indicate that the NH_2 bridge remains intact.

Although the mechanism of the oxidative-addition reaction has not been investigated in detail, our qualitative observations suggest that oxidative addition occurs via a coordinatively and electronically unsaturated species, presumably the 14e species $Ir(PEt_3)_2Cl$.[20] Ethylene loss from **1** occurs readily, at a much faster rate than the reaction with ammonia. The amido complex **2** could also be obtained from reaction of NH_3 with $Ir(PEt_3)_3Cl$ or $Ir(PEt_3)_2(C_2H_4)Cl$[21] at approximately the same rate, suggesting that ligand dissociation in not rate determining and that the same species, $Ir(PEt_3)_2Cl$, is involved in the rate-determining oxidative addition. This is in accord with the mechanism of H_2 oxidative addition to Rh(I), which has been shown to proceed via the 14e species $Rh(L)_2Cl$.[22] Furthermore, studies of C–H reductive elimination from octahedral Rh(III) complexes have shown that reductive elimination occurs through a five-coordinate, 16e, Rh(III) species, and therefore, by microscopic reversibility, C–H oxidative addition takes place via the 14e Rh(I) complex.[23] Further studies aimed at defining the mechanism and scope of this unique N–H cleavage reaction are now in progress.

Acknowledgment. We thank Barbara Larsen for her assistance in obtaining and interpreting FAB/MS data. Thanks are also extended to D. Reardon and M. Cushing for their excellent technical assistance.

Supplementary Material Available: Detailed report for structure determinations including tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, interatomic distances, intramolecular angles, and intermolecular distances and figures depicting the structures for compounds **3a** and **4** (12 pages); tables of calculated and observed structure factors (29 pages). Ordering information is given on any current masthead page.

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[19] **7a**: ^{1}H NMR (acetone-d_6) δ −5.71 (t, J_{H-P} = 17.0 Hz, 2 H, Ir–H), N–H obscured by P–CH_2 (~1.8 ppm); $^{31}P\{^1H\}$ NMR (acetone-d_6) δ −5.89 (s); IR (Nujol) 3394, 3325 (m, ν_{N-H}), 2126 (s, ν_{Ir-H}), 2026 cm^{-1} (s, ν_{CO}). **7b**: ^{1}H NMR (acetone-d_6) δ −7.94 (t, J_{H-P} = 18.5 Hz, 2 H, Ir–H), −0.05 (s (br), 2 H, N–H), 1.01 (s (br), 2 H, N–H); $^{31}P\{1H\}$ NMR (acetone-d_6) δ −8.52 (s); IR (Nujol) 3410, 3327 (m, N–H), 2175 cm^{-1} (s).

[20] Reaction steps involving the addition of NH_3 to ethylene can be excluded since ethylamines were not detected as reaction products.

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[24] The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

[25] Contribution No. 4107.

Articles

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Synthesis of Aminooxycarbene Complexes of Iron with *N*-Alkyl, -Allyl, and -Carbamoyl Groups

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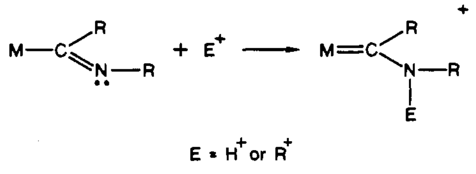
The aminooxycarbene complex $Cp(CO)_2Fe(=\overline{COCH_2CH_2N}H)^+$ (I) is deprotonated by NaH to give $Cp(CO)_2Fe(-\overline{COCH_2CH_2N})$ (II), whose nitrogen reacts with electrophiles. With Me_3O^+, II yields the *N*-methyl carbene $Cp(CO)_2Fe(=\overline{COCH_2CH_2N}Me)^+$ (III). Reaction of II with allyl bromide yields the *N*-allyl carbene $Cp(CO)_2Fe(=\overline{COCH_2CH_2N}CH_2CH=CH_2)^+$ (IV), which under UV photolysis loses CO, allowing the allyl group to coordinate in $Cp(CO)\underline{Fe(=\overline{COCH_2CH_2N}CH_2CH=}CH_2)^+$ (V). The nitrogen of II adds to the carbon of methyl isocyanate; this is followed by isocyanate nitrogen attack on a coordinated CO ligand to give a carbamoyl–carbene complex, $Cp(CO)\underline{Fe(=\overline{COCH_2CH_2N}C(=O)N(Me)C}=O$ (VI). Protonation of VI cleaves the carbamoyl ligand to give the *N*-carbamoyl carbene $Cp(CO)_2Fe(=\overline{COCH_2CH_2N}C(=O)NHMe)^+$ (VII). These interesting new complexes are characterized by their ^{1}H and ^{13}C NMR and IR spectra.

