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## Evidence for Nitrogen-Bonded Acrylonitrile to Iridium(I) in Acrylonitrilecarbonylbis (triphenylphosphine) iridium(I) perchlorate

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Analyses of <sup>1</sup>H-NMR, infrared and electronic spectral data for [Ir(CH<sub>2</sub>=CHCN)(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (**1**) prepared by the reaction of Ir(OCIO<sub>3</sub>)(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> with CH<sub>2</sub>=CHCN, agree with the suggestion that **1** is a mixture of the nitrogen-bonded acrylonitrile complex, [(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Ir-NCCH=CH<sub>2</sub>]ClO<sub>4</sub> and other compound which may be the C=C π-system-bonded acrylonitrile complex,  $\left\{ \text{(CO) (P(C}_6\text{H}_5\text{)}_3\text{)}_2\text{Ir} - \begin{array}{c} \text{CHCN} \\ \parallel \\ \text{CH}_2 \end{array} \right\} \text{ClO}_4$ .

### Introduction

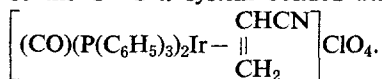
We recently reported the formation of a cationic acrylonitrile-iridium(I) complex, [Ir(CH<sub>2</sub>=CHCN)(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (**1**) by the reaction of Ir(OCIO<sub>3</sub>)(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> (**2**) with CH<sub>2</sub>=CHCN.<sup>1</sup> The bonding between iridium and acrylonitrile in **1**, however, has not been unequivocally understood thus far: CH<sub>2</sub>=CHCN may coordinate to metal through the nitrogen or through the π-system of the nitrile group or/and through the π-system of the olefinic group.<sup>2</sup> Vibrational spectral data are known to be very useful in determining the bonding types of unsaturated nitriles to metals. It is well established that ν<sub>C≡N</sub> increases when the coordination of a nitrile to a metal occurs through the nitrogen.<sup>2</sup> Coordination of a nitrile through the C≡N π-system should cause a significant decrease in ν<sub>C≡N</sub> as seen in succinonitrile (NCCH<sub>2</sub>CH<sub>2</sub>CN) complex of Mn(0).<sup>3</sup> To our knowledge, no acrylonitrile complexes where acrylonitrile is coordinated through the π-system of the nitrile group have been observed thus far. It is also well known that both ν<sub>C=C</sub> and ν<sub>C≡N</sub> of CH<sub>2</sub>=CHCN show considerable decreases (up to -168 cm<sup>-1</sup> for ν<sub>C=C</sub> and up to -55 cm<sup>-1</sup> for ν<sub>C≡N</sub>) upon coordination to metal through the C=C π-system.<sup>2</sup> In this paper, we wish to report that [Ir(CH<sub>2</sub>=CHCN)(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (**1**) prepared by the reaction of Ir(OCIO<sub>3</sub>)(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub> with CH<sub>2</sub>=CHCN is a mixture of nitrogen-bonded acrylonitrile complex,

[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>(CO)Ir-NCCH=CH<sub>2</sub>]ClO<sub>4</sub> and some amount of other compound which may be the C=C π-system-bonded acrylonitrile complex,  $\left[ \text{(P(C}_6\text{H}_5\text{)}_3\text{)}_2\text{(CO) Ir} - \begin{array}{c} \text{CH}_2 \\ \parallel \\ \text{CHCN} \end{array} \right] \text{ClO}_4$ .

### Results and Discussion

Infrared spectrum of **1** (in Nujol) prepared by the reaction of **2** with CH<sub>2</sub>=CHCN shows ν<sub>C≡N</sub> (weak and broad) at 2220~2240 cm<sup>-1</sup> and ν<sub>C=C</sub> (very weak and broad) at 1600~1620 cm<sup>-1</sup>, while free CH<sub>2</sub>=CHCN shows ν<sub>C≡N</sub> (sharp) and ν<sub>C=C</sub> (weak) at 2230 and 1609 cm<sup>-1</sup>, respectively. These infrared spectral data clearly suggest that the acrylonitrile in **1** does not coordinate through the C≡N π-system to iridium, but does not indicate whether the acrylonitrile coordinates through the nitrogen or through the C=C π-system. It should also be mentioned that infrared spectrum of **1** shows two ν<sub>CO</sub> bands at 2052 cm<sup>-1</sup> (medium) and 2047 cm<sup>-1</sup> (strong), which may imply that **1** is a mixture of two complexes since the related monocarbonyl iridium complexes always show a single strong ν<sub>CO</sub> band, respectively.<sup>4</sup> Then, the broad ν<sub>C≡N</sub> band at 2220~2240 cm<sup>-1</sup> observed for **1** may represent two bands: one at lower and the other at higher frequency than 2230 cm<sup>-1</sup> at which free CH<sub>2</sub>=CHCN shows ν<sub>C≡N</sub>. Accordingly, these infrared spectral data for **1** may suggest that **1** is a mixture of the nitrogen-bonded acrylonitrile complex, [(CO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Ir-NCCH=CH<sub>2</sub>]ClO<sub>4</sub> and other compound which may

