complex **42**. At first glance this is surprising. However, both oxygens in **42** can efficiently overlap with the carbene carbon, while the steric bulk of the tertiary amino groups in **43–45** prevents efficient overlap of the nitrogen with the carbene carbon, reducing its shielding effect. This steric interference with π-overlap and its effect on δ(^{53}Cr) is a common feature of all complexes studied[33] (see below).

By far most of the carbenes studied fell into Class II (Figure 2) and several different types of carbene complexes are represented here. However, the trends established with Class I complexes related to efficient overlap and steric hindrance thereof uniformly apply in this series as well. Carbenes **12–19** are among the least sterically hindered since one of the carbene carbon substituents is a hydrogen. Nevertheless, as α branching of the alkyl groups on nitrogen increases ($NH_2 \rightarrow N(i\text{-}Pr)_2 \rightarrow N(i\text{-}Bu)_2$, NBz_2) the chromium chemical shift moves progressively downfield, from 80 to 135 ppm. Similar effects are seen when comparing **17** (CH_2OMe) with **18** ($CH_2O\text{-}t\text{-}Bu$) with a difference of 20 ppm between them. This deshielding with an increase in steric bulk is attributed to steric inhibition to orbital colinearity required for efficient π-overlap of the heteroatom with the carbene carbon. The same trend is seen with the other types of carbenes.

Amino complexes **21–27** have a methyl group on the carbene carbon. Again, as steric congestion about the carbene center increases, the carbene ligand becomes less shielding, and δ(^{53}Cr) moves downfield. Thus, relatively unhindered cis monomethylamino complex **23** and free amino complex **21** are furthest upfield. The more sterically hindered trans monomethylamino complex **22** is moved ~40 ppm downfield. Dimethylaminocarbene **24**, morpholino carbene **25**, and isoindoline complex **27** appear another

Table I. Physical Data for $(CO)_5Cr(Y)(X)$ Complexes

complex	X	Y	$\delta(^{53}Cr)$, ppm	line width, Hz	$\lambda_{max}{}^{d-d}$	$\lambda_{max}{}^{MLCT}$	log *e*	$\delta(^{13}C)$, $=C(Y)(X)$, ppm	$\delta(^{13}C)$, CO, ppm		ν_{CO}, cm^{-1}			
									cis	trans	A_1	B_1	E	A_1
1	CH_3	OCH_3	187	900	320	376	3.85	361.0	216.5	223.3	2065		1963	1948
2	CH_3	OCH_2Ph	204	1500	318	377	3.92	358.8	216.5	223.3	2064		1961	1945
3	*t*-Bu	OCH_2CH_3	174	500	318	381	3.83	370.3	217.1	228.8	2059		1950	1942
4	$-(CH_2)_3O-$		123	1300	319	379	3.80	342.7	216.4	223.3	2066		1963	1949
5	Ph	OCH_3	245	1100	337	409	3.92	352.0	216.2	224.2	2064	1985	1961	1953
6	*p*-MeOPh	OCH_3	225	1150	340	430	3.94	342.6	216.9	223.8	2058	1981	1952	1941
7	*p*-CF_3Ph	OCH_3	258	1400	334	408	3.84	351.2	215.7	223.7	2066	1990	1971	1956
8	*o*-MeOPh	OCH_3	268	1900		400	3.96	355.1	216.1	225.1	2064	1987	1955	1948
9	2,6-Me_2Ph	OCH_3	236	1600	340	403	3.96	364.8	216.3	224.2	2066	1989	1964	1955
10	2,6-F_2Ph	OCH_3	303	1500	336	405	3.98	344.1	217.1	224.7	2070	1990	1973	1951
11	ferrocenyl	OCH_3	175	1700	332	418	3.89	331.0	217.4	222.9	2055	1975	1947	1936
12	H	NH_2	85	2000	324	369	3.83	285.5	217.0	223.3	2068		1955	1941
13	H	NMe_2	82	1300	323	364	3.90	265.2	217.6	223.9	2058		1943	1935
14	H	N(*i*-$Pr)_2$	96	1300	321	360	3.95	251.2	217.7	224.5	2056		1939	1933
15	H	N(*i*-$Bu)_2$	122	1000	322	363	3.92	262.9	217.8	224.1	2056		1939	1933
16	H	$N(CH_2Ph)_2$	121	2000	325	369	3.96	267.7	217.3	223.7	2058		1943	1938
17	H		80	3500	323	366	3.95	258.7	217.9	224.1	2056		1934	1934
18	H		100	1850	322	364	3.95	256.4	217.9	224.2	2055		1934	1934
19	H		135	1750	325	374	3.97	259.3	216.8	223.8	2058		1947	1940
20	H	NPh_2	156	3000	331	400	3.94	277.2	216.7	224.6	2057		1942	1942
21	CH_3	NH_2	103	1400	320	363	3.87	292.0	217.4	223.1	2057	1964	1949	1941
22	CH_3	$N(CH_3)H$ *E*	136	800	320	364	3.86	282.0	217.8	223.6	2057	1970	1938	1930
23	CH_3	$N(CH_3)H$ *Z*	93	750	318	357	3.86	277.8	217.8	223.6	2057	1970	1937	1932
24	CH_3	NMe_2	165	400	319	360	3.82	274.3	218.0	223.5	2055	1967	1933	1930
25	CH_3		177	490	321	365	3.86	273.0	217.6	223.4	2055	1970	1934	1929
26	CH_3	$N(CH_2Ph)_2$	202	920	321	367	3.85	280.0	217.7	223.3	2054		1932	1931
27	CH_3		156	530	320	362	3.76	274.3	218.8	224.0	2055		1936	1929
28	$PhCH_2OCH_2$	NMe_2	156	500	325	371	3.86	273.6	217.6	223.7	2055		1931	1931
29	$-(CH_2)_3N(CH_3)-$		54	750	311	351	3.87	266.4	218.2	223.1	2055		1934	1930
30	Ph	NH_2	159	1150	326	387	3.79	291.0	217.1	223.3	2058	1978	1944	1921
31	Ph	$NH(CH_3)$	166	1700	325	371	3.76	284.6	217.2	223.2	2057	1976	1940	1915
32	Ph	NMe_2	199	280	322	365	3.89	275.6	217.3	223.9	2056	1976	1939	1936
33	*p*-MeOPh	NMe_2	200	300	323	366	4.02	275.8	217.3	223.9	2054	1972	1940	1931
34	*p*-CF_3Ph	NMe_2	207	330	325	368	3.86	273.8	216.9	223.6	2057	1976	1940	1936
35	*o*-MeOPh	NMe_2	190	325	323	363	3.87	272.5	217.5	224.1	2054	1976	1933	1923
36	*m*-ClPh	NMe_2	202	300	321	371	3.86	271.9	216.9	223.6	2057	1975	1936	1927
37	2,6-F_2Ph	NMe_2	214	275	326	378	3.88	266.8	216.4	223.4	2059	1976	1939	1939
38	Ph	NEt_2	216	230	325	363	3.82	274.7	217.5	224.0	2056	1975	1934	1934
39	3-furyl	NMe_2	199	350	325	373	3.87	267.5	217.4	223.9	2056	1972	1936	1931
40	Ph		193	475	327	372	3.88	276.8	217.5	223.6	2055	1975	1940	1927
41	PhC≡C–		224	450	338	452	3.94	314.4	216.3	225.7	2055	1978	1943	1932
42	MeO	MeO	109	350	307	340	3.85	269.1	216.3	221.1	2068	1987	1953	1937
43	MeO	$N(CH_2Ph)_2$	155	305	296	342	3.66	248.3	217.0	221.7	2058		1932	1932
44	MeO	N(i-$Pr)_2$	154	165		348	3.45	246.0	217.3	221.6	2057		1930	1930
45	EtO	NEt_2	145	140		346	3.46	242.4	217.4	221.6	2057		1928	1928
46	$-N(Me)(CH_2)_2N(Me)-$		56	280		347	3.48	220.7	218.0	221.8	2056		1926	1926
47	$(CO)_5CrCNMe$		21	50		324	3.52							
48	$(CO)_5CrCNtBu$		20	90		336	3.46							
49	$(CO)_5CrCNPh$		23	150		341	4.00							
50	$(CO)_4Cr(CNMe)_2$		66	50		333	3.12							