Introduction

The general reaction[1] of electrophiles (E^+) with imidoyl ligands to form aminocarbene complexes (eq I) may be illustrated by the protonation of $Cp(CO)_2Fe(-C(H)(=NR))$, where Cp = η-C_5H_5,[2] $(CO)_2(PPh_3)_2(Cl)Os(-C(H)(=NMe))$,[3] and $Cl(PEt_3)_2Pt(-C(H)(=NR))$[4] to give the corresponding aminocarbene complexes. By treatment with base, these aminocarbenes



(I)

E = H$^+$ or R$^+$

are deprotonated to regenerate the imidoyl complexes. The above platinum imidoyl complex[4] is alkylated by Me_2SO_4 to give the aminocarbene, where E = Me (eq I). Werner and co-workers[5–7]

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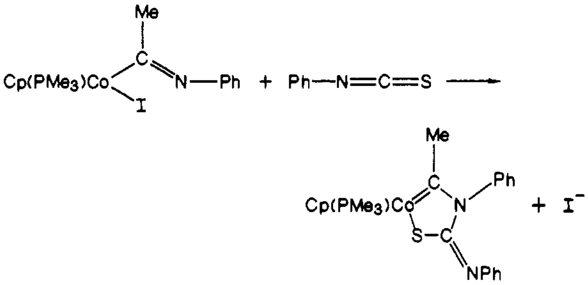
Table I. Infrared Spectra of the Complexes in CH_2Cl_2 Solvent

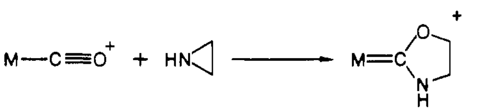
complex	ν(CO), cm^{-1}	ν(C=O), cm^{-1}
$[Cp(CO)_2Fe(=\overline{COCH_2CH_2N}H)]PF_6$ (I(PF_6))	2060 (vs), 2015 (vs)	
$Cp(CO)_2Fe(=\overline{COCH_2CH_2N})$ (II)	2035 (vs), 1980 (vs)	
$[Cp(CO)_2Fe(=\overline{COCH_2CH_2N}CH_3)]PF_6$ (III(PF_6))	2054 (vs), 2009 (vs)	
$[Cp(CO)_2Fe(=\overline{COCH_2CH_2N}CH_2CH=CH_2)]PF_6$ (IV(PF_6))	2055 (vs), 2008 (vs)	
$[Cp(CO)\underline{Fe(=\overline{COCH_2CH_2N}CH_2CH=}CH_2)]PF_6$ (V(PF_6))	2010 (vs)	
$Cp(CO)\underline{Fe(=\overline{COCH_2CH_2N}—C(=O)N(Me)C}=O)$ (VI)	1960 (vs)	1602 (s), 1675 (s)
$[Cp(CO)_2Fe(=\overline{COCH_2CH_2N}C(=O)NHCH_3)]PF_6$ (VII(PF_6))	2064 (vs), 2020 (vs)	1732 (s)

have reported reactions in which the imidoyl group in $Cp(PMe_3)(I)Co(—C(Me)(=NPh))$ adds to the electrophilic carbon center in a variety of unsaturated organic molecules (e.g., acetone, MeCN, CS_2, $Ph_2C=S$, and PhNCS). The reaction (eq II) with phenyl isothiocyanate is typical of this reactivity.[5]



(II)

Recently, we reported[8-10] a simple method for preparing aminooxycarbene complexes from relatively electron-poor metal carbonyl complexes and aziridine (eq III). The aminocarbene



(III)

ligand of $Cp(CO)_2Fe(=\overline{COCH_2CH_2N}H)^+$ (I) was deprotonated with NaH to give the imidoyl complex $Cp(CO)_2Fe(—\overline{COCH_2CH_2N})$ (II), whose nitrogen was sufficiently basic to form a complex, $[Cp(CO)_2Fe(=\overline{COCH_2CH_2N})Pd(\mu-Cl)Cl]_2$, upon reaction with $PdCl_2(NCMe)_2$.[11] In the present paper, we describe further studies of the nucleophilicity of the nitrogen in II in its reactions with organic electrophiles.

