

## Communications

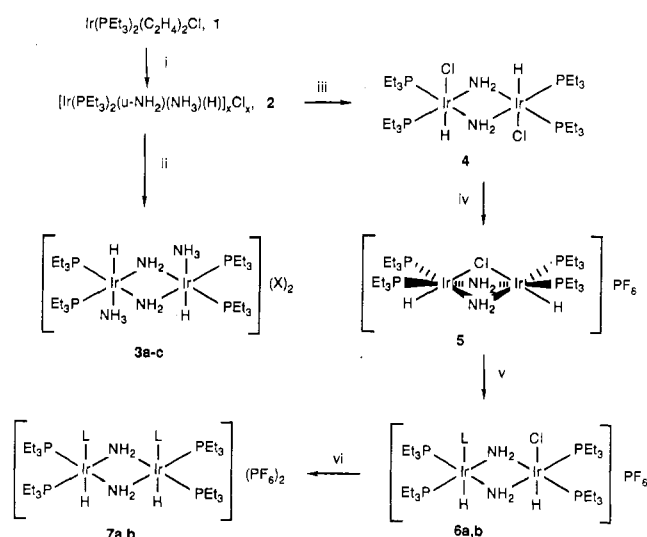
## N-H Activation. 1. Oxidative Addition of Ammonia to Iridium(I). Isolation, Structural Characterization, and Reactivity of Amidoiridium Hydrides

Sir:

Although the oxidative addition of N-H bonds may be an important step in the selective functionalization of ammonia, amines, and other N-H-containing molecules, examples of this reaction with nonactivated molecules are scarce. Reaction of NH<sub>3</sub> with the early-transition-metal complexes CpTiC<sub>5</sub>H<sub>4</sub>TiCp<sub>2</sub> and Cp<sub>2</sub>MH<sub>2</sub> (M = Zr, Hf) may involve N-H oxidative addition,<sup>1-3</sup> and M<sub>3</sub>(CO)<sub>12</sub> (M = Os, Ru) oxidatively adds ammonia and simple amines.<sup>4</sup> Molecules containing more activated N-H bonds such as amides, imides, and ammonium ions undergo N-H addition reactions to other group VIII (group 8-10<sup>24</sup>) complexes.<sup>5</sup>

In our study of the reactivity of amines and ammonia with transition-metal complexes, we chose to emphasize the late metals over the early metals. The weaker, late-metal M-N bond should be more reactive and enhance the potential for catalysis. We report here the first example of the oxidative addition of ammonia to a mononuclear late-transition-metal complex, including isolation, structural characterization, and reactivity of the product hydrido-amido complexes.

We have employed in our studies an electron-rich, low-valent, sterically unhindered iridium complex that contains labile ethylene ligands, Ir(PEt<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>Cl (**1**).<sup>6</sup> Reaction of a THF solution of **1** with an excess of liquid ammonia at 25 °C over 24 h gave C<sub>2</sub>H<sub>4</sub> and the iridium hydride complex **2** (Scheme I) as a white powder in ca. 90% isolated yield. Although solution NMR spectra of **2** could not be obtained due to its high insolubility,<sup>7</sup> the formulation of **2** is supported by solid-state <sup>31</sup>P MAS NMR (s, -8.4 ppm), IR (ν<sub>Ir-H</sub> = 2162 cm<sup>-1</sup> (s); ν<sub>N-H</sub> = 3355 (m), 3313 (m),

Scheme I<sup>a</sup>

<sup>a</sup> Reaction conditions: (i) NH<sub>3</sub>(l), 25 °C, 24 h; (ii) NaBPh<sub>4</sub>, AgBF<sub>4</sub> or TlPF<sub>6</sub> in acetone (**3a**, X = BPh<sub>4</sub>; **3b**, X = BF<sub>4</sub>; **3c**, X = PF<sub>6</sub>); (iii) 110 °C, pyridine; (iv) TlPF<sub>6</sub>, acetone; (v) L, acetone (**6a**, L = CO (50 psi); **6b**, L = *t*-BuNC); (vi) TlPF<sub>6</sub> + L in acetone.

3217 (s), 3115 cm<sup>-1</sup> (s); Nujol) and elemental analyses as well as by the compositions and structures of the related derivatives **3** and **4** (vide infra).