be the C=C  $\pi$ -system-bonded acrylonitrile complex,

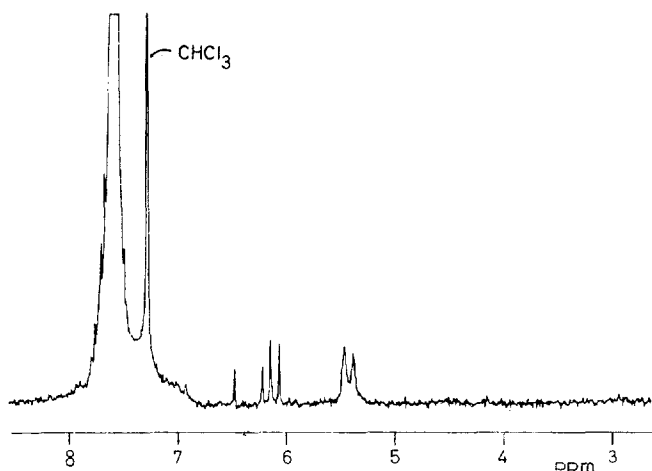


$^1\text{H-NMR}$  spectrum of **1** (Figure 1) prepared by the reaction of **2** with  $\text{CH}_2=\text{CHCN}$  clearly shows that the ratio of the phenyl protons (multiplet at 7.0~8.0 ppm, relative to TMS) to the acrylonitrile protons (multiplet at 5.3~6.5 ppm, relative to TMS) is 10:1, which confirms  $\text{Ir}(\text{CH}_2=\text{CHCN})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  moiety in **1**. The signals due to the coordinated acrylonitrile (5.3~6.5 ppm) in Figure 1 are not unequivocally interpreted as those due to the acrylonitrile in a single compound.<sup>5</sup> In short,  $^1\text{H-NMR}$  spectrum of **1** does not provide conclusive information on the nature of the bonding of acrylonitrile to iridium in **1** except the fact that  $\text{Ir}(\text{CH}_2=\text{CHCN})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  unit is in **1**.

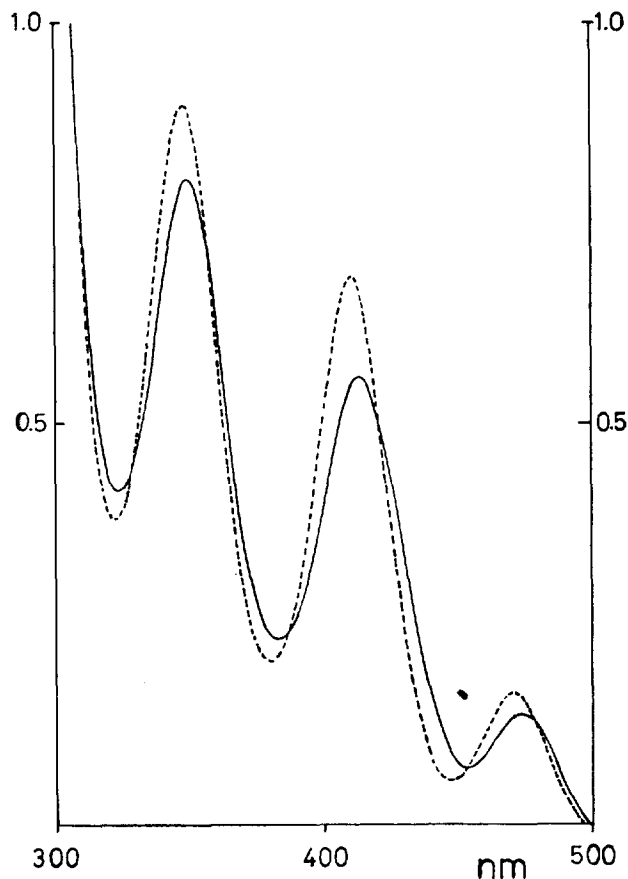
Figure 2 shows the electronic absorption spectrum of **1** in the visible region with three bands at 350, 414 and 475 nm. It is well known that the related four coordinated iridium (I) complexes,  $\text{IrA}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  (A=OH, halogen,  $\text{OClO}_3$ , NCO, NCS, CN *etc.*)<sup>6</sup> and  $[\text{Ir}(\text{L})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$  (L= $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{CH}_2\text{CN}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$ , *cis* and *trans*- $\text{CH}_3\text{CH}=\text{CHCN}$ ,  $\text{CH}_2=\text{CHCH}_2\text{CN}$ ) where L is coordinated to iridium (I) through the nitrogen<sup>7</sup> show the very similar three bands in the visible region. It is also known that  $\text{IrX}(\text{L})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  (X=halogen, L= $\text{CH}_2=\text{CHCN}$ , *trans*- $(\text{CN})\text{CH}=\text{CH}(\text{CN})$ ,  $(\text{CN})_2\text{C}=\text{C}(\text{CN})_2$ )<sup>8</sup> and  $[\text{Ir}(\text{trans}-(\text{CN})\text{CH}=\text{CH}(\text{CN}))(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$ <sup>9</sup> where L and *trans*- $(\text{CN})\text{CH}=\text{CH}(\text{CN})$  are coordinated to iridium through the C=C  $\pi$ -system show no absorption bands in the visible region. It is now evident that the three bands observed for **1** in the visible region (Figure 2) are due to the nitrogen-bonded acrylonitrile complex,  $[(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Ir}-\text{NCCH}=\text{CH}_2]\text{ClO}_4$  present in **1**, since the C=C  $\pi$ -system-bonded acrylonitrile complex,

