various adsorbates on supported catalysts is indicated by spectra of $CH_3C\equiv CCH_3$, $CF_3C\equiv CCF_3$, and $CF_3C\equiv CH^{21}$ in which ν_{CC} modes in analogous $\sigma_2\pi$ surface species are assigned to bands at 1576, 1540, and 1572 cm^{-1}, respectively.[22]   At least three mechanisms may account for the difference in surface species on the single crystal and the supported metal: (1) metal–support interactions change the nature of the binding of the adsorbate to the metal; (2) rearrangement and hydrogen transfer in the adsorbate require the cooperation of several neighboring sites and these sites are blocked at saturation coverage; (3) the finite size of the metal crystallite leads to changes in the electronic structure of the metal so that the adsorbate binding is fundamentally different.

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Phosphinoalkylsilyl Complexes. 6.[1] Isolation of a Silyl Complex of Iridium(I). Crystal and Molecular Structure of Dicarbonyl(triphenylphosphine)-[(((diphenylphosphino)ethyl)dimethylsilyl]iridium

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Hydrometalation of dicobalt octacarbonyl with triorganosilanes, -germanes, or -stannanes gives access[2] to thermally stable products $R_3MCo(CO)_4$ which may be regarded as heavy-element congeners of the extremely reactive[3] tetracarbonylcobalt alkyls $RCo(CO)_4$ (R = Me, Et, etc). By contrast, although alkyl-M^I(I) derivatives are known[4,5] for both rhodium and iridium, the extensive family of silyl, germyl, or stannyl compounds formed by these two metals are almost exclusively M^I(III) species.[6] Exceptions appear to be provided only by a series of complexes $R_3MIr(CO)_3(PPh_3)$ (M = Ge, R = Ph; M = Sn, R = Me or Ph) and $Me_3SnRh(CO)_2$-$(PPh_3)_2$ (1), synthesized from anionic M^I precursors by Collman et al.,[7] and by $Me_3GeIr(CO)(PPh_3)_2$ (2), a compound isolated by Glockling and Wilbey[8] through reaction of ethylene with a dihydridoiridium(III) complex, eq 1.   We have recently em-

$$H_2Ir(PPh_3)_2(CO)GeMe_3 + C_2H_4 =$$
$$Ir(PPh_3)_2(CO)GeMe_3 + C_2H_6 \quad (1)$$
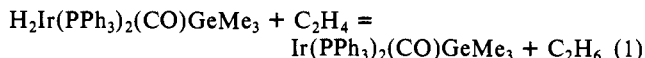
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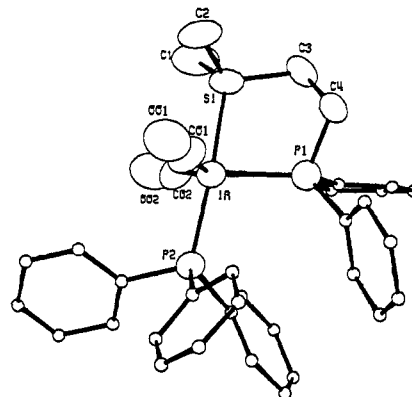(3) Heck, R. F. In "Organic Synthesis via Metal Carbonyls"; Wender, I.; Pino, P., Eds.; Wiley-Interscience: New York, 1968; Vol. I, p 373.
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Figure 1. ORTEP drawing of molecule 4. Selected bond distances and angles: Ir–Si, 2.454 (6); Ir–P(1), 2.342 (5); Ir–P(2), 2.371 (5); Ir–CO-(1), 1.873 (19); Ir–CO (2), 1.795 (24) Å. Si–Ir–P(1), 81.9 (2)°; Si–Ir–P(2), 175.7 (2)°; P(1)–Ir–P(2), 101.7 (2)°; Si–Ir–CO (1), 87.5 (8)°; Si–Ir–CO(2), 84.1 (8)°; P(1)–Ir–CO(1), 108.2 (7)°; P(1)–Ir–CO(2), 119.6 (6)°; P(2)–Ir–CO(1), 93.5 (8)°; P(2)–Ir–CO(2), 92.0 (8)°.

phasized[1] that corresponding silyl-M^I(I) compounds have remained unknown although such species are of potential significance in relation to silyl coupling reactions[9] and in spite of the fact that routes to silyl complexes of the platinum-group elements have been extensively researched[10] in relation to metal-catalyzed olefin hydrosilylation. Against this background we wish to describe the formation of a chelate-stabilized silyl–iridium(I) complex via reductive elimination from Ir(III): the stereochemistry of the product has also been established by an X-ray structure determination.

