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METAL COMPLEXES OF CYANOCARBONS
XI*. REACTIONS OF TETRACYANOETHYLENE WITH HYDRIDOIRIDIUM COMPLEXES

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SUMMARY

Reactions of tetracyanoethylene (TCNE) with a number of hydrido-complexes of iridium have been studied. Displacement reactions are observed for most of the tervalent, octahedral iridium substrates such as $IrHCl_2(CO)(PPh_3)_2$, $IrH_2Cl(CO)(PPh_3)_2$, $IrHCl(SnCl_3)CO(PPh_3)_2$, and $IrH_2(SnCl_3)CO(PPh_3)_2$ where HCl, H_2 $SnHCl_3$, and SnH_2Cl_2 respectively are eliminated and the iridium-containing product in all cases is $IrCl(CO)(TCNE)(PPh_3)_2$. In the case of the univalent, trigonal bipyramidal substrates $IrH(CO)(PPh_3)_3$ and $IrH(CO)_2(PPh_3)_2$ as well as tervalent $IrH_3(CO)(PPh_3)_2$, a 1,4-addition to TCNE is formally observed, and the novel cyano(dicyanomethyl)keteniminato complex $Ir(C_6N_4H)(CO)(TCNE)(PPh_3)_2$ is isolated when the solvent is benzene. The presence of alcohol in the reaction mixture results in the formation of the cyano-complex $Ir(CN)(CO)(TCNE)(PPh_3)_2$ as well as the keteniminato-complex. The nature of the keteniminato–iridium bond is discussed and a rationale for the 1,4-addition is proposed.

INTRODUCTION

Tetracyanoethylene is an unconventional olefin. This fact has been quite evident as various aspects of the reactions of TCNE with transition metal substrates have been studied in this laboratory. In the case of the reactions of TCNE with hydridoplatinum complexes[2], 1,2-addition to the TCNE does not occur as it does when the same complexes react with the conventional olefin ethylene, but rather the reaction proceeds according to eqn. (1).

$$PtHCl(PR_3)_2 + TCNE \rightarrow Pt(PR_3)_2TCNE + HCl \quad (1)$$

Because of the unprecedented nature of this reaction at the time it was first carried out, we decided to investigate the reactions of tetracyanoethylene with a wide variety of hydrido-complexes of transition metals. Reported herein are results obtained with iridium substrates. A novel keteniminato-complex, $Ir(C_6N_4H)(CO)(TCNE)(PPh_3)_2$, was isolated from the reaction of $IrH(CO)_2(PPh_3)_2$ and TCNE in the initial

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* For Part X see Ref. 1.

stages of this work, and its preparation and crystal structure have already been reported[3,4].

EXPERIMENTAL

I. Materials

Tetracyanoethylene was purchased from Columbia Organic Chemicals Co., Inc. It was recrystallized from chlorobenzene and sublimed prior to use.

Iridium-containing starting materials were prepared from either $IrCl_3 \cdot 3\ H_2O$ or $Na_3IrCl_6 \cdot 12\ H_2O$; these were purchased from Engelhard Industries and Alfa Inorganics, Inc. respectively.

Literature methods or modifications of these were used to prepare the following iridium complexes: $IrCl(CO)(PPh_3)_2$[5], $IrH(CO)(PPh_3)_3$[6]*, $IrH(CO)_2(PPh_3)_2$[7], $IrH_3(CO)(PPh_3)_2$[8], $IrCl(CO)(AsPh_3)_2$7, $IrH_3(CO)(AsPh_3)_2$[9]**, $IrHCl_2(CO)(PPh_3)_2$[10], $IrH_2Cl(CO)(PPh_3)_2$[11], $IrHCl(SnCl_3)(CO)(PPh_3)_2$[12], $IrH_2(SnCl_3)(CO)(PPh_3)_2$[12], $IrHCl_2(PPh_3)_3$[13], $IrH_2Cl(PPh_3)_3$[11], and $IrH_3(PPh_3)_3$[14].