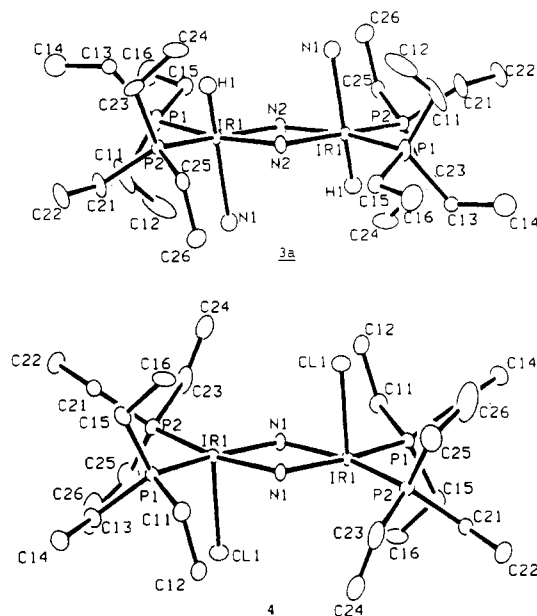
Treatment of **2** with 1 eq of NaBPh<sub>4</sub> in methanol followed by crystallization of the resulting white solid from acetone/diethyl ether (solvent/vapor diffusion) gave rectangular pale yellow crystals of **3a** in about 50% isolated yield. The BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> salts could be obtained in a similar fashion by treatment with AgBF<sub>4</sub> or TlPF<sub>6</sub>, respectively. Complex **4** was obtained by heating a stirred slurry of **2** in pyridine at 110 °C for about 1 h. The resulting yellow solution, which contained **4** quantitatively by NMR, was filtered, stripped in vacuo to a yellow precipitate, which was redissolved in toluene, and filtered again. Crystallization from toluene by vapor diffusion of pentane gave colorless, irregular block-shaped crystals of **4** in about 50% isolated yield.<sup>8</sup>

Since no other crystallographically characterized M(NH<sub>2</sub>)(H) complexes had been previously reported,<sup>9</sup> complexes **3a** and **4** were

- (1) Armor, J. N. *Inorg. Chem.* **1978**, *17*, 203.
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- (3) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.
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- (6) Tulip, T., unpublished results. The compound was synthesized from [Ir(cyclooctene)<sub>2</sub>Cl]<sub>2</sub>, PEt<sub>3</sub>, and C<sub>2</sub>H<sub>4</sub>.
- (7) **2** was found to be soluble in CH<sub>3</sub>OH; however, an unambiguous assignment of its NMR spectra in CD<sub>3</sub>OD was precluded by the rapid formation of other Ir species. NH<sub>2</sub>, NH<sub>3</sub>, and (Ir-H) resonances were observed, however, in the <sup>1</sup>H NMR spectrum.

(8) By removing the toluene in vacuo, **4** was obtained as a slightly impure solid in ca. 90% yield. This material was of sufficient purity for the syntheses of the derivatives **6a,b** and **7a,b**.

(9) Several M(NH<sub>2</sub>)(NH<sub>3</sub>) complexes have been structurally characterized. (a) Kretschmer, M.; Heck, L. Z. *Anorg. Allg. Chem.* **1982**, *490*, 215. (b) Schaefer, W. P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *39*, 1610. (c) Rotzinger, F. P.; Marty, W. *Inorg. Chem.* **1983**, *22*, 3593. (d) Clegg, W.; Sykes, A. G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *40*, 1820. (e) Curtis, N. J.; Hagen, K. S.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1571.