Experimental Section

All reactions were performed under an N_2 atmosphere with use of Schlenk techniques. Unless noted otherwise, reagent-grade chemicals were used as received. The solvent Et_2O was distilled from Na/benzophenone under N_2; CH_2Cl_2 was dried over CaH_2 and distilled under N_2. The solvents were stored over type 4A molecular sieves. $MgSO_4$ was dried in an oven before use. Complex I(PF_6), $[Cp(CO)_2Fe(=\overline{COCH_2CH_2N}H)]PF_6$, was prepared as reported previously.[11] The photolysis reactions were carried out in a Bradford Scientific unit equipped with a General Electric F4T4-BL ultraviolet light source emitting primarily 366 nm wavelength light. The quartz reaction vessel was water-cooled.

Infrared spectra were recorded on a Perkin-Elmer 281 or 681 spectrometer. Most ^1H and ^{13}C NMR spectra were obtained on a Nicolet NT-300 spectrometer. Spin-decoupled and 2-D NMR spectra were recorded on a Bruker WM-300 instrument. The mass spectrum of complex VI was obtained on a Finnigan 4000 GC/MS, while FAB mass spectra were run on samples in an ONPOE (*o*-nitrophenyl octyl ether) matrix with a Kratos MS-50 spectrometer. IR and NMR spectra of the complexes are collected in Tables I–IV.

Table II. ^1H NMR Data for the Complexes[a]

complex	OCH_2	NCH_2	Cp	other
I	4.60 (t)[d]	3.70 (t)[d]	5.30 (s)	9.50 (s) [NH]
II	3.75 (t)	3.60 (t)	5.00 (s)	
III	4.60 (t)[d]	3.77 (t)[d]	5.26 (s)	3.27 (s) [NCH_3]
IV	4.66 (t)[d]	3.76 (t)[d]	5.30 (s)	*b*
V	4.79 (m) 4.64 (m)	3.65 (m) 3.43 (m)	5.06	*b*
VI	4.66 (s, br)	4.02 (s, br)	4.84 (s)	3.00 (s) [NCH_3]
VII	4.78 (t)[d]	4.00 (t)[d]	5.24 (s)	6.61 (s) [NH], 2.81 (d)[c] [NCH_3]

[a] In CD_3CN; chemical shifts (δ) in ppm downfield from Me_4Si. Legend: t = triplet, d = doublet, s = singlet, br = broad, dd = doublet of doublets, m = multiplet. [b] See Table IV for allyl resonances. [c] J_{HH} = 4.6 Hz. [d] J_{HH} = 9–10 Hz.

Syntheses of the Complexes. $[Cp(CO)_2Fe(=\overline{COCH_2CH_2N}Me)]PF_6$ (III(PF_6)). The imidoyl complex $Cp(CO)_2Fe(—\overline{COCH_2CH_2N})$ (II) was generated[11] by adding 50% NaH (0.050 g, 1.0 mmol) in mineral oil to 0.050 g (0.13 mmol) of $[Cp(CO)_2Fe(=\overline{COCH_2CH_2N}H)]PF_6$ (I(PF_6)) in 20 mL of CH_2Cl_2 and stirring for 2 h. After the mixture was filtered under N_2 through $MgSO_4$, $(Me_3O)PF_6$ (0.026 g, 0.13 mmol) was added. After this mixture was stirred for 15 min, the solvent was evaporated under vacuum, and the residue was washed with small amounts of Et_2O until the washings were colorless. The residue was then dissolved in CH_2Cl_2 under N_2. After filtration through $MgSO_4$, the light yellow filtrate was evaporated under vacuum until a precipitate began to form. Further precipitation was induced by the addition of Et_2O. The mixture was allowed to stand at −20 °C overnight, and the solvent was decanted, leaving a light yellow powder of the product, III, which was washed with Et_2O and hexanes and then vacuum-dried; yield 0.029 g (57%). Anal. Calcd for $C_{11}H_{12}F_6FeNO_3P$: C, 32.46; H, 2.97. Found: C, 32.25; H, 2.64. FAB MS: *m/e* 262 (M^+), 234 (M^+ − CO), 206 (M^+ − 2CO), where M^+ is the cation in III.