Most of the reactions with TCNE were carried out in a nitrogen atmosphere but work-up of reaction mixtures was usually done in air.

II. Reactions of tetracyanoethylene

A. With $IrH(CO)_2(PPh_3)_2$. Drop-wise addition of a benzene solution (5 ml) of the complex (0.39 g, 0.5 mmoles) to a benzene solution (15 ml) of TCNE (0.26 g, 2.0 mmoles) at room temperature gave a deep orange solution as bubbles of CO gas were evolved, and simultaneously an orange-yellow solid separated. The mixture was stirred for 0.5 h, the solid was collected and washed with ethanol, and recrystallized from dichloromethane/benzene to give bronze-colored crystals of $Ir(C_6N_4H)(CO)(TCNE)(PPh_3)_2 \cdot \frac{1}{2}C_6H_6$***, 0.36 g (70%), m.p. 165–180° (dec.); IR**** (CH_2Cl_2 solution) 1355 w (N=C=C sym), 2080 vs (C≡O), 2168 vs (N=C=C asym), 2220 s (C≡N), and 2233 sh (C≡N). [Found: C, 58.68; H, 2.97; N, 10.68; P, 5.86; mol.wt., 904 (osmometric in $CHCl_3$). $C_{52}H_{34}IrN_8OP_2$ calcd.: C, 59.99; H, 3.29; N, 10.76; P, 5.95%; mol.wt., 1040.]

The complex $IrH(CO)_2(PPh_3)_2$ (0.39 g, 0.5 mmoles) was dissolved in 3 ml of benzene and TCNE (0.064 g, 0.5 mmoles) was added at room temperature. The solution turned deep orange as described above and a small amount of solid formed. Methanol (20 ml) was added immediately and a small amount of $Ir(C_6N_4H)(CO)(TCNE)(PPh_3)_2$, 0.10 g (20%) was collected on a filter. The filtrate was warmed to 50–60° and the volume of the solution was decreased to 10 ml under reduced pressure. Addition of ca. 0.1 g of TCNE to the solution caused a light yellow solid to precipitate. This solid was collected and washed with CH_2Cl_2. A white residue, 0.15 g (33%), of

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* The compound was prepared in over 90% yield by using $NaBH_4$ as the hydride source, and is an improvement over the original preparation (Ref. 6) using hydrazine.

** The literature method of Ref. 9 was modified by using $IrCl(CO)(AsPh_3)_2$ instead of its bromo-analogue.

*** The X-ray study shows that the crystals contain one molecule of benzene per two molecules of the complex (Ref. 3).

**** Abbreviations used to describe infrared band intensities and widths are: s, strong, vs, very strong, m, medium; w, weak; sp, sharp; br, broad. The abbreviation for shoulder is sh. All band positions are given in cm^{-1}. Mull spectra were recorded in either Nujol or hexachlorobutadiene.

$Ir(CN)(CO)(TCNE)(PPh_3)_2$ remained, m.p. >300° (dec.); IR (mull) 2080 s (C≡O), 2232 m (C≡N). [Found: C, 57.98; H, 3.16; N, 7.63; P, 6.79; mol.wt., 950 (osmometric in $CHCl_3$). $C_{44}H_{30}IrN_5OP_2$ calcd.: C, 58.80; H, 3.36; N, 7.79; P, 6.89%; mol.wt., 899.)

When 0.1 g (0.1 mmoles) of the complex $Ir(C_6N_4H)(CO)(TCNE)(PPh_3)_2$ was warmed a few minutes at 50° with excess KCN (0.016 g, 0.25 mmoles) in acetone (with sufficient CH_2Cl_2 to cause the complex to dissolve), a dark mixture resulted. The white complex $Ir(CN)(CO)(TCNE)(PPh_3)_2$ separated after the mixture had stood overnight. Yield, 0.08 g (90%).

The cyano-complex $Ir(CN)(CO)(TCNE)(PPh_3)_2$ was also obtained when $Ir(C_6N_4H)CO(TCNE)(PPh_3)_2$ (0.1 g, 0.1 mmoles) was dissolved in 50 ml of CH_2Cl_2/CH_3OH (1/5) and the mixture was refluxed for 1 h. Yield, 0.03 g (30%).