30 ppm downfield, and dibenzylamino complex **26** yet another 35 ppm downfield, resulting in a span of over 100 ppm for this single type of carbene complex.

Arylaminocarbene complexes **30**–**40** show similar trends. Free aminocarbene **30** has α-branching in the form of the phenyl group, and its ^{53}Cr NMR signal appears at the same chemical shift as that of complex **27**, having similar steric environments. As α branching on the nitrogen increases, the chemical shift again moves downfield—10 ppm for monomethylamino complex **31**, another 30 ppm for dimethylamino complex **32**, and a final 15 ppm for diethylamino complex **38**—a range of 55 ppm. Remarkably, the ^{53}Cr chemical shift values for this type of carbene complex indicate that the aryl group is *not* in conjugation with the carbene carbon, and substituents on the arene ring have little effect on ^{53}Cr

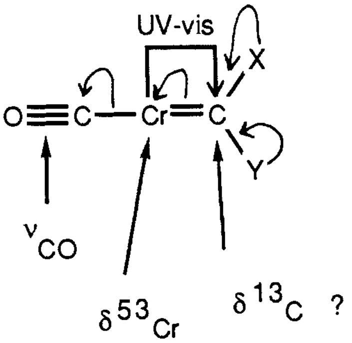


Figure 4.

chemical shift. Thus phenyl **32**, *o*-chlorophenyl **36**, *p*-methoxyphenyl **33**, *p*-(trifluoromethyl)phenyl **34**, *o*-methoxyphenyl **35**, and 3-furyl complexes **39** have chemical shift values within 10 ppm. Clearly, the methyl groups on the amine prevent the aryl group from achieving coplanarity with the carbene carbon. 2,6-Difluorophenyl complex **37** appears about 15 ppm downfield from the rest of the substituted aryl carbenes. This deshielding may involve the *inductive* electron-withdrawing effects of the fluoro groups.

(Alkyl)(alkoxy)carbenes **1–4** are the final members of the Class II carbene complexes. As expected from electronegativity arguments alone, they appear downfield from most of the amino carbenes. The simplest complex **1** appears at δ 190. The alkoxy carbenes appear much less subject to steric hindrance to efficient overlap, and the more bulky *tert*-butyl carbene **3** is actually shielded by about 15 ppm, indicating that the inductive effects of the alkyl groups override any potential steric problems. As with the amino carbenes, however, when the oxygen atom is locked into position for efficient overlap, as in complex **4**, a large increase in shielding is observed, and the chemical shift for **4** is 70 ppm upfield from that of **1**.

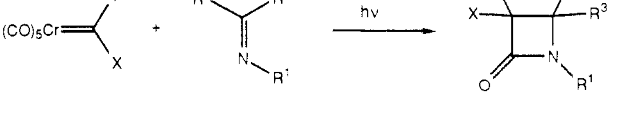
(Aryl)(alkoxy)carbene complexes **5–11** constitute a majority of the Class III carbene complexes. These are highly colored complexes having MLCT absorption bands above 400 nm and correspondingly long wavelength d–d bands. They also are the most deshielded of the carbene complexes. In contrast to the aryl(dialkylamino)carbene complexes, for which *no* aryl substituent effects on chemical shift were noted, the $\delta(^{53}Cr)$ chemical shifts of the (aryl)(alkoxy)carbenes **6–11** are strongly dependent on the electronic nature of the substituent and strictly mirror the donor–acceptor properties of these substituents. Thus the strongly electron donating ferrocenylcarbene **11** appears farthest upfield, followed by (*p*-methoxyphenyl)carbene **6**, (2,6-dimethylphenyl)carbene **9**, the parent phenyl carbene complex **5**, the electron-withdrawing (*p*-(trifluoromethyl)phenyl)carbene **7**, and the strongly electron-withdrawing 2,6-difluorophenyl complex **10**. Only (*o*-methoxyphenyl)carbene complex **8** appears anamolous. The methoxy group is electron donating, and **8** would be expected to be shielded (upfield) relative to parent complex **5**. While the *o*-methoxy group might sterically prevent efficient overlap of the aryl group with the carbene carbon, suppressing shielding, it is not clear why this substituent is actually deshielding relative to **5**. This point remains unresolved.

Two unusual aminocarbene complexes fall into Class III, (phenylacetylide)carbene **41** and (diphenylamino)carbene **20**. Each has a unique structural feature that accounts for its appearance in Class III. While steric hindrance prevents efficient π-overlap of the aryl group with the carbene carbon in aryl(dialkylamino)carbenes, replacing the phenyl group in **40** with the linear, conjugated phenylacetylide group in **41** results in a 30 ppm downfield shift in the ^{53}Cr resonance, indicating substantially more π interaction in **41** than in **40**. Similarly, conjugation of the aryl groups in complex **20** with the nitrogen results in modest (20 ppm) deshielding relative to other similar carbenes.