$[Cp(CO)_2Fe(=\overline{COCH_2CH_2N}CH_2CH=CH_2)]PF_6$ (IV(PF_6)). Excess 50% NaH (0.18 g, 3.8 mmol) in mineral oil was added to 0.18 g (0.46 mmol) of I in 40 mL of CH_2Cl_2 to generate II. After it was stirred for 2 h, the mixture was filtered through $MgSO_4$, and $CH_2=CHCH_2Br$ (0.56 g, 4.6 mmol) was added to the filtrate. The solution was refluxed for 4 h. Then, an excess of KPF_6 (1.5 g) was added, and the mixture was stirred for 30 min. The solvent was removed under vacuum, and the residue was dissolved in CH_2Cl_2 and purified by recrystallization as described in the preparation of III. The product, IV, was a light yellow powder, yield 0.065 g (33%). Anal. Calcd for $C_{13}H_{14}F_6FeNO_3P$: C, 36.06; H, 3.26; N, 3.23. Found: C, 36.25; H, 3.49; N, 3.27. FAB MS: *m/e* 288 (M^+), 260 (M^+ − CO), 232 (M^+ − 2CO).

$[Cp(CO)\underline{Fe(=\overline{COCH_2CH_2N}CH_2CH=}CH_2)]PF_6$ (V(PF_6)). Photolysis of a light yellow solution of IV (0.090 g, 0.2 mmol) in 35 mL of CH_2Cl_2 for 2 h changed the color to dark yellow. The solvent was evaporated under vacuum, and the residue was extracted with CH_2Cl_2 and purified as described in the isolation of III. The product, V, was a dark yellow powder, yield 0.069 g (82%). Anal. Calcd for $C_{12}H_{14}F_6FeNO_2P$: C, 35.58; H, 3.48; N, 3.46. Found: C, 35.47; H, 3.53; N, 3.21. FAB MS: *m/e* 260 (M^+), 232 (M^+ − CO).

$Cp(CO)\underline{Fe(=\overline{COCH_2CH_2N}C(=O)N(Me)C}=O)$ (VI). The oil was removed from 50% NaH (0.25 g, 63 mmol) in mineral oil by washing

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Table III. ^{13}C NMR Data for the Complexes[a]

complex	carbene	CO	Cp	OCH_2	NCH_2	other
I[b,c]	221.5	212.1	88.7	74.2	47.0	
II[b,d]	183.7[g]	214.3	85.6	64.9	56.2	
	f	*f*	88.0[c]	66.5[c]	57.3[c]	
III[c]	218.8	211.4	87.7	72.8	53.0	37.2 [NCH_3]
IV[c]	220.3	221.2	87.9	73.2	53.2	*h*
V[c]	225.5	218.5	87.2	75.9[i]	49.4[j]	*h*
VI[e]	184.5	214.4	88.3	71.6	46.4	29.0 [NCH_3], 153.0 [NC(=O)N], 247.7 [Fe(C=O)N]
VII[c]	*f*	210.9	88.3	74.9	50.4	27.9 [NCH_3], 147.5[g] [NC(=O)N]