B. With $IrH(CO)(PPh_3)_3$. Reaction of TCNE and $IrH(CO)(PPh_3)_2$ in benzene [with conditions as described in *II A* above for the reaction of $IrH(CO)_2(PPh_3)_2$ with TCNE] resulted in the formation of a dark gummy material. Removal of the gum, followed by addition of hexane to the remaining benzene solution, caused $Ir(C_6N_4H)$-$(CO)(TCNE)(PPh_3)_2$ to precipitate in low yield (10%). A higher yield of the keteniminato-complex was obtained in those reactions wherein solid TCNE was added to a benzene solution of $IrH(CO)(PPh_3)_3$ if ethanol was added to the reaction mixture, but the product was contaminated with $Ir(CN)(CO)(TCNE)(PPh_3)_2$.

When solid TCNE was added to a benzene solution of the deuterio-complex $IrD(CO)(PPh_3)_3$, a complex was obtained which had the same infrared spectrum in the 1900–2250 cm^{-1} region as described in *II A* above for $Ir(C_6N_4H)(CO)(TCNE)$-$(PPh_3)_2$.

C. With $IrH_3(CO)(PPh_3)_2$. A small yield (< 10%) of $Ir(C_6N_4H)(CO)(TCNE)$-$(PPh_3)_2$ precipitated when the complex and TCNE were warmed at 45–50° in benzene for 0.5 h. Addition of ethanol to the filtrate caused $Ir(CN)(CO)(TCNE)(PPh_3)_2$ to precipitate after several hours.

D. With $IrHCl_2(CO)(PPh_3)_2$. The complex (0.40 g, 0.5 mmoles) and TCNE (0.06 g, 0.50 mmoles) were suspended in 50 ml of $CHCl_3$ and the mixture was stirred at room temperature for 16 h. At this time unreacted material was removed by filtration and the green filtrate was taken to dryness under reduced pressure. Recrystallization of the residue from $CHCl_3$/C_2H_5OH gave pale yellow crystals (0.2 g, 43%) of $IrCl(CO)(TCNE)(PPh_3)_2$ whose infrared spectrum, melting point, and analysis agreed with published data[15] for this compound. Reaction of TCNE with the analogous deuterio-complex $IrDCl_2(CO)(PPh_3)_2$ gave the identical iridium-containing complex.

E. With $IrH_2Cl(CO)(PPh_3)_2$. The complex (0.30 g, 0.40 mmoles) was suspended in 25 ml of benzene and TCNE (0.05 g, 0.40 mmoles) in 20 ml of benzene was added. The yellow mixture was stirred at room temperature for 16 h by which time the color had faded and a white solid had separated. The solid was collected and recrystallized from $CHCl_3$/C_2H_5OH, yield 0.2 g (57%). Identification of the pale yellow crystals as $IrCl(CO)(TCNE)(PPh_3)_2$ was as described in *II D*. The analogous deuterio-complex $IrD_2Cl(CO)(PPh_3)_2$ also gave $IrCl(CO)(TCNE)(PPh_3)_2$ as the iridium-containing product.

F. With $IrHCl(SnCl_3)(PPh_3)_2$. Conditions and iridium-containing product same as *II D*; complex obtained in 45% yield.

G. With $IrH_2(SnCl_3)(CO)(PPh_3)_2$. This complex was found to be much less reactive toward TCNE than any of the complexes mentioned above. Stirring an equimolar mixture of the reactants in $CHCl_3$ for 12 h at room temperature did not result in a reaction, nor did refluxing of the mixture for 8 h. Five minutes of heating at 120° in xylene resulted in a dark solution. The cooled mixture, consisting of a tar mixed with light-colored crystals, was extracted with CH_2Cl_2. An infrared spectrum of the extract was identical to that of $IrCl(CO)(TCNE)(PPh_3)_2$, but further characterization was not possible due to the small amount of material obtained.