**Figure 1.** ORTEP drawings of **3a** (cation only) and **4** showing thermal ellipsoids at 20% probability level. Selected bond distances (Å) and angles (deg) are as follows. For **3a**: Ir<sub>1</sub>-N<sub>1</sub>, 2.244 (4); Ir<sub>1</sub>-N<sub>2</sub>, 2.128 (3); Ir<sub>1</sub>-N<sub>2</sub>, 2.127 (3); Ir<sub>1</sub>-H<sub>1</sub>, 1.61 (5); Ir<sub>1</sub>-P<sub>1</sub>, 2.274 (1); Ir<sub>1</sub>-P<sub>2</sub>, 2.280 (1); N<sub>2</sub>-Ir<sub>1</sub>-N<sub>2</sub>, 77.0 (1); N<sub>1</sub>-Ir<sub>1</sub>-N<sub>2</sub>, 84.3 (1); N<sub>1</sub>-Ir<sub>1</sub>-N<sub>2</sub>, 84.5 (1); P<sub>1</sub>-Ir<sub>1</sub>-N<sub>2</sub>, 170.1 (1); P<sub>2</sub>-Ir<sub>1</sub>-N<sub>2</sub>, 169.9 (1); H<sub>1</sub>-Ir<sub>1</sub>-N<sub>1</sub>, 157 (2). For **4**: Ir<sub>1</sub>-N<sub>1</sub>, 2.10 (1); Ir<sub>1</sub>-N<sub>1</sub>, 2.13 (1); Ir<sub>1</sub>-P<sub>1</sub>, 2.264 (4); Ir<sub>1</sub>-P<sub>2</sub>, 2.264 (4); Ir<sub>1</sub>-Cl<sub>1</sub>, 2.504 (4); Cl<sub>1</sub>-Ir<sub>1</sub>-P<sub>1</sub>, 96.4 (1); Cl<sub>1</sub>-Ir<sub>1</sub>-P<sub>2</sub>, 94.3 (1); Cl<sub>1</sub>-Ir<sub>1</sub>-N<sub>1</sub>, 87.8 (3); Cl<sub>1</sub>-Ir<sub>1</sub>-N<sub>1</sub>, 84.4 (3); P<sub>1</sub>-Ir<sub>1</sub>-N<sub>1</sub>, 168.6 (3); P<sub>2</sub>-Ir<sub>1</sub>-N<sub>1</sub>, 168.7 (3); N<sub>1</sub>-Ir<sub>1</sub>-N<sub>1</sub>, 75.3 (5).<sup>10</sup>

analyzed by single-crystal X-ray diffraction<sup>10</sup> (Figure 1). The overall structures of **3a** and **4** are very similar. Both complexes lie on crystallographic inversion centers, have  $C_{2h}$  symmetry, and exist as dimers in the solid state with the Ir atoms symmetrically bridged by two  $NH_2$  ligands. Each Ir atom is also coordinated to two  $PEt_3$  ligands, a terminal hydride, and X (**3a**, X =  $NH_3$ ; **4**, X = Cl), and has a distorted octahedral coordination geometry. The hydride and X ligands are trans. The  $Ir_2P_4N_2$  core atoms are planar within experimental error (largest deviation from planarity is 0.05 Å for both **3a** and **4**, respectively), and the Ir-X moieties are tipped 23 and 7° (**3a** and **4**, respectively) relative to the perpendicular of this plane and are tipped away from the  $PEt_3$  ligands. This distortion is presumably due to steric crowding of the  $PEt_3$  ligands. The Ir- $\mu$ -N and Ir-P bond distances (average 2.120, 2.270 Å, respectively) are nearly identical for **3a** and **4**.<sup>11</sup> For **3a**, the Ir- $NH_3$  distance is 0.12 Å longer than the Ir- $NH_2$  distance, an effect that may be attributed, in part, to the greater trans influence of a hydride relative to a  $PEt_3$  ligand but is also consistent with the high stability of the Ir- $NH_2$  bridge (vide infra). The Ir-Ir distances for **3a** and **4** are 3.33 and 3.34 Å, respectively, outside the range of normal Ir-Ir bonding distances.

IR and  $^1H$  and  $^{31}P$  NMR spectroscopic analyses of **3** and **4** were consistent with the solid-state structures. Ir-H stretching vibrations characteristic of terminal hydrides were detected at 2182 (s) (**3b**) and 2190 (s)  $cm^{-1}$  (**4**) (**3b** (Nujol)  $\nu_{N-H}$  = 3357 (br), 3312, 3295  $cm^{-1}$ ; **4** (Nujol)  $\nu_{N-H}$  = 3388  $cm^{-1}$ ). The presence of a

terminally bound Cl in **4** was confirmed by the observation of  $\nu_{Ir-Cl}$  at 245  $cm^{-1}$ .<sup>12</sup> Hydride resonances consistent with the cis H/P orientation were observed in the  $^1H$  NMR spectra of both complexes<sup>13</sup> (**3b** (acetone- $d_6$ )  $\delta$  -19.27 (t,  $J$  = 18.0 Hz); **4** ( $C_6D_6$ )  $\delta$  -19.62 (t,  $J$  = 18.0 Hz)), and well-separated  $NH_3$  and  $NH_2$  resonances were observed for **3** (**3b**  $\delta$  0.45 ( $NH_3$ , s(br)),  $\delta$  3.77 ( $NH_3$ , s(br)); **4**  $\delta$  0.45 ( $NH_2$ , s(br))).  $^{31}P$  NMR spectra of both complexes showed singlets at  $\delta$  -12.6 (**3b** (acetone- $d_6$ )) and -10.6 (**4**) ( $C_6D_6$ ), consistent with the  $C_{2h}$  symmetry observed in the solid state. Complex **4** was also successfully characterized by fast atom bombardment mass spectroscopy (FAB/MS), giving molecular ion peaks consistent with the dimeric formulation of **4** ( $m/e$  958,  $M^+$ ,  $^{191}Ir$ ,  $^{35}Cl$ ,  $^{191}Ir$ ).<sup>14</sup>