$\left[ (\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Ir} - \begin{array}{c} \text{CHCN} \\ \parallel \\ \text{CH}_2 \end{array} \right] \text{ClO}_4$  is expected to show no absorption bands in the visible region as  $[\text{Ir}(\text{trans}-(\text{CN})\text{CH}=\text{CH}(\text{CN}))(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$  does (see above and reference 9).

In summary, all these spectroscopic data ( $^1\text{H-NMR}$ ,



**Figure 1.** The 80 MHz-NMR spectrum of  $[\text{Ir}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$  in  $\text{CDCl}_3$  at 30 °C under nitrogen. Chemical shifts in ppm, relative to TMS.



**Figure 2.** Electronic absorption spectrum of  $[\text{Ir}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$  (**1**) ( $2.6 \times 10^{-4}$  M) (—) (for comparison, the spectrum of  $[\text{Ir}(\text{trans}-\text{CH}_3\text{CH}=\text{CHCN})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$  ( $2.6 \times 10^{-4}$  M) (.....) is also shown) in  $\text{CH}_2\text{Cl}_2$  at 20 °C under nitrogen. Cell path length=1.0 cm.

infrared and electronic) observed for **1** agree with the suggestion that  $[\text{Ir}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$  (**1**) prepared by the reaction of  $\text{Ir}(\text{OClO}_3)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  with  $\text{CH}_2=\text{CHCN}$  is a mixture of the nitrogen-bonded acrylonitrile complex,  $[(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Ir}-\text{NCCH}=\text{CH}_2]\text{ClO}_4$  and other compound which may be the C=C  $\pi$ -system-bonded acrylonitrile complex,  $\left[ (\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Ir} - \begin{array}{c} \text{CHCN} \\ \parallel \\ \text{CH}_2 \end{array} \right] \text{ClO}_4$ .

### Experimental

Infrared spectra, electronic absorption spectra and  $^1\text{H-NMR}$  spectra have been measured on a Shimadzu IR-440 Infrared Spectrophotometer using KBr cell in Nujol mull, Shimadzu UV-240 UV-VIS Spectrophotometer at 20 °C under nitrogen, and Bruker WP 80 MHz FT-NMR Spectrophotometer (at Chemistry Department, Sung Kyun Kwan University) in  $\text{CDCl}_3$  at room temperature under nitrogen. Elemental analyses were carried out in Spang Microanalytical Laboratory, Eagle Harbor, Michigan, U.S.A.

All solvents and acrylonitrile were dried and distilled before use.

Iridium compounds,  $\text{Ir}(\text{OClO}_3)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  (**2**) and  $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  which was used in the prepara-

tion of **2** were prepared by the literature methods.<sup>4k, 10</sup>  $[\text{Ir}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$  (**1**). 1.0 ml (1.2 mmole) of acrylonitrile was added into the benzene solution (15 ml) of  $\text{Ir}(\text{OCIO}_3)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  (84 mg, 0.1 mmole) under nitrogen at room temperature, and the resulting solution was stirred. The yellow solution turned into beige suspension within five minutes from which pale yellow solid was obtained by filtration. This pale yellow solid (**1**) was thoroughly dried in vacuum. The yield was 82mg or 91% based on  $[\text{Ir}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$ .

*Anal.* Calcd for  $\text{IrC}_{40}\text{H}_{33}\text{NOClP}_2$ : Ir, 21.43; C, 53.55; H, 3.68; N, 1.56; Cl, 3.95; P, 6.91. Found: Ir, 20.95; C, 54.01; H, 3.56; N, 1.40; Cl, 4.02; P, 6.80.

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