H. With $IrHCl_2(PPh_3)_3$. Mixing equimolar amounts of the α-form of this complex with TCNE in benzene or CH_2Cl_2 resulted in a dark green solution whose infrared spectrum showed a broad band at 2200 cm^{-1} with a shoulder at 2168 cm^{-1} as the only absorptions in the 1900–2300 cm^{-1} region. Removal of solvent under reduced pressure gave a red residue with similar infrared activity. Various attempts to isolate a crystalline material from the amorphous residue were not successful.

I. With $IrH_3(PPh_3)_3$. The complex (0.25 g, 0.25 mmoles) and TCNE (0.03 g, 0.25 mmoles) were dissolved in benzene and the solution was refluxed for 5 min to give an intense red color. An infrared spectrum of the solution showed absorptions at 2124 vs, sp, 2152 m, and 2210 sh. Attempts to isolate a compound from the solution gave a dark powder with broad, poorly-defined infrared absorptions in the 2100–2300 cm^{-1} region.

The complex $IrH_3(PPh_3)_3$ (0.5 g, 0.5 mmoles) and TCNE (0.05 g, 0.06 mmoles) were suspended in a mixture of methanol (60 ml) and benzene (10 ml). The mixture was stirred for 5 days at room temperature. After a small amount of solid material was removed by filtration the filtrate was taken to dryness to give a pale yellow solid. This solid was recrystallized from benzene/methanol to give 0.3 g (60%) of pale yellow crystals of $IrH_2CN(PPh_3)_3$, m.p. 150–152°. IR (mull: 2122 m, sp; 2176 vs, sp. [Found: C, 65.16; H, 4.61; N, 1.76; mol.wt., 1008 (osmometric in benzene). $C_{55}H_{47}IrNP_3$ calcd.: C, 65.53; H, 4.69; N, 1.38%; mol.wt., 1008.] The NMR spectrum in $CDCl_3$ shows a complex pattern in the τ 22–24 region as well as a signal at τ 30.4.

III. Analyses and instrumentation

Analyses for carbon, hydrogen, and nitrogen were carried out by Mr. R. Seab of the Department of Chemistry, Louisiana State University. Other analyses were performed by Galbraith Laboratories, Inc. of Knoxville, Tennessee.

Infrared spectra in the NaCl region were measured on a Beckman IR-7 spectrophotometer in Nujol or hexachlorobutadiene mulls, KBr pellets, and benzene and dichloromethane solutions.

Molecular weights were measured using a Hewlett–Packard osmometer, Model 302 A, with a 37° probe. Chloroform or benzene was used as solvent.

Nuclear magnetic resonance data were obtained with either a Varian A-60 or HA-100 instrument using $CDCl_3$ (low field) or CH_2Cl_2 (high field) as solvent with tetramethylsilane as an internal standard.

RESULTS AND DISCUSSION

Results of our study of reactions of tetracyanoethylene with hydridoiridium complexes are summarized in Table 1. In the case of the first complex studied, $IrH(CO)(PPh_3)_3$, other workers have shown that it reacts with the conventional olefin