We concluded on the basis of preliminary experiments[11] that UV irradiation was without effect on the *cis*-dihydridoiridium(III) complex $[Ir(PPh_2CH_2CH_2SiMe_2)(PPh_3)(CO)H_2]$ (3). In fact prolonged photolysis (250 h, 450-W medium-pressure Hg lamp) in an evacuated quartz tube of a THF solution of compound 3, which results in extensive decomposition, is accompanied by conversion in low yield (<30%) to a product for which IR and ^{31}P NMR data[12] were compatible with formulation as an iridium(I) species $[Ir(PPh_2CH_2CH_2SiMe_2)(PPh_3)(CO)_2]$ (4). Accordingly a similar reaction performed under an atmosphere of CO gas afforded compound 4 in over 80% yield in only 8 h. The same complex is recovered in ca. 80% yield after filtration and extraction into hexane following treatment of the precursor[8] $[Ir(PPh_2CH_2CH_2SiMe_2)(PPh_3)(CO)(H)(Cl)]$ (5) in THF solution with MeMgCl then CO gas. Careful recrystallization (ether/hexane mixture) provided colorless needles of compound 4 suitable for X-ray diffraction.[12] The crystal structure determination confirms the geometry proposed on the basis of the spectral data (ORTEP drawing, Figure 1). The molecule possesses no symmetry (centrosymmetric space group), adopting a five-coordinate arrangement in which Si is axial, trans to the triphenylphosphine P atom with the two CO ligands in the equatorial plane; bond angles are close to those in an idealized trigonal bipyramid. The Ir–Si bond length at 2.454 (6) Å is rather longer

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(12) Data for compound 4. Anal. Calcd for $C_{36}H_{35}IrO_2P_2Si$: C, 55.20; H, 4.51. Found: C 54.52; H, 4.40. IR (KBr pellet) ν_{CO} 1960, 1912 cm^{-1}. NMR: ^{1}H (C_6D_6, 250 MHz) δ 0.999 (s, 3 H), 0.992 (s, 3 H, SiCH$_3$), 0.64 (m, 2 H, SiCH$_2$), 2.28 (m, 2 H, PCH$_2$), 6.80–7.31 (m, 25 H, PH$_2$– and PPh$_3$ hydrogens); ^{31}P (THF, 24.3 MHz) δ –114.0 (PPh$_2$–), –140.0 (PPh$_3$, $^2J_{P-P}$ = 24 Hz). Crystal data: IrP$_2$SiO$_2$C$_{36}$H$_{35}$; M 781.9; monoclinic; space group P2$_1$/c; a = 13.376 (5) Å, b = 28.804 (8) Å, c = 10.023 (5) Å; β = 109.50 (4)°; V = 3640 Å^3; Z = 4; D_{calcd} = 1.43 g cm^{-3}; Picker four circle diffractometer, Mo Kα (λ = 0.71069 Å) radiation, μ = 36.6 cm^{-1}; 2743 observed reflections refined to a conventional R = 0.066 (R_w = 0.073).

than values we have observed in related Ir(III) derivatives.[13] The structure reported here for compound **4** closely resembles that suggested[7] for the rhodium–tin complex **1** on the basis of spectroscopic data.

It may be speculated that "anchoring" of the silyl group to Ir(III) in **3** results in reductive loss of H_2 or CH_4 (rather than a SiR_3-bound fragment) in a rate-determining step to give an extremely reactive square Ir(I) intermediate which is subsequently trapped as its CO adduct. Surprisingly, the same adduct is formed in photolysis experiments conducted in benzene or hexane in the absence of added CO, implicating compound **3** in an intermolecular CO transfer. We are continuing to examine potential routes to coordinatively unsaturated species where the electron-releasing character[1,14] of anchored silyl ligands may lead to novel reactivity.

Supplementary Material Available: Fractional atomic coordinates and temperature parameters, anisotropic temperature parameters, and tables of bond distances and angles for compound **4** (4 pages). Ordering information is given on any current masthead page.

(13) Compound 3, Ir–Si = 2.392 (3) Å; compound 5, Ir–Si = 2.404 (13) Å. Auburn, M. J.; Stobart, S. R.; Zaworotko, M. J.; Brennan, E. M.; Cameron, T. S., unpublished data.

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Ammonolysis of Cephamycins: 13C NMR Characterization of the Intermediates from β-Lactam Ring Cleavage Prior to Loss of the 3'-Group

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Recently Faraci and Pratt[1] provided the first evidence that loss of the 3'-group of a cephalosporin need not occur in concert with β-lactam opening. Such was accomplished via stopped-flow experiments on the reaction of TEM-2 β-lactamase with the cephalosporins PADAC and cephaloridine. We wish to report studies on the ammonolysis of cefoxitin and cephamycin C in which, for the first time, we have spectroscopically characterized the intermediates resulting from β-lactam cleavage prior to loss of the carbamic acid anion from position 3'. This was accomplished by examining the ammonolysis in liquid ammonia at –50 °C, using carbon-13 NMR spectroscopy.[2,3]

Experimental Section. Approximately 35–40% w/v solutions of cefoxitin[4] and cephamycin C[5] in anhydrous ammonia were prepared at –60 to –70 °C. These were placed in the spectrometer and warmed to –47 to –50 °C for the reaction studies. Carbon-13 NMR spectra were obtained at 25.16 MHz, using a Varian XL-100 spectrometer operated in the Fourier transform mode.

