

the nitrogen, then the paramagnetic term is relatively large for $-\text{NSO}$ with these ligands, which implies a lowering of the π^* relative to the n_{N} orbital.

Nitrogen-14 shifts were measured as before.¹¹ Literature methods were used for the preparation of $\text{S}(\text{NSO})_2$,¹⁵ PhNSO ,¹⁶ R_2NSAr ,¹⁷ and R_2NSNSO .¹⁸

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Registry No. Me_2NSPh , 24380-79-8; Et_2NSPh , 6667-19-2; Me_2NSNSO , 53520-63-1; $n\text{-Pr}_2\text{NSNSO}$, 65036-40-0; FSO_2NSO , 16829-30-4; $\text{S}(\text{NSO})_2$, 13840-74-9; PhNSO , 1122-83-4; PhNSNSO , 28968-93-6; Me_3SiNSO , 7522-26-1; Me_3CNSO , 38662-39-4.

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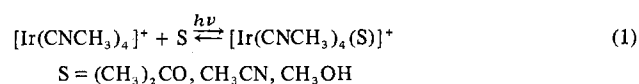
Contribution from the Department of Chemistry,
The Pennsylvania State University,
University Park, Pennsylvania 16802

Photoinduced Dissociation of Oligomeric Tetrakis(methyl isocyanide)iridium(I)

Gregory L. Geoffroy,* Mark G. Bradley, and Mark E. Keeney

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Bedford and Rouschias have briefly reported the photochemical properties of $[\text{Ir}(\text{CNCH}_3)_4]^+$.¹ The chloride salt of the complex was described as a blue-black air-sensitive solid which gave deep blue solutions (λ_{max} 610 nm; ϵ 22 000) in the absence of oxygen. These solutions were stable for several days in the dark, but they rapidly turned red-orange within minutes in light. On the basis of slight shifts in the NMR spectrum during photolysis and the somewhat reversible nature of the reaction, it was suggested that photoinduced association of solvent occurred to give a stable solvated complex, eq 1.¹ In



support of this proposal, it was shown that whereas aqueous

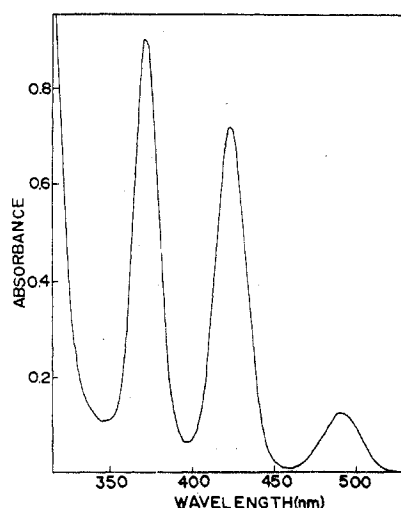


Figure 1. Electronic absorption spectrum of $[\text{Ir}(\text{CN-}t\text{-Bu})_4]\text{Cl}$ in CH_2Cl_2 solution.

solutions of $[\text{Ir}(\text{CNCH}_3)_4]^+$ did not react with CO or excess CNCH_3 in the dark, they did so when irradiated to give the corresponding $[\text{Ir}(\text{CNCH}_3)_5]^+$ and $[\text{Ir}(\text{CNCH}_3)_4\text{CO}]^+$ adducts.¹

It is our intent in this note to demonstrate that $[\text{Ir}(\text{CNCH}_3)_4]^+$ does not exist as a monomeric complex in solution but rather as oligomeric $[\text{Ir}(\text{CNCH}_3)_4]_n^{n+}$. We further show that the photochemical reaction is not photoinduced association as previously suggested¹ but rather photoinduced dissociation of the solution oligomers to generate monomeric $[\text{Ir}(\text{CNCH}_3)_4]^+$.^{2,5} It is then monomeric $[\text{Ir}(\text{CNCH}_3)_4]^+$ which subsequently undergoes addition of CNCH_3 or CO.

Results and Discussion

$[\text{Ir}(\text{CNCH}_3)_4]\text{Cl}$ can be prepared as previously described¹ by the addition of CNCH_3 to *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$. We have found a more convenient preparation to be through the addition of excess CNCH_3 to $[\text{IrCl}(1,5\text{-cyclooctadiene})_2]$. The blue-black solid obtained from this reaction is soluble in MeOH and H_2O and gives dark blue or blue-violet solutions. In addition to the dark solid, an amorphous, highly reflecting gold-colored material was obtained by very slow evaporation of solvent from methanol solutions. Dissolution of the gold-colored material gave the characteristic dark blue solutions which again yielded the blue-black powder upon rapid evaporation of solvent.