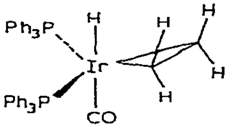
TABLE 1

RESULTS OBTAINED IN PREPARATIVE STUDIES OF THE REACTIONS[a]
HYDRIDOIRIDIUM COMPLEX + TCNE→

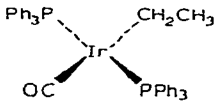
Hydridoiridium complex[b]	Result
$IrH(CO)L_3$	$Ir(C_6H_4H)(CO)(TCNE)L_2$ and $Ir(CN)(CO)(TCNE)L_2$[c] isolated
$IrH(CO)_2L_2$	$Ir(C_6H_4H)(CO)(TCNE)L_2$ and $Ir(CN)(CO)(TCNE)L_2$[c] isolated
$IrH_3(CO)L_2$	$Ir(C_6N_4H)(CO)(TCNE)L_2$ and $Ir(CN)(CO)(TCNE)L_2$[c] isolated
$IrH_3(CO)(AsPh_3)_2$	$Ir(CN)(CO)(TCNE)(AsPh_3)_2$[e] isolated
$IrHCl_2(CO)L_2$[d]	$IrCl(CO)(TCNE)(L)_2$ isolated
$IrH_2Cl(CO)L_2$[d]	$IrCl(CO)(TCNE)(L)_2$ isolated
$IrHCl(SnCl_3)(CO)L_2$	$IrCl(CO)(TCNE)(L)_2$ isolated
$IrH_2(SnCl_3)(CO)L_2$	$IrCl(CO)(TCNE)(L)_2$ isolated
$IrHCl_2L_3$	No complex isolated
IrH_3L_3	$IrH_2(CN)L_3$ isolated

[a] See Experimental for reaction conditions in each case. [b] $L = PPh_3$. [c] This compound is obtained when alcohol is added to the reaction mixture. [d] The complex $IrCl(CO)(TCNE)(L)_2$ is also isolated when the analogous deuteriocomplex is employed. [e] Not obtained analytically pure.

ethylene to give ethane[16,17]. An intermediate such as (I) may be formed in this process. Another intermediate, the alkyl complex (II), was detected by NMR studies[18].

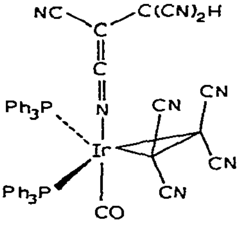


(I)



(II)

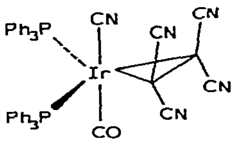
In contrast to the behavior of ethylene toward $IrH(CO)(PPh_3)_2$, activated olefins[18], *e.g.* fumaronitrile, react with the complex to give compounds with structures analogous to (I). In this work, however, we have found that the highly activated olefin tetracyanoethylene reacts with $IrH(CO)(PPh_3)_3$, and also with $IrH(CO)_2(PPh_3)_2$ and $IrH_3(CO)(PPh_3)_2$, to give a complex containing the elements of two molecules of TCNE per iridium atom. The compound is formulated as $Ir(C_6N_4H)(CO)(TCNE)(PPh_3)_2$ on the basis of elemental analysis, infrared spectrum [Fig. 1; 2233 sh, (C≡N); 2220 s, (C≡N); 2168 vs, (N=C=C asym.); 2080 vs, (C≡O); and 1355 w, (N=C=C sym)] and the NMR spectrum (singlet, τ 5.8, with intensity ca. 1/30 that of the phenyl protons). An X-ray study[3,4] has shown the compound to have structure (III).



(III)

Preparation of (III) from the reaction of TCNE with $IrH(CO)_2(PPh_3)_2$ is the method of choice since the yield is good (70%) and the reaction is clean. The trihydrido-complex $IrH_3(CO)(PPh_3)_2$, unlike $IrH(CO)_2(PPh_3)_2$, does not react readily with TCNE at room temperature in benzene, but rather the reaction mixture must be warmed to ca. 50°. Use of $IrH(CO)(PPh_3)_3$ is complicated by a side reaction between TCNE and triphenylphosphine which leads to formation of a tar and a lower yield of product (10%).

A second iridium-containing complex is obtained from the reactions of TCNE with $IrH(CO)_2(PPh_3)_2$, $IrH(CO)(PPh_3)_3$, and $IrH_3(CO)(PPh_3)_2$ if alcohol is added to the reaction mixture. The new complex is white in color and has a lower nitrogen content than (III); the nitrogen to phosphorus ratio is 5 to 2. Structure (IV) is suggested.



