

- ibid.*, **70**, 4277 (1979); (c) T. A. Weber and E. Helfand, *ibid.*, **71**, 4760 (1979); (d) *ibid.*, **72**, 4014 (1980).
- (14) (a) J. P. Ryckaert, G. Ciccotti and H. J. C. Berendsen, *J. Comput. Phys.*, **23**, 327 (1977); (b) J. P. Ryckaert and A. Bellemans, *Chem. Phys. Letters*, **30**, 123 (1975); (c) Faraday Discuss. *Chem. Soc.*, **66**, 95 (1978).
- (15) S. H. Jeon, I. J. Oh and T. Ree, *J. Phys. Chem.*, **87**, 2980 (1983).
- (16) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, 1969, Chap. 1-3.
- (17) W. J. Taylor, *J. Chem. Phys.*, **16**, 257 (1948).
- (18) M. Vacatello, G. Avitabile, P. Corradini and A. Tuzi, *J. Chem. Phys.*, **73**, 548 (1980).
- (19) L. Verlet, *Phys. Rev.*, **159**, 98 (1967).
- (20) P. A. Egelstaff, "Introduction to the Liquid State", Academic Press, London, 1967, p. 16.
- (21) A. Rahman, *Phys. Rev.*, **136**, A405 (1964).
- (22) D. A. McQuarrie, "Statistical Mechanics," Harper and Row, New York, 1976, p. 468.
- (23) J. H. Dymond and B. J. Alder, *J. Chem. Phys.*, **45**, 2061 (1966).

}

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

Soonheum Park, Hwa-Kun Park and Chong Shik Chin¹

Department of Chemistry, Sogang University, IPO Box 1142, Seoul 121, Korea (Received May 9, 1984)

Analyses of ¹H-NMR, infrared and electronic spectral data for [Ir(CH₂=CHCN)(CO)(P(C₆H₅)₃)₂]ClO₄ (**1**) prepared by the reaction of Ir(OCIO₃)(CO)(P(C₆H₅)₃)₂ with CH₂=CHCN, agree with the suggestion that **1** is a mixture of the nitrogen-bonded acrylonitrile complex, [(CO)(P(C₆H₅)₃)₂Ir-NCCH=CH₂]ClO₄ and other compound which may be the C=C π-system-bonded acrylonitrile complex, [(CO)(P(C₆H₅)₃)₂Ir- $\begin{matrix} \text{CHCN} \\ \parallel \\ \text{CH}_2 \end{matrix}$]ClO₄.

Introduction

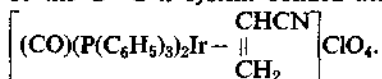
We recently reported the formation of a cationic acrylonitrile-iridium(I) complex, [Ir(CH₂=CHCN)(CO)(P(C₆H₅)₃)₂]ClO₄ (**1**) by the reaction of Ir(OCIO₃)(CO)(P(C₆H₅)₃)₂ (**2**) with CH₂=CHCN.¹ The bonding between iridium and acrylonitrile in **1**, however, has not been unequivocally understood thus far: CH₂=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.² 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_{C≡N} increases when the coordination of a nitrile to a metal occurs through the nitrogen.² Coordination of a nitrile through the C≡N π-system should cause a significant decrease in ν_{C≡N} as seen in succinonitrile (NCCH₂CH₂CN) complex of Mn(0).³ 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_{C=C} and ν_{C≡N} of CH₂=CHCN show considerable decreases (up to -168 cm⁻¹ for ν_{C=C} and up to -55 cm⁻¹ for ν_{C≡N}) upon coordination to metal through the C=C π-system.² In this paper, we wish to report that [Ir(CH₂=CHCN)(CO)(P(C₆H₅)₃)₂]ClO₄ (**1**) prepared by the reaction of Ir(OCIO₃)(CO)(P(C₆H₅)₃)₂ with CH₂=CHCN is a mixture of nitrogen-bonded acrylonitrile complex,

[(P(C₆H₅)₃)₂(CO)Ir-NCCH=CH₂]ClO₄ and some amount of other compound which may be the C=C π-system-bonded acrylonitrile complex, [(P(C₆H₅)₃)₂(CO)Ir- $\begin{matrix} \text{CH}_2 \\ \parallel \\ \text{CHCN} \end{matrix}$]ClO₄.