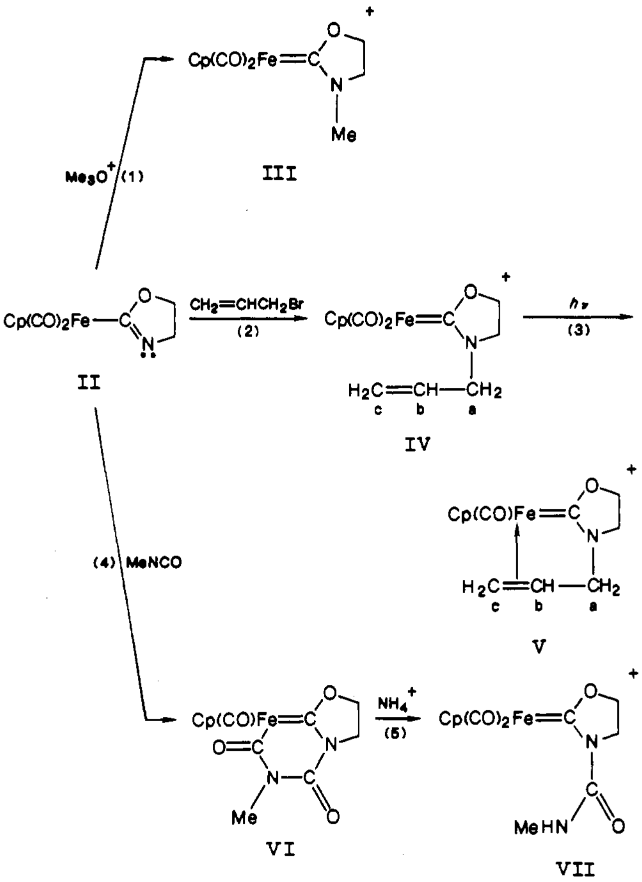
[a] Chemical shifts in ppm, referenced from CD_3CN (δ 1.29). [b] Reference 11. [c] In CD_3CN solvent. [d] In C_6D_6 solvent. [e] In CD_2Cl_2 solvent. [f] Not observed. [g] Assignment uncertain due to low signal to noise ratio. [h] See Table IV for allyl resonances. [i] t, J_{CH} = 157.5 Hz. [j] t, J_{CH} = 144.5 Hz.

Table IV. ^1H and ^{13}C NMR Data for the Allyl Groups in IV and V[a]

complex	C_a	C_b	C_c
		^1H NMR	
IV	4.32 (d)[e]	5.90 (m)	5.41 (m) 5.39 (m)
V	3.65 (d) 2.92 (d)[f]	5.48 (m)	3.04 (dd)[g] 3.97 (dd)[h]
		^{13}C NMR	
IV	50.4	131.3	121.1
V	48.1[b]	72.5[c]	52.7[d]

[a] Solvents and abbreviations are the same as in Tables II and III for these compounds; carbon atoms a, b, and c are identified in Scheme I. [b] t, J_{CH} = 148 Hz. [c] d, J_{CH} = 161.6 Hz. [d] t, J_{CH} = 164.6 Hz. [e] J_{HH} = 5.9 Hz. [f] J_{HH} = 13.0 Hz. [g] J_{HH} = 12.0 and 5.8 Hz. [h] J_{HH} = 12.1 and 6.8 Hz.

Scheme I



four times with 10-mL portions of hexanes; the NaH was then dried under vacuum for 2 h. After it was dried under vacuum for 2 h, 0.25 g (0.64 mmol) of I was dissolved in 20 mL of CH_2Cl_2 under N_2. This solution was added to the dry NaH to form II; the mixture was stirred for 2 h and then filtered through $MgSO_4$. To this solution was added 54 μL (0.92 mmol) of MeNCO; this solution was stirred for 1.5 h. In order to protonate any unreacted II and thereby facilitate its removal, 0.5 g (3 mmol) of NH_4PF_6 was added to the solution, which was stirred for 3 min and then quickly filtered through $MgSO_4$. The filtrate, which contained a mixture of complexes I, VI, and VII, was evaporated under vacuum to leave a residue, which was dissolved in Et_2O (I and VII are mostly insoluble). The Et_2O solution was filtered through $MgSO_4$ and evaporated under vacuum. The yellow residue was dissolved in acetone and chromatographed on a 2.5 × 10 cm Kieselgel column with acetone as the eluent. The yellow fraction was evaporated to leave bright yellow VI, yield 0.045 g (23%). The product decomposes slowly in solution so that an analytically pure product could not be obtained by recrystallization. It was characterized by its IR and NMR spectra (Tables I–III) and by MS: *m/e* 304 (M^+), 247 (M^+ − NCOMe).