(IV)

The infrared spectrum of (IV) is shown in Fig. 1 in the 2000–2250 cm^{-1} range. This spectrum is very similar to spectra of $IrX(CO)(TCNE)(PPh_3)_2$ (X=Cl, Br, I). For a structure such as (IV) at least three bands would be expected in the 1800–2300 cm^{-1} regions. The bands at 2080 and 2230 cm^{-1} are probably ν(C≡O) and ν(C≡N of TCNE) respectively by comparison with similar compounds[15]. A band ascribable to the

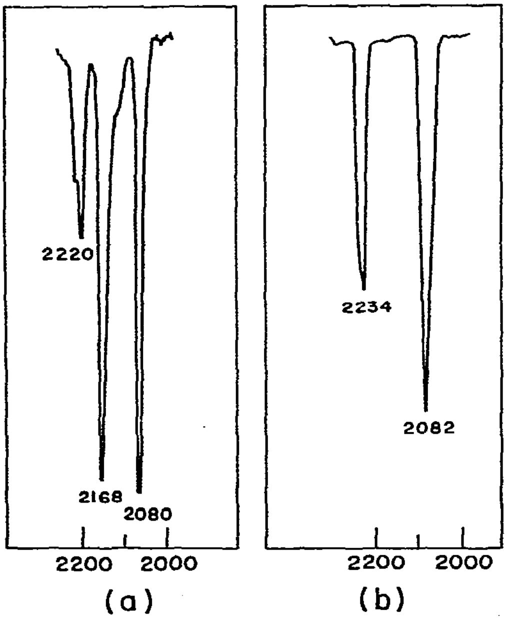
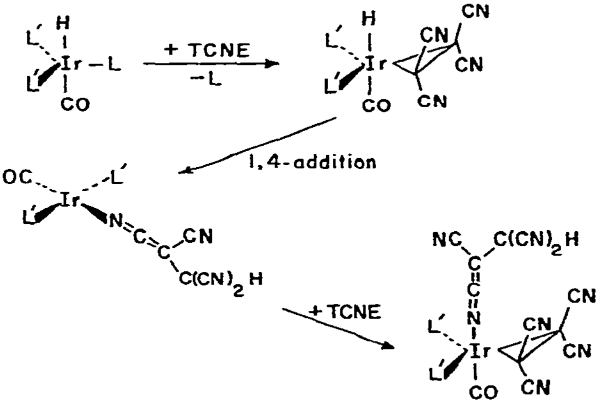


Fig. 1. (a), Infrared spectrum (CH_2Cl_2) of $Ir(C_6H_4H)(CO)(TCNE)(PPh_3)_2$ in the 1900–2300 cm^{-1} region. (b), Infrared spectrum ($CHCl_3$) of $Ir(CN)(CO)(TCNE)(PPh_3)_2$ in the 1900–2300 cm^{-1} region.

cyano-group bound to iridium is not discernible in the spectrum. It may be that this band overlaps with the band at 2230 cm^{-1} due to ν (C≡N) of the TCNE cyano groups since this band showed either a slight splitting or a shoulder in the various spectra that were examined. Further evidence for the formulation of the white product as (IV) comes from other methods of preparation of the compound. When (III) is mixed with KCN in acetone and warmed at 50° for a few minutes a white compound identical in properties to that formulated as (IV) is obtained. This transformation could arise from nucleophilic displacement of the cyano(dicyanomethyl)keteniminato moiety by cyanide ion, and is analogous to displacement reactions which *N*-stannylketenimines undergo when $R'CH_2{-}C(CN){=}C{=}N{-}SnR_3$ and reactive alkyl halides $R''Cl$ react to give substituted malononitriles and $SnClR_3$[19]. The same white material was obtained in low yield when (III) was refluxed in methanol for 1 h. A reasonable reaction path would involve alcoholysis of the Ir–N bond (analogous to the alcoholysis which *N*-stannylketenimines undergo[19]) with formation of an iridium alkoxide intermediate which could then undergo nucleophilic displacement by cyanide ion generated in solution by degradation of the cleaved $-N{=}C{=}C(CN)_2H$ moiety.

The triphenylarsine analog of (IV) in an impure form (2% low in carbon) was obtained when $IrH_3(CO)(AsPh_3)_2$ was allowed to react with TCNE in refluxing benzene. Presumably a keteniminato-complex analogous to (III) is formed as an intermediate. This intermediate may be unstable under these reaction conditions, and decomposition to $Ir(CN)(CO)(TCNE)(AsPh_3)_2$ could result.