Results and Discussion

Infrared spectrum of **1** (in Nujol) prepared by the reaction of **2** with CH₂=CHCN shows ν_{C≡N} (weak and broad) at 2220~2240 cm⁻¹ and ν_{C=C} (very weak and broad) at 1600~1620 cm⁻¹, while free CH₂=CHCN shows ν_{C≡N} (sharp) and ν_{C=C} (weak) at 2230 and 1609 cm⁻¹, 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_{CO} bands at 2052 cm⁻¹ (medium) and 2047 cm⁻¹ (strong), which may imply that **1** is a mixture of two complexes since the related monocarbonyl iridium complexes always show a single strong ν_{CO} band, respectively.⁴ Then, the broad ν_{C≡N} band at 2220~2240 cm⁻¹ observed for **1** may represent two bands: one at lower and the other at higher frequency than 2230 cm⁻¹ at which free CH₂=CHCN shows ν_{C≡N}. Accordingly, these infrared spectral data for **1** may suggest that **1** is a mixture of the nitrogen-bonded acrylonitrile complex, [(CO)(P(C₆H₅)₃)₂Ir-NCCH=CH₂]ClO₄ and other compound which may

be the C=C π -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.⁵ 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, OClO_3 , NCO, NCS, CN *etc.*)⁶ and $[\text{Ir}(\text{L})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$ (L= CH_3CN , $\text{CH}_3\text{CH}_2\text{CN}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$, *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 nitrogen⁷ 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*- $(\text{CN})\text{CH}=\text{CH}(\text{CN})$, $(\text{CN})_2\text{C}=\text{C}(\text{CN})_2$)⁸ and $[\text{Ir}(\text{trans}-(\text{CN})\text{CH}=\text{CH}(\text{CN}))(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$ ⁹ where L and *trans*- $(\text{CN})\text{CH}=\text{CH}(\text{CN})$ are coordinated to iridium through the C=C π -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 π -system-bonded acrylonitrile complex,

$[(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Ir} - \begin{array}{c} \text{CHCN} \\ \parallel \\ \text{CH}_2 \end{array}]\text{ClO}_4$ 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 ($^1\text{H-NMR}$,

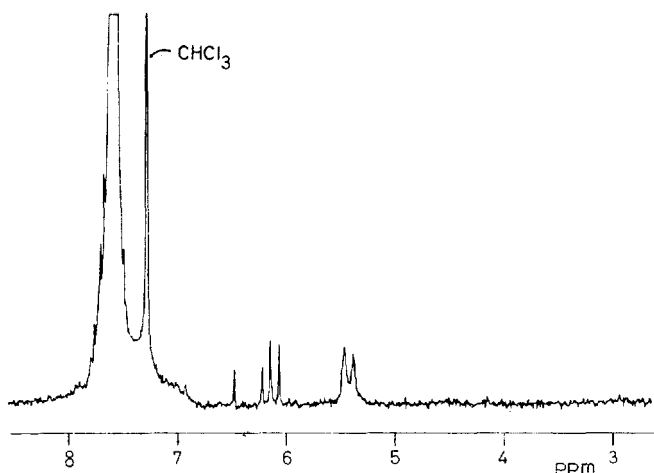


Figure 1. The 80 MHz-NMR spectrum of $[\text{Ir}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$ in CDCl_3 at 30 °C under nitrogen. Chemical shifts in ppm, relative to TMS.

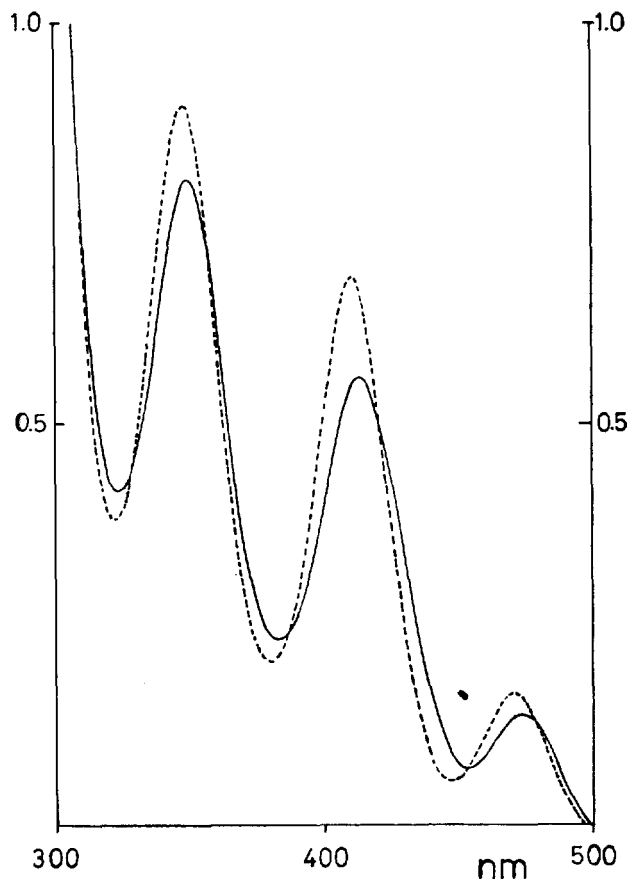


Figure 2. Electronic absorption spectrum of $[\text{Ir}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$ (**1**) (2.6×10^{-4} M) (—) (for comparison, the spectrum of $[\text{Ir}(\text{trans}-\text{CH}_3\text{CH}=\text{CHCN})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$ (2.6×10^{-4} M) (.....) is also shown) in CH_2Cl_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 π -system-bonded acrylonitrile complex, $[(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Ir} - \begin{array}{c} \text{CHCN} \\ \parallel \\ \text{CH}_2 \end{array}]\text{ClO}_4$.