$[Cp(CO)_2Fe(=\overline{COCH_2CH_2N}C(=O)NHMe)]PF_6$ (VII(PF_6)). Excess NH_4PF_6 (~0.5 g, 3 mmol) was added to a solution of 0.0070 g (0.023 mmol) of VI in 8 mL of CH_2Cl_2. After the mixture was stirred 4 h, the solvent was removed under vacuum, and the orange residue was extracted into CH_2Cl_2 and purified as described for the isolation of III. The yield of the orange VII was 0.0078 g (75%). Anal. Calcd for $C_{12}H_{13}O_4FeF_6PN_2$: C, 32.03; H, 2.91; N, 6.22. Found: C, 31.73; H, 2.85; N, 6.14. FAB MS: *m/e* 305 (M^+), 277 (M^+ − CO), 248 (M^+ − 2CO).

Results and Discussion

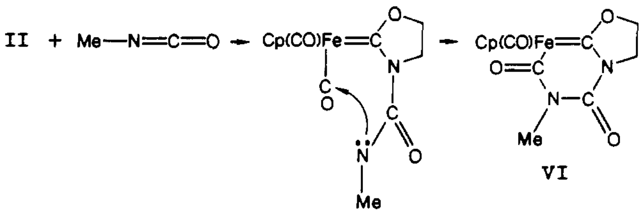
The reactions of the imidoyl complex $Cp(CO)_2Fe(\overline{-COCH_2CH_2N})$ (II) reported in this paper are summarized in Scheme I; equations discussed below are those numbered in Scheme I. All of the products are air-stable in the solid state for a period of at least several months.

The nitrogen of II is methylated (eq 1) by $[Me_3O]PF_6$ within 15 min at room temperature to give the *N*-methyl carbene III in 57% isolated yield. As expected, the ν(CO) values (Table I) for III are higher than those of II; however, they are not quite as high as those for I, indicating that Me is more electron-donating than H. In the ^1H NMR spectrum (Table II) of III, the two sets of CH_2 protons in the carbene ring each occur as triplets, as expected for an A_2B_2 system; this pattern is characteristic of I, II, and aminooxycarbene complexes of other metals.[8-11]

Allyl bromide reacts (eq 2) with II in refluxing CH_2Cl_2 to give the *N*-allyl carbene complex IV in 33% isolated yield. The same complex was prepared similarly from allyl iodide. The ν(CO) frequencies of IV are very similar to those of the *N*-methyl complex III. Ultraviolet photolysis (eq 3) of IV results in the loss of a CO ligand and coordination of the olefinic bond of the allyl group to the Fe to give V in 82% yield. As expected, V shows only one ν(CO) band in its IR spectrum.

Notable changes occur in the ^1H NMR spectrum in the conversion of IV to V. In IV, the OCH_2CH_2N sets of protons each occur as triplets as found in other simple aminooxycarbene complexes (e.g., I and III). However, in V, the asymmetry at the Fe causes all four of the OCH_2CH_2N protons to become inequivalent, and the OCH_2 and NCH_2 resonances become complex multiplets. The allyl ^1H and ^{13}C signals of IV and V are summarized in Table IV. The ^{13}C chemical shift assignments were made on the basis of spectra of related derivatives in this study; for V, a proton-coupled ^{13}C spectrum gave J_{CH} values (Tables III and IV), which were helpful in making the proposed assignments. The ^1H NMR assignments for IV were based on integrations and the close similarity of the allyl portion of the spectrum to that of allylamine. For V, the assignments were made on the basis of integration, chemical shift values, coupling patterns, and, most importantly, a proton-correlated 2D NMR experiment. The two CH_a protons

Scheme II



(Table IV) occur as a simple doublet due to coupling with H_b in IV but become inequivalent in V. The chemical shifts of the olefinic protons in IV move upfield upon coordination to the Fe in V; the upfield shift is very similar to that observed for propene when it becomes coordinated in $CpFe(CO)_2(propene)^+$.[12] The olefinic ^{13}C resonances (C_b and C_c) of IV have chemical shifts typical of those of free alkenes,[13] but in V, these resonances move upfield into the range observed for $CpFe(CO)_2(olefin)^+$ complexes.[12] It should be noted that it is possible in V for the olefin to be oriented relative to the other ligands in two ways; NMR spectra of the complex show, however, the presence of only one isomer.