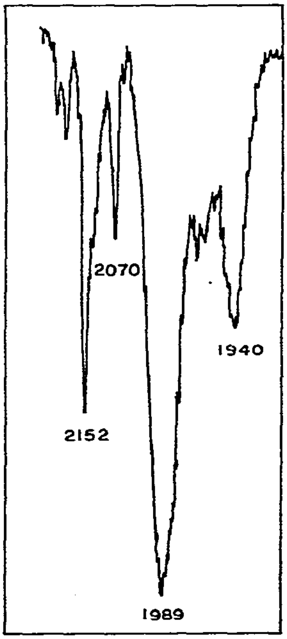


Fig. 2. Proposed reaction path for keteniminato-complex formation from TCNE and $IrH(CO)LL'_2$ (L = CO, L' = PPh_3; L = L' = PPh_3).

Fig. 3. Infrared spectrum of the 1/1 reaction mixture of $IrH(CO)_2(PPh_3)_2$ and TCNE in benzene in the 1900–2300 cm^{-1} region.

A possible reaction path for the formation of $Ir(C_6N_4H)(CO)(TCNE)(PPh_3)_2$ from $IrH(CO)LL'_2$ ($L=CO, L'=PPh_3$; $L=L'=PPh_3$) and TCNE is shown in Fig. 2, and would involve initial formation of a hydrido-π-olefinic complex, followed by 1,4-addition of Ir–H to the coordinated TCNE to give a coordinatively unsaturated, planar iridium(I) complex. Subsequent reaction of this coordinatively unsaturated substrate with a second molecule of TCNE would give compound (III). Qualitative evidence consistent with this pathway comes from infrared monitoring of a 1/1 reaction mixture of $IrH(CO)_2(PPh_3)_2$ and TCNE in benzene. In the spectrum of the mixture (Fig. 3) it is noted that the band at 2152 cm^{-1}, which is believed to be ν(N=C=C), is considerably more intense than the carbonyl band at 2070 cm^{-1} whereas in the final product of the reaction, the ν(N=C=C) and ν(C≡O) are about equal in intensity. The bands at 1940 and 1989 cm^{-1} of Fig. 3 are at about the same positions as ν(C≡O) in the starting material $IrH(CO)_2(PPh_3)_2$[7]. However, in $IrH(CO)_2(PPh_3)_2$ the lower energy band is more intense than the higher energy band and the two are about the same in breadth. These observations are interpreted in terms of the reaction mixture consisting of the starting materials $IrH(CO)_2(PPh_3)_2$ and TCNE, the intermediate $Ir(C_6N_4H)(CO)(PPh_3)_2$, and the final product $Ir(C_6N_4H)(CO)(TCNE)(PPh_3)_2$. That the absorption at 2152 cm^{-1} is more intense than the 2070 cm^{-1} absorption suggests to us that the former one includes ν(N=C=C) of both the final product $Ir(C_6N_4H)(CO)(TCNE)(PPh_3)_2$ and the intermediate $Ir(C_6N_4H)(CO)(PPh_3)_2$ whereas the intensity and broadness of the 1989 cm^{-1} absorption suggests that it corresponds to ν(C≡O) of both $IrH(CO)_2(PPh_3)_2$ and the keteniminato-intermediate $Ir(C_6N_4H)(CO)(PPh_3)_2$. Related evidence that $Ir(C_6N_4H)(CO)(PPh_3)_2$ is a likely precursor to (III) is that a very similar keteniminato-compound $Ir(C_4N_3)(CO)(PPh_3)_2$ (C_4N_3 is the anion derived from cyanoform) has been prepared[36] which reacts readily with TCNE to give $Ir(C_4N_3)CO)(TCNE)(PPh_3)_2$ which is analogous to (III).