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 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.^{4k,10} $[\text{Ir}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$ (**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.

Acknowledgement. We wish to thank the Korean Science and Engineering Foundation for the financial support. We are indebted to professor Wanchul Ju for FT-NMR spectra measurements.

References

- (1) J. C. Woo, S. H. Kim and C. S. Chin, *J. Polymer Science*, **20**, 1947 (1982).
- (2) S. J. Bryan, P. G. Huggart, J. A. Daniels and J. R. Jennings, *Coordination Chem. Rev.*, **44**, 149 (1982) and references therein.
- (3) M.F. Farona and K.F. Kraus, *Inorg. Chem.*, **9**, 1700 (1970).
- (4) (a) R. Brady, W.H. Decamp, B.R. Flynn, M.L. Scheider, J.D. Scott, and L. Vaska, *Inorg. Chem.*, **14**, 2669 (1975); (b) B.R. Flynn and L. Vaska, *Chem. Commun.*, 703 (1974); (c) B.R. Flynn and L. Vaska, *J. Amer. Chem. Soc.*, **95**, 5801 (1973); (d) L. Vaska, *Inorg. Chem. Acta*, **5**, 295 (1971); (e) L. Vaska and J. Peone, Jr., *Chem. Commun.*, 418 (1971); (f) L. Vaska, W. V. Miller and B. R. Flynn, *Chem. Commun.*, 1615 (1971); (g) L. Vaska and L. S. Chen, *Chem. Commun.*, 1080 (1971); (h) L. Vaska and M. F. Weneke, *Trans. N.Y. Acad. Science*, **33**, 70 (1971); (i) L. Vaska, L. S. Chen and C. V. Senoff, *Science*, **174**, 587 (1971); (j) L. Vaska and J. Peone, Jr., *Suomen Kemistilehti*, **B44**, 317 (1971); (k) J. Pecna, Jr. and L. Vaska, *Angew. Chem. Int. Ed. Engl.*, **10**, 511 (1971).
- (5) ^1H -NMR of free acrylonitrile shows a complicated 13-line ABC pattern centered at 6.0 ppm (relative to TMS). This complicated ABC pattern has been also observed (with relatively small changes in chemical shifts and coupling constants) for coordinated acrylonitrile in $[\text{Ru}(\text{CH}_2=\text{CHCN})(\text{NH}_3)_5]^{2+}$ and $[\text{Rh}(\text{CH}_2=\text{CHCN})(\text{NH}_3)_5]^{3+}$ where acrylonitrile is coordinated through the nitrogen (see R. D. Foust, Jr. and P. C. Ford, *J. Amer. Chem. Soc.*, **94**, 5686 (1972)). On the other hand, nitrogen-bonded acrylonitrile in $[\text{Rh}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]^+$ shows a simple 8-line spectrum with relatively large changes in chemical shifts in both directions of upfield and downfield and in coupling constants upon coordination of $\text{CH}_2=\text{CHCN}$ (see M. K. Lee, T. Kwon and C. S. Chin, *Bull. Korean Chem. Soc.*, in print). Protons of acrylonitrile coordinated to metal through the π -system of the olefinic group show upfield shifts compared with those of free acrylonitrile.² In all cases above, every signals due to the coordinated acrylonitrile are clearly assigned.
- (6) R. Brady, B. F. Flynn, G. L. Geoffroy, H. B. Gray, J. Peone, Jr. and L. Vaska, *Inorg. Chem.*, **15**, 1485 (1976).
- (7) C. S. Chin, S. Park, W-K. Park, I. B. Kim and M. K. Lee, to be submitted for publication.
- (8) L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968).
- (9) C. S. Chin, S. Park and H-K. Park, unpublished results: infrared spectrum of $[\text{Ir}(\text{trans}-(\text{CN})\text{CH}=\text{CH}(\text{CN}))(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2]\text{ClO}_4$ shows $\nu_{\text{C}=\text{N}}$ at 2244 and 2221 cm^{-1} while free $\text{trans}-(\text{CN})\text{CH}=\text{CH}(\text{CN})$ shows $\nu_{\text{C}=\text{N}}$ at 2262 and 2242 cm^{-1} , which suggests $\text{trans}-(\text{CN})\text{CH}=\text{CH}(\text{CN})$ is coordinated to iridium through the $\text{C}=\text{C}$ π -system in the complex. $\nu_{\text{C}=\text{C}}$ of $\text{trans}-(\text{CN})\text{CH}=\text{CH}(\text{CN})$ is infrared inactive both for free $\text{trans}-(\text{CN})\text{CH}=\text{CH}(\text{CN})$ and coordinated $\text{trans}-(\text{CN})\text{CH}=\text{CH}(\text{CN})$ in **1**.
- (10) K. Vrize, J. P. Collman, C. T. Tears, Jr. and M. Kubota, *Inorg. Synthesis*, **11**, 101 (1968).