Reaction of II with methyl isocyanate, Me—N=C=O (eq 4), gives VI, which was not sufficiently stable in solution to allow purification. However, its spectra are consistent with the formulation shown in Scheme I. The mass spectrum of VI shows a parent ion corresponding to the correct composition. The IR spectrum shows three $\nu(CO)$ absorptions; the highest (1960 cm^{-1}) may be assigned to the CO ligand. $\nu(C{=}O)$ of the carbamoyl group is assigned to the band at 1602 cm^{-1}, because this frequency is similar to those observed in the related carbamoyl complexes $Cp(CO)_2Fe(—C({=}O)NHR)$: R = H, 1593 cm^{-1}; R = CH_3, 1625 cm^{-1}.[14] The $\nu(CO)$ band at 1675 cm^{-1} is assigned to the urea-like carbonyl. Organic ureas have $\nu(CO)$ absorptions in the region around 1660 cm^{-1}, e.g., 1695 cm^{-1} for tetramethylurea.[15]

The ^1H NMR spectrum (Table II) is consistent with structure VI; in particular, the four OCH_2CH_2N protons in the carbene ring are inequivalent because of the asymmetry at Fe, as they were in V, giving rise to broad, highly split signals. In the ^{13}C NMR spectrum of VI, the chemical shifts are reasonably assigned as given in Table III. Only the carbamoyl carbon $FeC({=}O)N$ assignment at δ 247.7 is somewhat surprising because it is so different from the δ 195.2 signal observed for the carbamoyl carbon in $Cp(CO)_2Fe(—C({=}O)NHMe)$;[16] however, the carbamoyl group in VI is quite unusual and its chemical shift may not fall in the normal carbamoyl range. Presumably, the formation of VI in eq 4 occurs by initial addition (Scheme II) of the imidoyl nitrogen to the isocyanate carbon followed by nucleophilic attack of the isocyanate nitrogen on the carbon of a CO ligand.

Typically, acids react[17,18] with carbamoyl ligands by protonating the nitrogen with loss of the amine, which leaves a coordinated CO ligand. Similarly, VI reacts with NH_4^+, a very weak acid, to protonate the nitrogen and generate a CO ligand to give VII in 75% isolated yield (eq 5).[19] The presence of two CO ligands in VII is established by the presence of two $\nu(CO)$ bands at 2064 and 2020 cm^{-1} in the terminal CO region; the urea-like $\nu(CO)$ absorption at 1732 cm^{-1} has a relatively high value,[15] presumably due to delocalization of electron density from the ring nitrogen into the carbene carbon, which reduces donation to the urea carbonyl group. Both the ^1H and ^{13}C NMR spectra are consistent with structure VII shown in Scheme I. The NCH_3 protons occur as a doublet due to coupling with the NH proton as demonstrated by adding 2 drops of D_2O to an acetonitrile solution of VII, which causes the NCH_3 doublet to collapse to a singlet and the NH signal to disappear. If NaH in mineral oil is added to a CH_2Cl_2 solution of VII, the nitrogen is deprotonated and VI is regenerated.

A variety of other electrophiles were reacted with II. In all of these reactions, it is important that the solutions be rigorously dry; otherwise II is protonated to give the carbene I. This occurred when the following commercial chemicals were used: $CH_3C({=}O)Cl$, $CH_3(C{=}O)Br$, $Et_2O{\cdot}BF_3$, BF_3 gas, CO_2, CS_2, and $(CF_3CO)_2O$. When $CH_3(C{=}O)Cl$ was purified by refluxing and distilling over PCl_5 and then over *N,N*-dimethylaniline,[20] it reacted with an equimolar amount of II to give a small amount of I, but most of II remained unreacted. Phenyl isocyanate, purified by vacuum distillation over P_2O_5,[20] reacted with II to give a small amount of I, but the IR spectrum of the reaction mixture also suggested the formation of the phenyl analogue of VI, as well as other products. Dry diphenylketene ($Ph_2C{=}C{=}O$) reacted with II to give a mixture of products, which were not identified. There was no reaction of II with ethylene oxide, styrene oxide, ethylene sulfide, or *i*-PrN=C=N-*i*-Pr in refluxing CH_2Cl_2. Nor was there a reaction with MeNCS or PhNCS at room temperature. Thus, II is only moderately nucleophilic, certainly not as nucleophilic as amines or alkoxides.

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