On the basis of these data, a structure similar to **3**, containing outer-sphere Cl, would be reasonable for **2**, although other isomers or oligomers cannot be ruled out. A monomeric structure seems unlikely since  $\nu_{Ir-Cl}$  was absent from the IR spectrum of **2**. Unlike early transition-metal-amido complexes, N-M  $\pi$  bonding is not expected to contribute to the stabilization of the relatively electron-rich late-transition-metal-amido complexes, and it has been suggested that this accounts for the general lack of late-transition-metal complexes that contain terminal amido ligands.<sup>15</sup>

The stability of complexes **2** and **3** toward loss of ammonia is surprising. Ammonia loss from **2** in pyridine did not occur at a significant rate at temperatures below 100 °C, and slurries of **2** in toluene remained completely unchanged after several hours of reflux. Complex **3** exhibited only slight decomposition after 4 h in refluxing acetone, but complete decomposition occurred at 85 °C. These decomposition products have not been fully characterized.

Preliminary studies of the complexes **2-4** suggest the reactivity of these complexes is dominated by the stability of the Ir- $NH_2$ -Ir bridge. These complexes were inert to ligands such as CO,  $CO_2$ ,  $PEt_3$ , and  $C_2H_4$  at moderate temperatures and pressures. As shown in Scheme I, the introduction of other simple ligands has been achieved by Cl abstraction from complex **3**, although no insertion into the Ir-N bond has been observed. Treatment of an acetone solution of **4** with excess  $TiPF_6$  resulted in the removal of only one Cl and the quantitative formation of the  $\mu$ -Cl complex **5**.<sup>16</sup> It is notable that **5** is stable in acetone, exhibiting no propensity to insert or deprotonate acetone at a significant rate.<sup>17</sup> Treatment of **5** with excess CO (50 psi) or  $t$ -BuNC gave the monosubstituted adducts **6a,b**.<sup>18</sup> Further treatment of **6** with CO or  $t$ -BuNC in the presence of  $TiPF_6$  generated the disubstituted adducts **7a,b**.<sup>19</sup>  $^1H$  NMR spectra of all of these complexes

- (10) Crystal data for **3a**·( $CH_3$ )<sub>2</sub>CO: space group  $P\bar{1}$ ,  $a$  = 12.501 (2) Å,  $b$  = 14.052 (2) Å,  $c$  = 11.902 (2) Å,  $\alpha$  = 91.98 (1)°,  $\beta$  = 92.57 (1)°,  $\gamma$  = 69.24 (1)°,  $V$  = 1952.7 Å<sup>3</sup>,  $Z$  = 1,  $T$  = -100 °C. Crystal data for **4**: space group  $P\bar{1}$ ,  $a$  = 12.428 (6) Å,  $b$  = 14.953 (6) Å,  $c$  = 10.714 (5) Å,  $\alpha$  = 97.96 (4)°,  $\beta$  = 114.35 (3)°,  $\gamma$  = 83.50 (4)°,  $V$  = 1793.0 Å<sup>3</sup>,  $Z$  = 2,  $T$  = -100 °C. The crystal structure of **4** consists of two molecules that lie on different centers of symmetry. The two independent half-molecules differ only in the conformations of the ethyl groups of the  $PEt_3$  ligands. Distances and angles within these two molecules did not differ significantly and are reported as averages.
- (11) A similar M-N distance at 2.09 (2) Å was found for the related complex *cis*-Pt( $PEt_3$ )<sub>2</sub>( $NPh_2$ )Cl: Eadie, D. T.; Pidcock, A.; Stobart, S. R.; Brennan, E. T.; Cameron, S. T. *Inorg. Chim. Acta* **1982**, *65*, L111.