Preparation of $[\text{Ir}(\text{CN-}t\text{-Bu})_4]\text{Cl}$ by an exactly analogous procedure using excess *tert*-butyl isocyanide gave an orange solid in contrast to the dark material obtained with CNCH_3 . Its infrared spectrum showed a single $\nu_{\text{C}\equiv\text{N}}$ at 2160 cm^{-1} similar to that of $[\text{Ir}(\text{CN-}t\text{-Bu})_4]\text{PF}_6$ previously prepared by a somewhat different procedure.⁴ The electronic absorption spectrum of $[\text{Ir}(\text{CN-}t\text{-Bu})_4]\text{Cl}$ in CH_2Cl_2 solution, Figure 1, shows bands at 490 (ϵ 743), 423 (ϵ 4264), 372 (ϵ 5428), and 309 nm (ϵ 16 787). It is precisely the type of spectrum shown by the other planar Ir(I) complexes which we previously examined,⁸⁻¹⁰ and it is virtually identical with the spectrum of $[\text{Ir}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$. Thus $[\text{Ir}(\text{CN-}t\text{-Bu})_4]^+$ behaves exactly as expected for a monomeric $\text{Ir}^{\text{I}}\text{L}_4$ complex.

The electronic absorption spectrum of a dark blue methanol solution of $[\text{Ir}(\text{CNCH}_3)_4]\text{Cl}$ is shown in Figure 2. It is not at all similar to the spectrum of $[\text{Ir}(\text{CN-}t\text{-Bu})_4]\text{Cl}$ or to the spectra of other planar Ir(I) complexes⁸⁻¹⁰ but instead shows a maximum at 630 nm with an apparent ϵ of 16 000, calculated for a solution $1.77 \times 10^{-3}\text{ M}$ in monomeric $[\text{Ir}(\text{CNCH}_3)_4]\text{Cl}$. The band maximum varies between 600 and 650 nm, depending on concentration and the method of sample preparation. The intensity of the 630-nm band does not follow

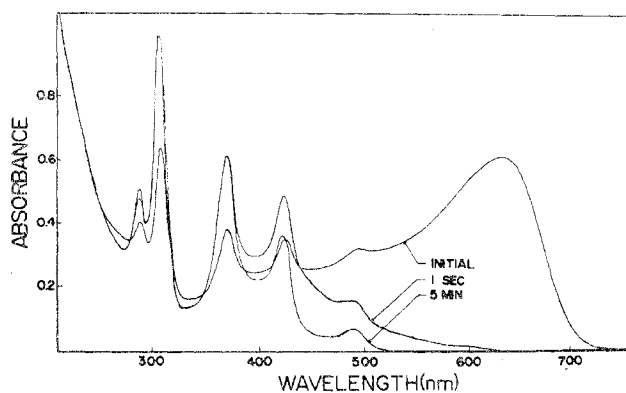
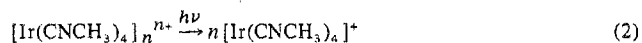


Figure 2. Electronic absorption spectral changes during $\lambda > 525$ nm photolysis of a 4.02×10^{-5} M MeOH solution of $[\text{Ir}(\text{CNCH}_3)_4]\text{Cl}$.

Beer's law, although very dilute solutions still appear blue and show an absorption maximum at about 610 nm.

An isopiestic molecular weight of 1769 was obtained for a solution containing 2.06×10^{-4} mol of $[\text{Ir}(\text{CNCH}_3)_4]\text{BPh}_4$ in CH_3CN . This compares well with the values 1580–3400 obtained by Kawakami et al.³ for the $[\text{Ir}(\text{CNAr})_4]\text{Cl}$ complexes which they examined. Since the expected molecular weight for monomeric $[\text{Ir}(\text{CNCH}_3)_4]\text{BPh}_4$ is 675, the experimental value of 1769 indicates association of the cations in solution. The established tendency of rhodium(I) isocyanide complexes to oligomerize in solution,⁷ our molecular weight measurements and those of Kawakami et al.,³ the blue-black color of $[\text{Ir}(\text{CNCH}_3)_4]\text{Cl}$, its absorption spectrum which is *not* that expected for monomeric $[\text{Ir}(\text{CNCH}_3)_4]^+$ and which does not obey Beer's law, and our ability to obtain reflecting gold-colored material by slow solvent evaporation all strongly indicate that $[\text{Ir}(\text{CNCH}_3)_4]^+$ exists predominantly in the form of oligomers both in solution and in the solid state. The oligomers presumably arise from simple stacking of the planar complexes in a manner similar to that which has been demonstrated for $[\text{IrCl}(\text{CO})_3]$.¹¹ The complexes must be held together through interaction of the d_z^2 and the a_{2u} π molecular orbitals, and an MO diagram such as that previously drawn⁷ for $[\text{Rh}(\text{CNPh})_4]_n^{n+}$ seems appropriate.