Figure 4 presents the sites in a carbene complex for which various spectroscopic techniques provide information. Of these, only ^{53}Cr NMR spectroscopy directly provides information about the metal center itself, and, as such, it provides a sensitive probe for the extent of electronic interaction of the carbene ligand with the metal center and for the effects of changes of substituents about the carbene carbon on the degree of this interaction. The ^{53}Cr chemical shift value provides detailed information about the efficiency of π-overlap of the carbene carbon with its substituents and emphasizes the sensitivity of this π-overlap to steric crowding about the carbene carbon. It correlates very well with accepted views of electron-donating and electron-withdrawing properties of various functional group substituents across the entire range of the 46 carbene complexes studied, in contrast to other spectroscopic techniques, which are restricted to comparisons within a single type of carbene complex (e.g., infrared spectroscopy) or to gross (but not detailed) comparisons between two types (e.g., UV–visible spectroscopy for N vs O carbenes).

Provided the correlation times and solution viscosities are similar, ^{53}Cr NMR measurements also provide information concerning the degree of symmetry of the electron distribution about the Cr nucleus, in the form of line width data.[34] A symmetrical electronic environment about the metal produces sharp lines, as is observed for the standard, $Cr(CO)_6$. As the electronic environment becomes less symmetrical, the line width increases. Thus, with replacement of one or two CO in $Cr(CO)_6$ by an isonitrile, a ligand with bonding properties similar to those of CO (complexes **47–50**), the line width increases to 50–150 Hz. The line widths of carbene complexes **1–46** span a range of over 3000 Hz. Carbenes **42–46**, containing two heteroatoms, have the narrowest lines, in the 150–300 Hz range, with (dibenzylamino)carbene **43** having the broadest line. Aryl(dialkylamino)carbenes **32–41** also have relatively narrow (250–500 Hz) lines, as do alkyl(dialkylamino)carbenes **24–28** (400–500 Hz). The one exception is (dibenzylamino)carbene **26**, with a line width of 920 Hz. The line-broadening effects of benzylamino groups are general and, at present, inexplicable. Methyl(*N*-methylamino)carbenes **22** and **23** as well as the cyclic aminocarbene complex **29** have intermediate line widths, in the range of 750–800 Hz. The remainder of the aminocarbenes **12–21**, **30**, and **31** have broad lines, in excess of 1000 Hz. Alkoxycarbenes **1–11** also have broad lines, with the exception (*tert*-butyl)(ethoxy)carbene **3**. Although these line widths are systematically dependent on the substitution pattern about the carbene carbon, they do not correlate with other spectroscopic properties such as $\delta(^{53}Cr)$, λ_{max}, or ν_{CO}, and rationalization of observed line widths in terms of donor–acceptor properties of the carbene ligand is not possible. However, since line widths *are*, at least in part, a measure of the degree of asymmetry of the electronic environment about the metal, and since most synthetically interesting reactions of carbene complexes involve reactions of the metal–carbene bond, some relation of line width to reactivity might be anticipated. Preliminary results suggest that this is the case.

During the development, in these laboratories, of the photolytic reaction of chromium carbene complexes with imines to give β-lactams (eq 5)[15–17] it had been observed that a number of chromium carbene complexes failed to react under a variety of conditions. These included bis-heteroatom carbenes **42–46**, (dialkylamino)(alkyl)carbenes **24**, **25**, and **27–29**, and (dialkyl-



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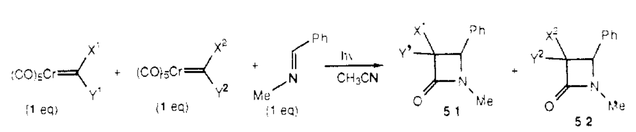
[34] All chemical shift and line width measurements were made in the same solvent, at the same temperature and concentration. Although correlation times were not measured, the structural similarity of complexes **1–46** ($(CO)_5Cr{=}(Y)(X)$), combined with the observation that line width was not a function of steric bulk or the presence or absence of hydrogen bonding capability, implies that neither aggregation phenomena nor intramolecular steric bulk effects produce differences in correlation times large enough to account for the observed variation in line width.

[35] Martin, M. L.; Delpuech, J. J.; Martin, G. J. *Practical NMR Spectroscopy*; Heyden: London, 1980; p 246.



Complex	X^1	Y^1	Line Width	Complex	X^2	Y^2	Line Width	Ratio 51 52
16	NBz$_2$	H	2000	**15**	N(i-Bu)$_2$	H	1000	10 1
16	NBz$_2$	H	2000	**13**	NMe$_2$	H	1300	16:1
20	NPh$_2$	H	3000	**13**	NMe$_2$	H	1300	7:1
20	NPh$_2$	H	3000	**16**	NBz$_2$	H	2000	2.1
16	NBz$_2$	H	2000	**1**	MeO	Me	900	1:1
5	OMe	Ph	1100	**1**	MeO	Me	900	1.6.6

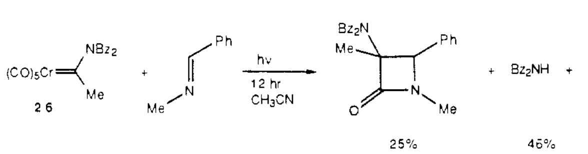
Figure 5.

amino)(aryl)carbenes **32–41**. The lack of reactivity of carbenes **42–46** was not surprising since they are among the most stable chromium carbene complexes and since their spectroscopic properties (λ_{max}^{MCLT}, $\delta(^{13}C)$) are somewhat different from the remainder of the complexes in Table I. However, there were *no* obvious differences between the *rest* of the unreactive complexes and those that did react. One of the major motivations for the ^{53}Cr NMR studies discussed herein was to determine if *this* technique could provide insight into reactivity differences among various chromium carbene complexes. ^{53}Cr chemical shift data clearly did not correlate in any discernible fashion with reactivity. For example, carbenes ranging from δ 80 (**17**) through δ 245 (**5**) underwent efficient photochemical reaction with imines to give β-lactams; but carbene **32** (δ 199) was virtually unreactive while carbene **2** (δ 204) was quite reactive. However, unreactive carbenes had one feature in common—relatively narrow line widths ranging from 150 to 500 Hz—while reactive carbenes had line widths in excess of 1000 Hz. Of the 46 carbenes examined there were only two exceptions: complex **3**, with a line width of 500 Hz but reactive toward imines, and complex **29**, with a line width of 750 Hz but unreactive toward imines. Two sets of experiments were carried out to test this correlation. First, *pairs* of carbene complexes, each of which individually underwent reaction with imines, were allowed to compete for a single equivalent of imine, and the ratio of β-lactams formed was taken as a crude estimate of relative reactivity. These results are summarized in Figure 5.