- (12) Nujol mull on polyethylene plates. See: Schramm, K. D.; Tulip, T. H.; Ibers, J. A. *Inorg. Chem.* **1980**, *19*, 3183.
- (13) The hydride resonance at **3** underwent an unusual but reversible change when acetone- $d_6$  solutions of **3** were allowed to stand for a few hours. A new multiplet, which has been tentatively identified as a triplet of triplets ( $J$  = 9, 18 Hz), slowly grew in the same chemical shift while the original triplet disappeared. The remainder of the  $^1H$  NMR spectrum was unchanged. Crystallization of **3** from the solution followed by redissolution in acetone- $d_6$  gave the original triplet resonance in the  $^1H$  NMR spectrum of **3**. The significance of this behavior is not clearly understood and is being investigated.
- (14) An isotope pattern compatible with the presence of  $^{35,37}Cl$  and  $^{191,193}Ir$  was observed.
- (15) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273.
- (16) **5**:  $^1H$  NMR (acetone- $d_6$ )  $\delta$  -25.86 (t,  $J_{H-P}$  = 18 Hz, 2 H, Ir-H), 0.15 (s (br), 2 H, N-H), 1.43 (s (br), 2 H, N-H);  $^{31}P$  { $^1H$ } NMR (acetone- $d_6$ )  $\delta$  -9.5 (s); IR (Nujol) 2226 (m,  $\nu_{Ir-H}$ ), 3395, 3331  $cm^{-1}$  ( $\nu_{N-H}$ ); FAB/MS,  $m/e$  923 ( $M^+$ ,  $^{191}Ir$ ,  $^{35}Cl$ ,  $^{191}Ir$ ). The observed isotope pattern of the  $M^+$  ion was identical with the calculated isotope pattern.
- (17) For a discussion of insertion behavior of metal amides see: Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, U.K., 1980.
- (18) **6a**:  $^1H$  NMR (acetone- $d_6$ )  $\delta$  -6.00 (t,  $J_{H-P}$  = 18.0 Hz, 1 H, Ir-H trans to CO), -20.27 (t,  $J_{H-P}$  = 17.7 Hz, 1 H, Ir-H trans to Cl), 0.35 (s (br), 2 H, NH), 0.45 (s (br), 2 H, N-H);  $^{31}P$  { $^1H$ } NMR (acetone- $d_6$ )  $\delta$  -7.54 (s, 2 P), -10.25 (s, 2 P);  $^{13}C$  { $^1H$ } NMR of  $^{13}C$ -labeled **6a** (acetone- $d_6$ )  $\delta$  176.4 (t,  $J_{C-P}$  = 4.5 Hz, Ir-CO); IR (acetone) 2176 (m,  $\nu_{Ir-H}$ ), 2110 (s,  $\nu_{Ir-h}$ ), 2008  $cm^{-1}$  (s,  $\nu_{CO}$ ). **6b**:  $^1H$  NMR (acetone- $d_6$ )  $\delta$  -20.35 (t,  $J_{H-P}$  = 17.8 Hz, 1 H, Ir-H trans to Cl), -8.39 (t,  $J_{H-P}$  = 17.8 Hz, 1 H, Ir-H trans to  $t$ -BuNC), 0.15 (s (br), 2 H, N-H), 0.31 (s (br), 2 H, N-H), 1.72 (s, ( $CH_3$ )<sub>2</sub>NC);  $^{31}P$  { $^1H$ } NMR (acetone- $d_6$ )  $\delta$  -8.91 (s, 2 P), -10.7 (s, 2 P); IR (acetone): 2178 (s), 2138  $cm^{-1}$  (w).

indicate that the NH<sub>2</sub> 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<sub>3</sub>)<sub>2</sub>Cl.<sup>20</sup> 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<sub>3</sub> with Ir(PEt<sub>3</sub>)<sub>3</sub>Cl or Ir-(PEt<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)Cl<sup>21</sup> at approximately the same rate, suggesting that ligand dissociation is not rate determining and that the same species, Ir(PEt<sub>3</sub>)<sub>2</sub>Cl, is involved in the rate-determining oxidative addition. This is in accord with the mechanism of H<sub>2</sub> oxidative addition to Rh(I), which has been shown to proceed via the 14e species Rh(L)<sub>2</sub>Cl.<sup>22</sup> 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.<sup>23</sup>