$[\text{Ir}(\text{CNCH}_3)_4]_n^{n+}$ is extremely photosensitive. Dilute solutions (10^{-4} M) change from blue to orange within seconds of irradiation. The color change can be induced by fluorescent room light, sunlight, or flashlight irradiation or by photolysis with 254, 313, 366 nm and light filtered to pass only $\lambda > 525$ nm. The electronic absorption spectral changes which obtain during irradiation are shown in Figure 2. After 1-s irradiation with $\lambda > 525$ nm, the 630-nm band had decreased appreciably, and it completely disappeared after 5 min of photolysis. The final spectrum shows bands at 490, 425, 370, and 305 nm and is exactly the type of spectrum expected⁸⁻¹⁰ for a monomeric $\text{Ir}^{\text{I}}\text{L}_4$ complex. The band positions compare quite well to those of $[\text{Ir}(\text{CN}-t\text{-Bu})_4]^+$. The electronic absorption spectral changes thus strongly indicate that photolysis induces cleavage of the oligomers and generates monomeric $[\text{Ir}(\text{CNCH}_3)_4]^+$, eq 2.



The 436-nm quantum yield *per monomer unit*, determined by monitoring the decrease in intensity of the 610-nm band, is 0.3.

Although a definitive excited-state argument cannot be presented, it is likely that irradiation simply provides enough vibrational energy to dissociate the weakly bound oligomers. Alternatively, as recently suggested by Ginsberg¹² for $[\text{IrCl}(\text{CO})_3]$, oligomers of sufficient length may have the bonding orbital resulting from interaction of the monomer a_{2u} orbitals drop below the antibonding d_z^2 combination. The least en-

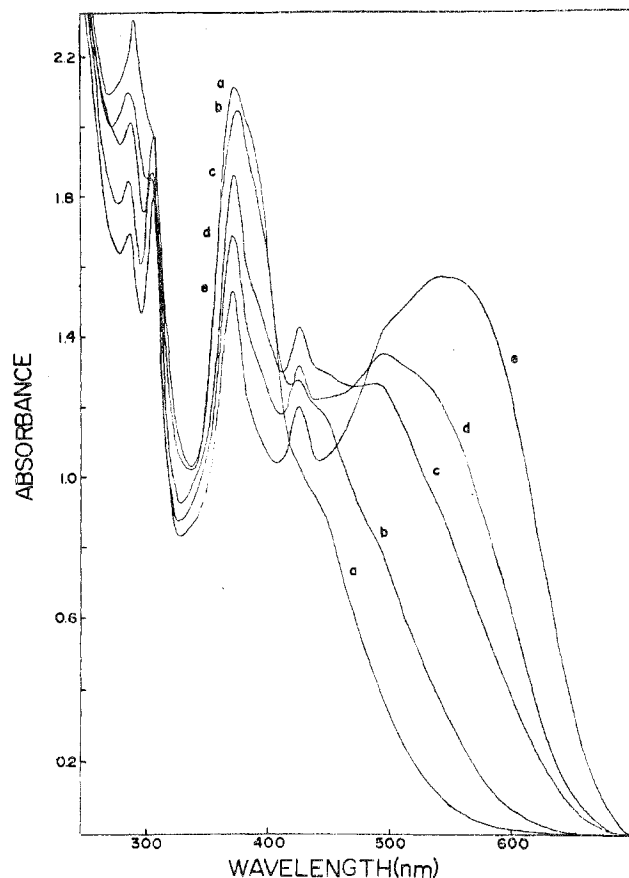


Figure 3. Electronic absorption spectral changes following irradiation of $[\text{Ir}(\text{CNCH}_3)_4]\text{Cl}$ in methanol solution. Spectra were recorded at the following time intervals after cessation of photolysis: (a) immediately; (b) 95 min; (c) 6.25 h; (d) 8.75 h; (e) 18.25 h. The sample was equilibrated at 23 °C in the dark between spectral recordings.

ergetic transition resulting from such a structure would promote an electron from a bonding to an antibonding orbital, and dissociation would be expected.