The first entry is striking. Complexes **16** and **15** have virtually the same $\delta(^{53}Cr)$ (121 vs 122), the same λ^{d-d} (325 vs 322), the same λ^{MLCT} (369 vs 363), and the same $\delta(^{13}C)$ (268 vs 263), but **16** has twice the line width of **15** and forms β-lactams much more efficiently. The same holds true for the first four entries, with the carbene having the broader line being more reactive. However, the remaining two entries show that this potential correlation of reactivity with line width clearly does *not* hold when methoxycarbenes are involved. In these cases (methoxy)(methyl)carbene **1** with a relatively narrow (900 Hz) line is more reactive than both aminocarbenes and other alkoxycarbenes with substantially broader lines. The reasons for this are currently being examined.

As noted above, (dialkylamino)(alkyl)carbene complexes have relatively narrow lines and fail to react with imines to form β-lactams. In the course of ^{53}Cr NMR measurements it was observed that aminocarbene complexes having *N*-benzyl substituents always had broader lines than those having other *N*-alkyl groups. To determine if this line broadening effect translated into an increase in reactivity, (dibenzylamino)(methyl)carbene complex **26** (line width 920 Hz) was compared with (dimethylamino)(methyl)carbene complex **24** (line width 400 Hz) in its photolytic reaction with *N*-methylbenzylidenimine (eq 6 and 7). After 12 h of irradiation, complex **26**, with its broad ^{53}Cr line, was completely consumed, producing a low yield of β-lactam and substantial amounts of dibenzylamine. In contrast, complex **24**, with its narrower line, was completely unreactive and could be recovered unchanged, even after 24 h of irradiation.

The photolytic reactions of chromium carbene complexes are thought to involve, as a key first step, a photolytically driven CO insertion process to form a metal–ketene complex (eq 8).[17] The



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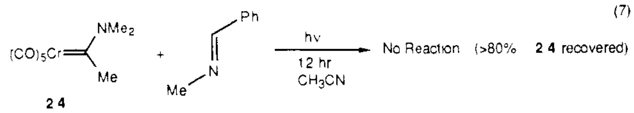

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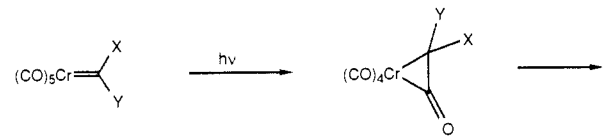

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facility of this photo process may be related to the ^{53}Cr line width and may account for the observed relation of reactivity to ^{53}Cr line width. Although the yield of β-lactams was low in eq 6, complex **26** was completely consumed, indicating that photolytic activation was facile but that reaction of the metal ketene with the imine was inefficient. In contrast, the complete lack of reactivity of complex **24** under identical conditions suggests that CO insertion did not occur under photolysis in this case. Thus, ^{53}Cr line widths appear to be related to reactivity under photolytic conditions. The generality of this phenomenon and its application to the enhancement of photoreactivity of normally unreactive carbenes by introduction of line-broadening groups are currently under study.

Experimental Section

Spectroscopic Studies. All reported ^{53}Cr NMR measurements except those for complexes **11**, **38**, and **45** were performed at 20.33 MHz on a Nicolet NT-360 wide bore spectrometer (B_0 = 8.456 T) with a single-frequency home-built probe. The samples were measured as ~0.4 M solutions in acetone in 12-mm tubes sealed under nitrogen, at 293 ± 1 °K, unless otherwise specified. To minimize errors in line widths and chemical shifts due to temperature differences (see below) the radio frequency power level was held approximately constant for all measurements. The 90° pulse, at 50 W, corresponds to a pulse length of 180 μs. To suppress acoustic ringing, a preacquisition delay of 140 μs was used. To optimize the accuracy of peak postions, the spectra were Gaussian broadened by between $^1/_5$ and $^1/_{10}$ of their natural line widths. In a typical case, $\Delta\nu_{1/2}$ = 1150 Hz, a signal-to-noise ratio of 10 was achieved in 25 min. The ^{53}Cr measurements of complexes **11**, **38**, and **45** were performed by A. Hafner in the laboratories of Professor W. von Philipsborn, University of Zurich, on a Bruker AM-400 wide-bore spectrometer B_0 = 9.9395 T at 22.58 MHz with a 20 mm broad-band probe head (12–100 MHz) under the same conditions as above. Chemical shifts were recorded on the δ scale relative to external Cr(CO)$_6$ in THF measured at the same temperature. Positive shifts denote decrease shielding.

The effect of temperature on chemical shift was measured by recording the ^{53}Cr NMR of $(CO)_5Cr{=}C(NMe_2)(Ph)$ (0.4 M in acetone) relative to external Cr(CO)$_6$ in THF at different temperatures (from −40 to +40 °C after an equilibration time of 20 min). Less than 2 Hz chemical shift difference was observed over this range, while the line width ranged from 1000 Hz at −40 °C to 250 Hz at +40 °C.

The T_1 value of $(CO)_5CrC(CH_3)(\overline{NCH_2CH_2OCH_2CH_2})$ was determined by the inversion recovery technique[35] with use of 13 different τ values. For the calculation of T_1 a three parameter Gaussian fit was used, and gave a T_1 value of 750 ± 50 μs. From line width measurements a T_2 of 650 μs was estimated, making $T_1 \simeq T_2$.

^{13}C NMR measurements were performed on an IBM-Bruker WP 270 instrument, with CDCl$_3$ solvent. Infrared spectra were recorded on a Perkin-Elmer 983 infrared spectrometer in *n*-hexane solution and have an accuracy of ±0.5 cm^{-1}. UV–visible spectra were recorded on a Perkin-Elmer λ 4B spectrometer in *n*-hexane solution in 1-cm cells. Absorption maxima for the lowest energy d–d transitions were assigned by taking into account both a Gaussian analysis and the first derivative of the spectra. (In the case of overlapping signals with different intensities, the energy of the minor transition is very close to the maximum of the first derivative of the absorption band.)[36] The values given in the table are mean values of these two values.

