

ca. -264 (OPA) which is characteristic of the strongly deshielded  $^{31}\text{P}$  atom in the cation.

The noncyclic cation may be compared in some sense to the allyl radical which has a bonding ( $\alpha + 1.41\beta$ ), a nonbonding ( $\alpha$ ), and an antibonding  $\pi$  orbital ( $\alpha - 1.41\beta$ ).

Applying the usual first-order corrections for energy differences in the p levels of N and P atoms one again obtains the expected bonding level

$$E = \alpha - \left( \frac{\lambda - \sqrt{\lambda^2 + 8}}{2} \right) \beta$$

nonbonding

$$E = \alpha$$

and the antibonding level

$$E = \alpha - \left( \frac{\lambda + \sqrt{\lambda^2 + 8}}{2} \right) \beta$$

where  $\alpha$  = the Coulomb integral of the nitrogen atom,  $\beta$  = the  $\text{N}_{2p}-\text{P}_{3p}$  overlap integral, and  $(\alpha - \lambda\beta)$  is the Coulomb integral of the phosphorus atom. The bonding and nonbonding levels are filled. The photochemistry of the ion system is under investigation.

The cation is both a Lewis acid and a Lewis base. It has a rather rich chemistry which will be delineated in subsequent reports. For example, very small amounts of the noncyclic cation in a solution containing the  $\text{PF}_6^-$  ion will make the  $^{31}\text{P}$  spectrum of the normally stable  $\text{PF}_6^-$  ion collapse to a broad single peak at room temperature. The cyclic cation does not bring about this labilization of fluorines on the  $\text{PF}_6^-$  ion. Other sharp differences associated with the onset of rotation around the P-N bond will be outlined.

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## Novel Cyclic Carbene Complexes of Iron

Sir:

It is well known that isocyanides coordinate to a variety of transition metals.<sup>1</sup> One of the current interests in the coordination chemistry of isocyanides has been focused on the insertion reaction.<sup>2,3</sup> Studies on this subject have been done in several laboratories.

During our extensive studies on the insertion reactions of alkyl iron complexes with isocyanides, we found new carbene complexes which resulted from unexpected insertion of isocyanide into the C-H bond of an alkyl group. In this communication we report the new finding and give the revised structure for "tris imino type complexes"<sup>4</sup> obtained from dicarbonyl- $\pi$ -cyclopentadienylbenzyliron and cyclohexyl isocyanide.

When the bis imino type complex **1**<sup>5</sup> is treated with

(1) L. Malatesta and F. Bonati, "Isonitrile Complexes of Metals," Wiley, New York, N. Y., 1969.

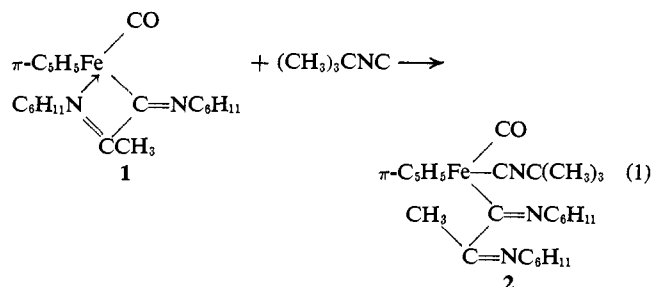
(2) Y. Yamamoto and H. Yamazaki, *Coord. Chem. Rev.*, **8**, 225 (1972).

(3) P. M. Treichel, *Advan. Organometal. Chem.*, **11**, 21 (1973).

(4) Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, **11**, 211 (1972).

(5) Compound **1** can be prepared by two different methods: (1) the photochemical reaction of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CNC}_6\text{H}_{11})\text{COCH}_3$  and

*tert*-butyl isocyanide in benzene at 40° for 8 hr, the reaction results in elimination of the coordinated nitrogen atom and coordination of an incoming isocyanide to the iron atom, giving **2**<sup>6</sup> (eq 1). On treat-



ment of **2** in benzene at 70° for 38 hr, the reddish brown crystals, **3**, having the same empirical formula as that of **2** are formed and characterized by the absence of a coordinated isocyanide group in its infrared spectrum.

Crystals of **3** belong to the monoclinic space group  $P2_1/c$ . Unit cell data are  $a = 11.732$ ,  $b = 10.380$ ,  $c = 22.831$  Å,  $\beta = 112.97^\circ$ , and  $Z = 4$ . A crystal of dimensions  $0.1 \times 0.3 \times 0.7$  mm was mounted on the  $c$  axis, and the 3298 reflections having  $F_o > 3\sigma(F_o)$  and  $2\theta < 130^\circ$  were collected using Cu  $K\alpha$  radiation and a four-circle diffractometer. The position of the Fe atom was determined by a Patterson method using the Harker line and sections, and the H, C, N, and O atoms appeared in successive electron-density maps. The final unweighted  $R$  value was 0.064. Distances and angles in the novel chelate system appear in Figure 1. The five-membered ring containing the iron atom is essentially planar with N(1), N(2), and N(3). The C(3)-C(4), C(2)-N(2), and C(4)-N(3) bond lengths are shorter than expected for normal single bonds, and the C(2)-C(3) bond length is longer than that found for the normal double bond, indicating the existence of a  $\pi$  system involving mainly the N(2)-C(2)-C(3)-C(4)-N(3) atoms. The complex is considered as a kind of carbene complex. The Fe-carbene carbon(4) distance of 1.926 (5) Å is similar to the Fe-C(1)  $\sigma$ -bonded length of 1.973 (5) Å and is relatively shorter than the Fe-C(carbene) distances of 2.02 and 2.03 Å reported for the carbene complex<sup>7</sup>  $[(\text{CH}_3\text{NC})_4\text{Fe}(\text{C}_2\text{N}_4)(\text{CH}_3)_3\text{H}_2]\text{PF}_6)_2$ .

The proton nmr spectrum of **3** is consistent with the X-ray structure determination and provides evidence for the location of protons. The spectrum consists of resonances at  $\tau$  8.57(singlet,  $(\text{CH}_3)_3\text{C}$ ), 7.6-9.2(broad,  $\text{C}_6\text{H}_{10}$ ), 6.4-7.2(b,  $\text{C}_6\text{H}$ ), 5.67(s,  $\text{C}_3\text{H}_5$ ), 4.15(s, CH), and 2.9-3.2(b, NH). The resonance due to two NH protons disappears on treatment with  $\text{D}_2\text{O}$ .

An apparent insertion of an incoming reagent into the C-H bond rather than into the Ru-C bond has been noted in the reaction of  $\pi\text{-C}_5\text{H}_5\text{Ru}(\text{PPh}_3)_2[\text{C}(\text{CO}_2\text{CH}_3)=\text{CH}(\text{CO}_2\text{CH}_3)]$  with  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ .<sup>8</sup>

It is less easy to rationalize the mechanism of formation of the carbene complex. Although there is no

(2) the photochemical reaction between  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  and  $\text{C}_6\text{H}_{11}\text{NC}$ . The elemental analysis and the spectroscopic studies are in agreement with the proposed structure.

(6) The elemental analysis and the mass spectrum gave satisfactory results.

(7) J. Miller, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, **93**, 4613 (1971).

(8) T. Blackmore, M. I. Bruce, F. G. A. Stone, R. E. Davis, and A. Garza, *Chem. Commun.*, 852 (1971).