The photoreaction is partially reversible. Storage of the orange irradiated solutions in the dark results in a return of the blue color *but never to the original extent*. The rate of return is highly dependent on conditions, occurring faster at elevated temperatures with greater complex concentration. Electronic absorption spectral changes which obtain during the oligomerization reaction are shown in Figure 3. Although quite complex, the progressive appearance of bands at lower energy indicates a rather high degree of oligomerization. The system can only be cycled through the photoinduced de-oligomerization–thermal oligomerization process two or three times before it fails to yield oligomers because of decomposition. The $[\text{Ir}(\text{CNCH}_3)_4]\text{BPh}_4$ and $[\text{Ir}(\text{CNCH}_3)_4]\text{BF}_4$ salts in CH_3CN , DMF, and Me_2SO solutions are also photosensitive and change from dark blue to red-orange upon irradiation. These reactions, however, are not at all reversible, and the electronic absorption spectra of the irradiated solutions are not those of square-planar $\text{Ir}^{\text{I}}\text{L}_4$ complexes but resemble that of $[\text{Ir}(\text{CNCH}_3)_5]^+$. As previously noted,¹ we found that the latter complex can be prepared by photolysis of $[\text{Ir}(\text{CNCH}_3)_4]_n^{n+}$ in the presence of excess CNCH_3 . It appears that photolysis in these donor solvents, and in the presence of excess CNCH_3 and CO , gives cleavage of the oligomers and generation of monomeric $[\text{Ir}(\text{CNCH}_3)_4]^+$. It is the monomeric complex which subsequently adds CNCH_3 , CO , or solvent to give stable five-coordinate complexes in a thermal process similar to that of other reactive $\text{Ir}(\text{I})$ complexes. Specifically,

it is not an excited-state association reaction as originally suggested.¹ All attempts to develop a photochromic system which could be repeatedly cycled have failed.

Experimental Section

Methyl isocyanide,¹³ *tert*-butyl isocyanide,¹⁴ and $[\text{IrCl}(1,5\text{-cyclooctadiene})_2]_2$ ¹⁵ were prepared by published procedures, and solvents were purified by standard methods. All experiments and manipulations of compounds were conducted under vacuum or under a purified N_2 atmosphere.

Preparation of $[\text{Ir}(\text{CNCH}_3)_4]\text{Cl}$ and $[\text{Ir}(\text{CN-}t\text{-Bu})_4]\text{Cl}$. Excess CH_3NC was distilled into a Schlenk tube containing $[\text{IrCl}(1,5\text{-cyclooctadiene})_2]$ (0.30 g; 0.4 mmol) in 20 mL of CH_2Cl_2 , and the mixture was stirred for 1 h. The solvent, excess CNCH_3 , and 1,5-cyclooctadiene were removed under vacuum. The crude product was dissolved in methanol and filtered. Evaporation of solvent gave a blue-black solid. Other salts were prepared by metathesis in methanol using NaBPh_4 and NaBF_4 . $[\text{Ir}(\text{CN-}t\text{-Bu})_4]\text{Cl}$ was obtained as an orange solid by an exactly analogous procedure using excess *tert*-butyl isocyanide.

General Irradiation Procedures. Irradiations were conducted using a 450-W Hanovia medium-pressure Hg lamp in a quartz well equipped with one of the following Corning glass filters: 5-74 (λ 436 nm); 7-83 (λ 366 nm); 3-70 ($\lambda \geq 525$ nm). The complex to be studied was placed in an degassable quartz UV cell or a Schlenk tube, and after degassing on a vacuum line, the appropriate solvent was distilled onto the sample. Solutions for infrared studies were transferred in an inert-atmosphere glovebox to 0.5-mm NaCl-solution infrared cells. Lamp intensities were measured using ferrioxalate actinometry¹⁶ and were of the order of 4.0×10^{-7} einstein/min (436 nm).

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Registry No. $[\text{Ir}(\text{CNCH}_3)_4]\text{Cl}$, 40226-52-6; $[\text{Ir}(\text{CN-}t\text{-Bu})_4]\text{Cl}$, 34389-90-7; $[\text{IrCl}(1,5\text{-cyclooctadiene})_2]$, 12112-67-3.