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Chemical Studies. Materials. Tetrahydrofuran (Fisher, reagent grade) and diethyl ether (ASP, analytical reagent) were predried over CaH_2 and distilled from benzophenone ketyl under a nitrogen atmosphere just prior to use. Hexane (technical grade) was distilled at atmospheric pressure. Ethyl acetate (technical grade) was distilled over CaH_2. Methylene chloride was distilled over CaH_2 or filtered through aluminum oxide (Baker Analyzed, 5 g per 100 mL). Acetonitrile (Fisher) was distilled over CaH_2 and stored over 4Å molecular sieves. Methanol (Fisher) was dried over Mg and distilled.

Chromium hexacarbonyl (Pressure Chemicals), naphthalene (Baker), *N,N*-diisopropylformamide (Aldrich), dibenzylamine (Aldrich), acetamide (Baker), and *N*-methylamine (Matheson) were used as received. *N,N*-Diisobutylformamide,[37] bis(1,3-dimethylimidazolidin-2-ylidene),[38] *n*-methylbenzylidenimine,[15a] and isoindoline[39] were prepared by literature procedures.

Carbene Complexes. Carbene complexes **13**, **16**, **19**, **24**, **25**, **28**, **29**, **32**, **36**, and **39** were prepared by the reaction of $Na_2Cr(CO)_5$, the corresponding amide, and trimethylsilyl chloride, following the literature procedure.[7] Carbenes **14**, **15**, and **26** were made by the same procedure. Pertinent physical data for these new complexes are reported below. See Table I for UV, infrared, and ^{13}C data.

Complex 14: from 80 mL of a 0.12 M THF solution of $Na_2Cr(CO)_5$, 0.73 mL (5.0 mmol) of *N,N*-diisopropylformamide, and 1.9 mL (15 mmol) of trimethylsilyl chloride, 1.30 g (85%) of **14**, as a yellow solid, mp 91 °C, was obtained. ^1H NMR ($CDCl_3$): δ 1.20 (d, J = 6 Hz, 6, CH_3), 1.44 (d, J = 6 Hz, 6, CH_3), 3.92 (sept, J = 6 Hz, 1, CH), 5.04 (sept, J = 6 Hz, 1, CH), 11.06 (s, 1, =CH). Anal. Calcd for $C_{12}H_{15}NO_5Cr$: (C, H, N).

Complex 15: From 60 mL of a 0.12 M THF solution of $Na_2Cr(CO)_5$, 0.875 mL (5.0 mmol) of *N,N*-diisopropylformamide, and 2 mL (16 mmol) of trimethylsilyl chloride, 1.14 g (68%) of **15**, as a yellow oil, was obtained. ^1H NMR ($CDCl_3$): δ 0.90 (d, J = 5 Hz, 6, CH_3), 1.00 (d, J = 5 Hz, 6, CH_3), 2.00 (hept, J = 5 Hz, 1, $(CH_3)_2CH$), 2.21 (hept, J = 5 Hz, 1, $(CH_3)_2CH$), 3.35 (d, J = 8 Hz, 2, CH_2), 3.80 (d, J = 8 Hz, 2, CH_2), 10.87 (s, 1, =CH). Anal. Calcd for $C_{14}H_{19}NO_5Cr$: (C, H, N).

Complex **26**: On twice the scale (10 mmol of amide) as above, 1.62 g (36%) of **26** was obtained as a yellow oil. ^1H NMR ($CDCl_3$): δ 2.92 (s, 3, $=CCH_3$), 4.77 (s, 2, CH_2), 5.50 (s, 2, CH_2), 6.90–7.5 (m, 10, ArH). Anal. Calcd for $C_{21}H_{17}NO_5Cr$: (C, H, N).

Complexes **1**,[2] **4**,[40] **5**,[2] **6**,[41] **7**,[41] **8**,[41] **11**,[42] **21**,[43] **22**,[44] **23**,[44] **30**,[45] **42**,[7] **45**,[46] and **46**[47] were synthesized by literature procedures. Complexes **17**, **18**, and **20** were prepared by the reaction of $Na_2Cr(CO)_5$ with the appropriate Vilsmeir's salt of the formamide.[16] Their physical properties are reported below.

Complex **17**: from (2*S*)-*N*-formyl-2-methoxymethylpyrrolidine (0.54 g, 3.5 mmol), oxalyl chloride (0.98 g, 7.7 mmol), and $Na_2Cr(CO)_5$ (48 mL of a 0.09 M solution in THF, 4.6 mmol), 0.60 g (62%) of **17** was obtained as a yellow solid, mp 40–41 °C. ^1H NMR ($CDCl_3$): δ 1.9–2.3 (m, 4, CH_2), 3.2–3.5 (m, 2, NCH_2), 3.35 (s, 3, OCH_3), 3.81 (m, 1, NCH), 4.08 (m, 2, NCH_2), 11.54 (s, 1, =CH). Anal. Calcd for $C_{12}H_{13}NO_6Cr$: (C, H, N).

Complex **18**: From (2*S*)-*N*-formyl-2-(*tert*-butoxymethyl)pyrrolide, oxallyl chloride, and $Na_2Cr(CO)_5$ exactly as above, 0.57 g (45%) of **18** as a yellow solid, mp 52–53 °C, was obtained. ^1H NMR ($CDCl_3$): δ 1.16 (s, 9, O-*t*-Bu), 1.9–2.4 (m, 4, CH_2), 3.3–3.5 (m, 2, CH_2N), 4.06 (m, 2, CH_2O-*t*-Bu), 11.00 (s, 1, =CH). Anal. Calcd for $C_{15}H_{19}NO_6Cr$: (C, H, N).

Complex **20**: From *N,N*-diphenylformamide (2.58 g, 12 mmol), oxalyl chloride (2.92 g, 23 mmol), and $Na_2Cr(CO)_5$ (10 mmol) was obtained 1.48 g (33%) of **20** as a yellow solid, mp 93–94 °C. ^1H NMR ($CDCl_3$): δ 7.0–7.7 (m, 10, ArH), 12.03 (s, 1, =CH). Anal. Calcd for $C_{18}H_{11}NO_5Cr$: (C, H, N).