- (19) **7a**: <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ -5.71 (t, *J*<sub>H-P</sub> = 17.0 Hz, 2 H, Ir-H), N-H obscured by P-CH<sub>2</sub> (~1.8 ppm); <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>) δ -5.89 (s); IR (Nujol) 3394, 3325 (m, ν<sub>N-H</sub>), 2126 (s, ν<sub>Ir-H</sub>), 2026 cm<sup>-1</sup> (s, ν<sub>CO</sub>). **7b**: <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ -7.94 (t, *J*<sub>H-P</sub> = 18.5 Hz, 2 H, Ir-H), -0.05 (s (br), 2 H, N-H), 1.01 (s (br), 2 H, N-H); <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>) δ -8.52 (s); IR (Nujol) 3410, 3327 (m, N-H), 2175 cm<sup>-1</sup> (s).
- (20) Reaction steps involving the addition of NH<sub>3</sub> to ethylene can be excluded since ethylamines were not detected as reaction products.
- (21) Tulip, T., unpublished results. The monoethylene adduct can be generated directly from **1** by heating **1** in hexane under N<sub>2</sub>.
- (22) Halpern, J.; Wong, C. S. *J. Chem. Soc. Chem. Commun.* 1973, 629.

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.

- (23) (a) Milstein, D. *J. Am. Chem. Soc.* 1982, 104, 5227. (b) Milstein, D. *Acc. Chem. Res.* 1984, 17, 221.
- (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.

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## Articles

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### Synthesis of Aminoxy-carbene Complexes of Iron with *N*-Alkyl, -Allyl, and -Carbamoyl Groups

Lynda K. Johnson and Robert J. Angelici\*

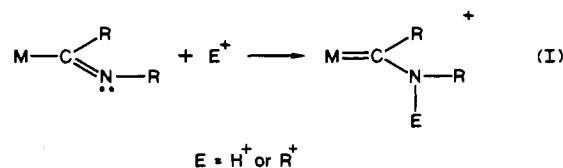
Received August 11, 1986

The aminoxy-carbene complex Cp(CO)<sub>2</sub>Fe(=COCH<sub>2</sub>CH<sub>2</sub>NH)<sup>+</sup> (I) is deprotonated by NaH to give Cp(CO)<sub>2</sub>Fe(=COCH<sub>2</sub>CH<sub>2</sub>N) (II), whose nitrogen reacts with electrophiles. With Me<sub>3</sub>O<sup>+</sup>, II yields the *N*-methyl carbene Cp(CO)<sub>2</sub>Fe(=COCH<sub>2</sub>CH<sub>2</sub>NMe)<sup>+</sup> (III). Reaction of II with allyl bromide yields the *N*-allyl carbene Cp(CO)<sub>2</sub>Fe(=COCH<sub>2</sub>CH<sub>2</sub>NCH<sub>2</sub>CH=CH<sub>2</sub>)<sup>+</sup> (IV), which under UV photolysis loses CO, allowing the allyl group to coordinate in Cp(CO)Fe(=COCH<sub>2</sub>CH<sub>2</sub>NCH<sub>2</sub>CH=CH<sub>2</sub>)<sup>+</sup> (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)Fe(=COCH<sub>2</sub>CH<sub>2</sub>NC(=O)N(Me)C=O) (VI). Protonation of VI cleaves the carbamoyl ligand to give the *N*-carbamoyl carbene Cp(CO)<sub>2</sub>Fe(=COCH<sub>2</sub>CH<sub>2</sub>NC(=O)NHMe)<sup>+</sup> (VII). These interesting new complexes are characterized by their <sup>1</sup>H and <sup>13</sup>C NMR and IR spectra.

#### Introduction

The general reaction<sup>1</sup> of electrophiles (E<sup>+</sup>) with imidoyl ligands to form aminocarbene complexes (eq I) may be illustrated by the protonation of Cp(CO)<sub>2</sub>Fe(=C(H)(=NR)), where Cp = η-C<sub>5</sub>H<sub>5</sub>,<sup>2</sup> (CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(Cl)Os(=C(H)(=NMe)),<sup>3</sup> and Cl-(PEt<sub>3</sub>)<sub>2</sub>Pt(=C(H)(=NR))<sup>4</sup> to give the corresponding amino-

carbene complexes. By treatment with base, these aminocarbenes



are deprotonated to regenerate the imidoyl complexes. The above platinum imidoyl complex<sup>4</sup> is alkylated by Me<sub>2</sub>SO<sub>4</sub> to give the aminocarbene, where E = Me (eq I). Werner and co-workers<sup>5-7</sup>

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