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Correspondence

Reinvestigation of the Coordination Geometry of Eight-Coordinate Metal Tetrakis(acetylacetonates)

Sir:

Although several sets of parameters have been devised to measure the shape of a discrete eight-coordinate complex with reference to idealized geometric forms,¹⁻⁴ some confusion still exists in the assignment of an idealized geometry to an observed eight-coordinate complex. A case in point is the series of acetylacetonate (acac) complexes with actinides, lanthanides, and group 4B elements. The individual eight-coordinate tetrakis(acetylacetonate) complexes exist in either of two crystalline modifications (the α and β forms); the coordination geometry of the β form has been described as primarily square antiprismatic,⁵⁻⁸ while that of the α form has been described as predominantly dodecahedral^{9,10} and as predominantly antiprismatic.¹¹

We have reexamined the tetrakis(acetylacetonate) series by calculating the ϕ and δ shape parameters^{3,4,12} for $\alpha\text{-Ce}(\text{acac})_4$, $\alpha\text{-Th}(\text{acac})_4$, $\beta\text{-Zr}(\text{acac})_4$, $\beta\text{-Ce}(\text{acac})_4$, $\beta\text{-U}(\text{acac})_4$, and $\beta\text{-Np}(\text{acac})_4$. The results are given in Table I. The results of mean-planes calculations, assuming both dodecahedral and antiprismatic geometries for both series of complexes, are listed in Table II. Tables III and IV give the atomic coordinates and the definition of the planes used in the calculation of the shape parameters for the α and β forms, respectively.

The idealized geometry most closely approximated by the coordination groups of $\alpha\text{-Ce}(\text{acac})_4$ and $\alpha\text{-Th}(\text{acac})_4$ is neither the D_{2d} dodecahedron nor the D_{4d} square antiprism but rather the C_{2v} bicapped trigonal prism, as shown by the shape parameters in Table I. The assignment of primarily dodecahedral geometry to the coordination group of the α complexes by Allard⁹ was based on a comparison of observed normalized polyhedral edge lengths with the corresponding edge lengths

Table I. Shape Parameters (deg) for $M(\text{acac})_4$ Complexes^a

Compd	ϕ_1	ϕ_2	δ_1	δ_2	δ_3	δ_4
D_{2d} dodecahedron ^b	0.0	0.0	29.5	29.5	29.5	29.5
C_{2v} bicapped trigonal prism ^b	14.1	14.1	0.0	21.8	48.2	48.2
D_{4d} square antiprism ^b	24.5	24.5	0.0	0.0	52.4	52.4
$\alpha\text{-Ce}(\text{acac})_4$	12.8	15.3	9.7	21.1	44.0	42.9
$\alpha\text{-Th}(\text{acac})_4$	15.6	17.3	5.4	19.8	44.5	44.9
$\beta\text{-Zr}(\text{acac})_4$	22.8	22.4	3.2	3.2	49.6	49.6
$\beta\text{-Ce}(\text{acac})_4$	19.7	19.3	5.3	5.3	46.7	46.7
$\beta\text{-U}(\text{acac})_4$	22.1	17.8	6.8	6.8	49.2	49.2
$\beta\text{-Np}(\text{acac})_4$	22.3	20.6	4.5	4.5	50.5	50.5

^a The planes defining the ϕ and δ angles are given for the α complexes in Table III and for the β complexes in Table IV.

^b Values of the shape parameters for the idealized geometries were taken from ref 4.

for the "most favorable polyhedra".¹ However, it is very difficult on this basis to assign an idealized geometry to the α complexes since their edge lengths are approximately midway between those of the dodecahedron and the square antiprism. If anything, there appears to be a slight tendency toward antiprismatic coordination. Our calculation of the ϕ and δ shape parameters assigns the geometry of the α complexes as quite close to bicapped trigonal prismatic. Moreover, since the bicapped trigonal prism is along the reaction pathway between the dodecahedron and square antiprism,^{3,4} our calculation is in quite good agreement with the polyhedral edge lengths given by Allard.

The mean-planes calculations for $\alpha\text{-Ce}(\text{acac})_4$ and $\alpha\text{-Th}(\text{acac})_4$ (see Table II) show a large degree of nonplanarity for the BAAB trapezoids, again indicating that the α complexes do not closely approximate dodecahedral geometry. One of the square faces for the antiprismatic model is also relatively nonplanar. Note, however, that the deviations of the atoms from the plane of the other square face, the face corresponding