Complex **12** was prepared by aminolysis of (diphenylamino)carbene **20**. Dry, gaseous ammonia was bubbled slowly through 10 mL of a 1:1 mixture of 95% ethanol/dimethoxyethane containing 0.57 g (1.53 mmol) of complex **20** for 6 h. The solvent was removed under vacuum, and the product was purified by column chromatography (30 g silica gel, 60–200 mesh eluted with 2:1 methylene chloride/hexane) to give 0.24 g (70%) of **12**, as a pale yellow solid, mp 182 °C dec. ^1H NMR ($CDCl_3$): δ 8.6–9.3 (br s, 2, NH_2), 11.69 (dd, J = 13, 23, 1 Hz, =CH). Anal. Calcd for $C_6H_3NO_5Cr$: (C, H, N).

Isoindoline complexes **27**, **40**, and **41** were prepared by amine/methoxy exchange from the corresponding methoxy carbenes with the same general procedure.

Complex **27**: Isoindoline (220 μL, 2.0 mmol) was added to a solution of methoxycarbene **1** (0.50 g, 2.0 mmol) in 10 mL of THF. After stirring at 25 °C for 3 h, the solvent was removed under vacuum, and the residue was purified by column chromatography (25 g of silica gel, 200–400 mesh, hexane/CH_2Cl_2 4:1) to give 0.41 g (60%) of **27** as a light yellow solid. ^1H NMR ($CDCl_3$): δ 2.84 (s, 3, CH_3), 4.96 (s, 2, CH_2), 5.49 (s, 2, CH_2), 7.26, 7.28, 7.36, 7.39 (m, 4, ArH). Anal. Calcd for $C_{15}H_{11}NO_5Cr$: (C, H, N).

Complex **40**: From 0.93 g (2.97 mmol) of methoxycarbene **5** and 0.35 mL (3.17 mmol) of isoindoline was obtained 1.15 g (94%) of **40** as a yellow solid. ^1H NMR ($CDCl_3$): δ 4.56 (s, 2, CH_2), 5.64 (s, 2, CH_2), 6.80 (d), 7.06 (d), 7.3–7.48 (m, 9, ArH). Anal. Calcd for $C_{20}H_{13}NO_5Cr$: (C, H, N).

Complex **41**: From 0.18 g (0.54 mmol) of methoxy(phenylacetylide)carbene complex[48] and 60 μL (0.54 mmol) of isoindoline at −78 to +25 °C was obtained 55 mg (25%) of **41** as an orange-red solid. ^1H NMR ($CDCl_3$): δ 5.22 (s, 2, CH_2), 5.62 (s, 2, CH_2), 7.2–7.6 (m, 9, ArH). Anal. Calcd for $C_{22}H_{13}NO_5Cr$: (C, H, N).

Aminoalkoxycarbene complexes **43** and **44** were prepared following the procedure of Fischer.[49]

Complex **43**: From chromium hexacarbonyl (2.20 g, 10.0 mmol), lithium dibenzylamide (10.0 mmol), and trimethoxonium tetrafluoroborate (2.22 g, 15.0 mmol) was obtained 1.35 g (33%) of **43** as a cream solid. ^1H NMR ($CDCl_3$): δ 4.25 (s, 3, OCH_3), 4.54 (s, 2, CH_2), 5.21 (s, 2, CH_2), 6.8–7.5 (m, 10, ArH). Anal. Calcd for $C_{21}H_{17}NO_6Cr$: (C, H, N).

Complex **44**: From chromium hexacarbonyl (1.10 g, 5.0 mmol), lithium diisopropylamide (5.0 mmol, from diisopropylamine and *n*-butyllithium), and trimethyloxonium tetrafluoroborate (1.11 g, 7.5 mmol) was obtained 0.63 g (38%) of **44** as a cream 7.1 Hz, ^1H NMR ($CDCl_3$): δ 1.24 (d, J = 7.6 Hz, $CHCH_3$), 1.32 (d, J = 7.6 Hz, $CHCH_3$), 3.50 (sept, J = 7.1 Hz, $CHCH_3$), 4.20 (s, 3, OCH_3), 5.02 (sept, J = 7.1 Hz, $CH(CH_3)$). Anal. Calcd for $C_{13}H_{17}NO_6Cr$: (C, H, N).

Complexes **33**, **34**, **35**, and **38** were prepared by amine/methoxy exchange from complexes **6**, **7**, **8**, and **5**, respectively.

Complex **33**: At −60 °C, dimethylamine (3 mL, liquid) was added to solid complex **6** (2.00 g, 5.60 mmol), and the mixture was allowed to slowly warm to 25 °C, venting gaseous amine as the mixture warmed. The resulting yellow solid was taken up in CH_2Cl_2 and passed through a short (1 in.) plug of silica gel. Removal of solvent gave >95% yield of pure carbene **33**, mp 74 °C. ^1H NMR ($CDCl_3$): δ 3.02 (s, 3, NCH_3), 3.79 (s, 3, OCH_3), 3.95 (s, 3, NCH_3), 6.63, 6.90 (d, J = 6 Hz, 4, ArH). Anal. Calcd for $C_{15}H_{13}NO_6Cr$: (C, H, N).

Complex **34**: The reaction was carried out exactly as above, starting with 2.00 g of complex **7**, mp 90 °C. ^1H NMR ($CDCl_3$): δ 3.05 (s, 3, NCH_3), 4.01 (s, 3, NCH_3), 6.80, 7.62 (d, J = 8 Hz, 4, ArH). Anal. Calcd for $C_{15}H_{10}F_3NO_5Cr$: C, H, N).

Complex **35**: The reaction was carried out exactly as above, starting with 2.00 g of complex **8**. ^1H NMR ($CDCl_3$): δ 3.06 (s, 3, NCH_3), 3.80 (s, 3, OCH_3), 3.98 (s, 3, NCH_3), 6.7–7.2 (m, 4, ArH). Anal. Calcd for $C_{15}H_{12}NO_6Cr$: (C, H, N).

Complex **38**: Prepared from complex **5** following the procedure used to prepare complex **41** above. ^1H NMR ($CDCl_3$): δ 1.09 (t, J = 7 Hz, 3, NCH_2CH_3), 1.52 (t, J = 7 Hz, 3, NCH_2CH_3), 3.37 (q, J = 7 Hz, 2, NCH_2), 4.29 (q, J = 7 Hz, 2, NCH_2), 6.69 (d, J = 7 Hz, 2), 7.13 (t, J = 7 Hz, 1), 7.34 (t, J = 7 Hz, 2, ArH). Anal. Calcd for $C_{16}H_{15}NO_5Cr$: (C, H, N).