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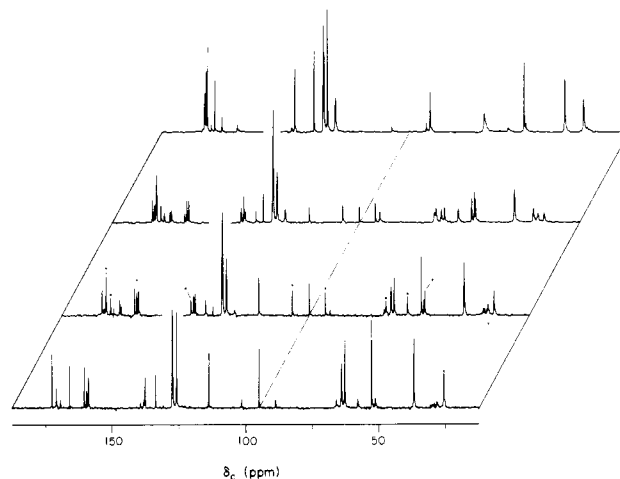
Figure 1. Elapsed reaction time plot for cefoxitin in liquid ammonia at approximately –50 °C. Reaction times are 11, 23.5, 45.5, and 185 min, respectively, from bottom to top. The accumulation interval is 10 min in each case, and absolute intensity presentations are shown at constant scale factor. Key carbon atoms in **2a** are starred; diagonals of constant chemical shift are shown.

Reaction solutions were observed in 10-mm tubes placed inside 12-mm tubes with annular CD_3COCD_3 lock. Spectral widths, acquisition times (and exponential smoothing parameters), and pulse nutation angles were 10 kHz, 0.4 s, and 23°, respectively.

Results and Discussion. The ammonolyses of **1a** and **1b** were straightforward. Initially both compounds undergo β-lactam cleavage to intermediates **2a** and **2b** in accord with the reaction path proposed by Faraci and Pratt.[1] Both **2a** and **2b** retain their carbamate groups and have lifetimes sufficient for carbon-13 spectral characterization. Subsequent reactions yield **3a** and **3b**,

1a R = (thiophen-2-yl)-CH_2- Cefoxitin

1b R = $^-O_2CCH-(CH_2)_3$- Cephamycin C
         |
        $^+NH_3$
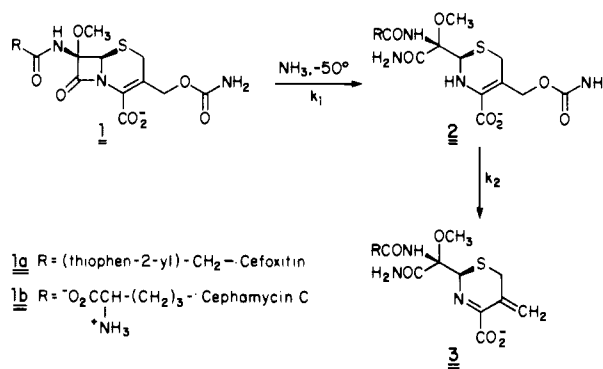
which are stable to the ammonolysis conditions, and readily characterized by carbon-13 spectroscopy. This is the first time that intermediates such as **2a** and **2b** have been observed, thus establishing the formation of **3a** and **3b** via two-step processes.

Identification of **2a** is based on the carbon-13 data presented in Figure 1. In the bottom trace the strongest signals are those of **1a**. The same signals persist in the center traces with decreasing intensities. They are virtually absent in the top trace, which is essentially the spectrum of **3a** and the anion of carbamic acid at δ_c 168.4. Comparison of the traces reveals an additional set of signals ascribed to **2a** (Table I). Off-resonance proton decoupling supported all assignments listed in Table I. Examination of traces corresponding to other reaction times establishes the gradual increase and subsequent decrease of the signals, as a group, ascribed to **2a**. Key carbon-13 shift effects identifying **2a** are the increased shielding of C_3 by 12.6 ppm, now conjugated to an amine rather than an amide nitrogen, and large changes in shielding of C_4, C_6, C_7, and C_8, the latter having been converted to a primary amide carbonyl. Conversion to **3a** produces some 30 ppm deshielding of C_3 and C_4 with smaller but significant effects at C_6 and the 4-carboxylate. The exo-methylene carbon becomes olefinic and appears downfield. Analogous spectral changes occur when