Complex **2**: Tetramethylammonium ate complex $[(CO)_5Cr{=}C(O)CH_3]^-NMe_4$ (4.74 g, 12.77 mmol) in 100 mL of CH_2Cl_2 was treated with pivaloyl chloride (1.54 g, 12.77 mmol) at −40 °C, and the resulting mixture was stirred at −30 °C for 0.75 h. Benzyl alcohol (1.52 g, 14.05 mmol) was added, and the mixture was stirred at −30 °C for an additional 0.75 h and then warmed to 25 °C. Silica gel (3.5 g) was added to the mixture and the volatiles were removed under vacuum. Purifica-

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tion by column chromatography (silica gel, hexane) gave 3.32 g (80%) of **2** as a low melting yellow solid. ^{1}H NMR ($CDCl_3$): δ 2.99 (s, 3, CH_3), 5.92 (br s, 2 CH_2), 7.45 (s, 5, ArH). Anal. Calcd for $C_{14}H_{10}O_6Cr$: (C, H).

Complex **3** was prepared by the standard Fischer procedure[2] from chromium hexacarbonyl (0.985 g, 5.00 mmol), *tert*-butyllithium (2.5 mL, 2 M) and triethyloxonium tetrafluoroborate (1.05 g, 5.5 mmol) to give 1.10 g (67%). ^{1}H NMR ($CDCl_3$): δ 1.23 (s, 9, $C(CH_3)_3$), 1.61 (t, J = 7 Hz, 3, CH_2CH_3), 5.17 (q, J = 7 Hz, 2, OCH_2). Anal. Calcd for $C_{12}H_{14}O_6Cr$: (C, H).

Complex **9**, mp 81 °C: ^{1}H NMR ($CDCl_3$): δ 2.16 (s, 6, CH_3), 4.02 (br s, 3, OCH_3), 7.0–7.5 (m, 3, ArH).

Complex **10**: In a dry, 100-mL Airless Ware flask, 2,5-difluorobenzene (2.90 g, 15.0 mmol) was dissolved in 40 mL of THF, and 2 equiv (15 mL, 2 M) of *tert*-butyllithium was added at −78 °C. The mixture was stirred for 2 h at −78 °C, and the resulting solution was added to chromium hexacarbonyl (3.30 g, 15.0 mmol) in 200 mL of THF at −78 °C. After 0.5 h at this temperature, the reaction mixture was allowed to warm to room temperature, and the solvent was removed under vacuum. The dark red residue was dissolved in 30 mL of water, and trimethyloxonium tetrafluoroborate (3.32 g, 22.5 mmol) was added in portions. After 0.25 h, a two-phase mixture was formed. The aqueous mixture was extracted three times with ether, and the ether phase was dried over Na_2SO_4. Removal of solvent, followed by purification by column chromatography (silica gel, hexane/CH_2Cl_2 3:5/1) gave 3.50 g (67%) of complex **10**. ^{1}H NMR ($CDCl_3$): δ 4.37 (br s, 3, OCH_3), 7.0, 7.3 (m, 3, ArH). Anal. Calcd for $C_{13}H_6FO_6Cr$: (C, H).

Complex **37** was prepared by aminolysis of complex **10**, as above. ^{1}H NMR ($CDCl_3$): δ 3.22 (s, 3, NCH_3), 4.05 (s, 3, NCH_3), 6.95 (t), 7.22 (m, 5, ArH). Anal. Calcd for $C_{14}H_9F_2NO_5Cr$: (C, H, N).

Competition Experiments (Figure 5). General Procedure. All experiments were performed in oven- or flame-dried 20-mL Pyrex ($\lambda > 280$ nm) test tubes. After weighing in equimolar amounts of the carbenes, the test tubes were capped with a septum and purged with argon for at least 1 min. Dry and degassed CH_3CN (5 mL) was transferred via a canula to produce a 0.02–0.04 M solution. *N*-Methylbenzylidenimine (1 equiv) was added via syringe and the samples irradiated for the indicated period of time (3–7 h) without stirring at a distance of 10 cm from a 450-W lamp. After the irradiation, the solvent was evaporated under reduced pressure. The residue, redissolved in 30 mL of EtOAc and transferred into an Erlenmeyer flask, was air oxidized in a light box fitted with 6–20 W Vitalight fluorescent tubes and/or in the direct sunlight. The chromium residues were removed by filtration through Celite and the filtrate evaporated under reduced pressure. The crude reaction mixture was analyzed by ^{1}H NMR (200 MHz) and the relative amounts of produced β-lactams (E/Z isomers combined) were obtained by integration over well-resolved peaks of the individual compounds. The ^{1}H NMR (200 MHz) spectra of the pure β-lactams were obtained from independent experiments. β-Lactams, with reported ^{1}H NMR spectra at a field of 60 MHz, were synthesized and purified according to literature procedures to obtain their ^{1}H NMR spectra at 200 MHz. [For the sake of simplicity the β-lactams were named after their substituent on carbon 3.]

(a) [(Dibenzylamino)methylene]chromium(0) pentacarbonyl **16**, [(diisobutylamino)methylene]chromium(0) pentacarbonyl **15**, and *N*-methylbenzylidenimine were irradiated for 3 h. (Dibenzylamino)-β-lactam[16] and (diisobutylamino)-β-lactam were produced in a ratio greater than 10:1. *cis*-1-Methyl-3-(diisobutylamino)-4-phenyl-β-azetidinone: ^{1}H NMR ($CDCl_3$) δ 0.78 (d, J = 7 Hz, 6 CH_3), 0.82 (d, J = 7 Hz, 6, CH_3), 1.50–1.70 (m, 2, CH), 2.20–2.40 (m, 4, CH_2), 2.73 (s, 3 NCH_3), 3.91 (d, J = 2 Hz, 1 PhCHN), 4.41 (d, J = 2 Hz, 1, NCHCO), 7.1–7.3 (m, 5, ArH); IR (hexane) ν_{CO} 1770 cm^{-1}.

(b) [(Dibenzylamino)methylene]chromium(0) pentacarbonyl **16**, [(dimethylamino)methylene]chromium(0) pentacarbonyl **13**, and *N*-methylbenzylidenimine were irradiated for 7 h. (Dibenzylamino)-β-lactam[16] and (dimethylamino)-β-lactam[16] were obtained in a 16:1 ratio. An experiment with only 1 h of irradiation gave exclusively (dibenzylamino)-β-lactam.

(c) [(Dimethylamino)methylene]chromium(0) pentacarbonyl **13**, [(diphenylamino)methylene]chromium(0) pentacarbonyl **20**, and *N*-methylbenzylidenimine were irradiated for 5 h. (Dimethylamino)-β-lactam[16] and (diphenylamino)-β-lactam were obtained in a 1:7 ratio. Authentic (diphenylamino)-β-lactam was prepared as follows. A solution of 0.20 g (0.54 mmol) of [(diphenylamino)methylene]chromium(0) pentacarbonyl **20** and 66 μL of *N*-methylbenzylidenimine (0.54 mmol) in 10 mL of dry and degassed CH_3CN were irradiated for 10 h and air oxidized for 18 h in the "light box" and 4 h in direct sunlight. The crude reaction mixture (176 mg) was chromatographed twice on 8 g of SiO_2 (200–400 mesh) with hexane/EtOAc 3:2 to give 140 mg (79%) of *cis*-1-methyl-3-(diphenylamino)-4-phenyl-β-azetidinone. ^{1}H NMR ($CDCl_3$): δ 2.90 (s, 3, NCH_3), 4.98 (d, J = 2, 1 Hz, PhCHN), 5.48 (d, J = 2 H, 1, Ph_2NCHCO), 6.69 (d), 6.8–7.24 (m, 15, ArH); IR (CCl_4) ν_{CO} 1760 cm^{-1} (C=O). Anal. Calcd for $C_{22}H_{20}N_2O$: (C, H, N).

(d) [(Dibenzylamino)methylene]chromium(0) pentacarbonyl **16**, [(diphenylamino)methylene]chromium(0) pentacarbonyl **20**, and *N*-methylbenzylidenimine were irradiated for 7 h. (Dibenzylamino)-β-lactam[16] and (diphenylamino)-β-lactam were obtained in a 1:2 ratio.

(e) [(Dibenzylamino)methylene]chromium(0) pentacarbonyl **16**, [methylmethoxycarbene]chromium(0) pentacarbonyl, and *N*-methylbenzylidenimine were irradiated for 7 h. (Dibenzylamino)-β-lactams[16] and (methoxymethyl)-β-lactam were obtained in a 1:1 ratio.

(f) [Methylmethoxycarbene]chromium(0) pentacarbonyl, [phenylmethoxycarbene]chromium(0) pentacarbonyl, and *N*-methylbenzylidenimine were irradiated for 5.5 h. (Methoxymethyl)-β-lactam and (methoxyphenyl)-β-lactam were obtained in a 6.6:1 ratio.

A solution of 0.34 g (0.83 mmol) of [(dibenzylamino)methyl]chromium(0) pentacarbonyl **26** and 0.10 mL of *N*-methylbenzylidenimine (0.83 mmol) was irradiated for 12 h and air oxidized in direct sunlight for 19 h. The crude reaction mixture (0.21 g) was chromatographed on 20 g of SiO_2 (200–400 mesh) with benzene/EtOAc 6:1. The β-lactam (29 mg, 25%) and dibenzylamine (75 mg, 46%) were isolated. 1,3-Dimethyl-3-(dibenzylamino)-4-phenyl-β-azetidinone: ^{1}H NMR ($CDCl_3$): δ 1.63 (s, 3, CH_3), 2.82 (s, 3, NCH_3), 3.50 (d, J = 14 Hz, 2, PhCH_2N), 3.72 (d, J = 14 Hz, 2, PhCH_2N), 4.38 (s, 1, PhCHNMe), 6.7 (d), 7.0 (m), 7.4 (m), 15 (ArH); IR (CCl_4) ν_{CO} 1760 cm^{-1}. Anal. Calcd for $C_{25}H_{26}NO$: C, H, N).

Irradiation of [(dimethylamino)methylcarbene]chromium(0) pentacarbonyl **24** with *N*-methylbenzylidenimine under identical conditions resulted in recovery of 80% **24** after irradiation but before oxidation.

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Registry No. 1, 20540-69-6; **2**, 117041-03-9; **3**, 117041-04-0; **4**, 54040-15-2; **5**, 27436-93-7; **6**, 27437-03-2; **7**, 27637-27-0; **8**, 27436-99-3; **9**, 72532-29-7; **10**, 110517-74-3; **11**, 117041-05-1; **12**, 117041-06-2; **13**, 38893-15-1; **14**, 117041-07-3; **15**, 117041-08-4; **16**, 106502-05-0; **17**, 117041-09-5; **18**, 117041-10-8; **19**, 112044-06-1; **20**, 112068-79-8; **21**, 22852-50-2; **22**, 117178-70-8; **23**, 117141-90-9; **24**, 22852-52-4; **25**, 112044-04-9; **26**, 117041-11-9; **27**, 117041-12-0; **28**, 112068-80-1; **29**, 112044-05-0; **30**, 32370-44-8; **31**, 35797-14-9; **32**, 30971-68-7; **33**, 117041-13-1; **34**, 117041-14-2; **35**, 117041-15-3; **36**, 112044-02-7; **37**, 117041-16-4; **38**, 117041-17-5; **39**, 112044-01-6; **40**, 117041-18-6; **41**, 117041-19-7; **42**, 112044-07-2; **43**, 117041-20-0; **44**, 117041-21-1; **45**, 28471-37-6; **46**, 67012-34-4; **47**, 33726-04-4; **48**, 37017-55-3; **49**, 14782-94-6; **50**, 113217-99-5; $AcN(CH_2Ph)_2$, 10479-30-8; $(CO)_5Cr{=}C(MeO)(C{\equiv}CPh)$, 99824-96-1; $[(CO)_5Cr{=}C(O)CH_3]^-NMe_4$, 15975-93-6; *N*,*N*-diisopropylformamide, 2700-30-3; *N*,*N*-diisobutylformamide, 2591-76-6; (2*S*)-*N*-formyl-2-methoxymethylpyrrolidine, 63126-45-4; (2*S*)-*N*-formyl-2-(*tert*-butoxymethyl)pyrrolidine, 116997-59-2; *N*,*N*-diphenylformamide, 607-00-1; isoindoline, 496-12-8; lithium dibenzylamide, 116997-60-5; lithium diisopropylamide, 4111-54-0; 1,3-difluorobenzene, 372-18-9; *cis*-1-methyl-3-(diisobutylamino)-4-phenyl-β-acetidinone, 116997-56-9; *N*-methylbenzylidenimine, 622-29-7; *cis*-1-methyl-3-(diphenylamino)-4-phenyl-β-azetidinone, 116997-57-0; 1,3-dimethyl-3-(dibenzylamino)-4-phenyl-β-azetidinone, 116997-58-1.