Wojcicki and co-workers have reported that several alkyls of π-cyclopentadienylchromium nitrosyl, iron carbonyl, and molybdenum carbonyl react with TCNE via 1,4-addition[20]. The results described herein where 1,4-addition of Ir–H to TCNE occurs instead of 1,2-addition may be related to the electronic structure of cyanocarbon anions[21,22]. Cyanocarbons such as pentacyanopropene are remarkably strong acids, and it has been suggested that this is due to resonance stabilization in the anion. Resonance stabilization is not possible in the conjugate acid. Molecular orbital calculations on cyanocarbon anions indicate extensive electronic delocalization[23,24]. Of particular interest to the discussion here is that these calculations show that the terminal nitrogen atoms are considerably more negative than carbon atoms in the framework. While the very stable cyanocarbon anions with their highly delocalized structures are generated from cyanocarbon acids by proton loss, we suggest that a coordinated "cyanocarbon anion" may be generated in the reactions of TCNE with these hydridoiridium complexes by hydride transfer to the coordinated TCNE. This transfer of electronic charge to the cyanocarbon moiety would be expected, by analogy with cyanocarbon anions, to result in increased electronic density on the nitrile nitrogen atoms and an enhancement of their nucleophilicity. Internal attack at the electrophilic iridium center by one of the nitrogen atoms would then complete the 1,4-addition process.

A number of compounds containing the $M-N=C=C\langle$ linkage, where M is either a transition metal[20,25–29] or a main group metal[30–33], have been prepared. The compounds reported herein are the first examples of keteniminato-derivatives of noble transition metals. From an X-ray study of compound (III) it was noted that the Ir–N distance of 2.04 Å appears to be that of a normal single bond[4]. It was also suggested, on the basis of a comparison of Ir–P bond lengths in (III) and $IrBr(CO)(TCNE)(PPh_3)_2$ that the cyano(dicyanomethyl)keteniminato ligand is very similar to the bromide ligand in its bonding characteristics. Data shown in Table 2 are also informative in regard to the nature of the $Ir{-}N{=}C{=}C\langle$ linkage. The fact that $\nu(C{\equiv}O)$ values in complexes (III) and (IV) are identical, and also somewhat higher than for analogous complexes listed in Table 2, might be interpreted to mean that the $-N{=}C{=}C(CN)C(CN)_2H$ group is similar in electronic characteristics as a ligand to the cyanide ion, *i.e.* a strong π-acceptor. However, this idea is not consistent with the crystallographic evidence (Ir–N bond distance), nor with the apparent instability of (III) with respect to cleavage of the keteniminato-moiety in the presence of alcohol. One also notes from Table 2 that there is a noticeable disparity between the thermal stabilities of (III) and the other complexes. We interpret these various observations to mean that the cyanocarbon moiety in (III) is weakly bonded to the iridium, and that it is a hard ligand with weak σ and negligible π-bonding properties. Such properties would give rise to a higly polar Ir–N linkage in (III), and such a charge distribution would be consistent with the high carbonyl stretching frequency.

TABLE 2

CARBONYL STRETCHING FREQUENCIES AND THERMAL DECOMPOSITION TEMPERATURES OF COMPLEXES OF THE TYPE $IrX(CO)(TCNE)(PPh_3)_2$

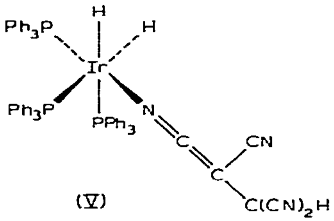
X	$\nu(C{\equiv}O)$[a]	M.p. (dec.)	Ref.
 $-N{=}C{=}C(CN)C(CN)_2H$	2080	165–180°	[b]
$-CN$	2080	>300°	[b]
$-N{=}C{=}S$	2067	240–250	15
$-N{=}C{=}O$	2061	285–289	15
Cl	2060	265–270	15

[a] In cm^{-1}. [b] This work.

In contrast to results cited above where keteniminato-complexes were isolated from reactions of TCNE with three hydridoiridium complexes, the tervalent, octahedral complexes $IrHCl_2(CO)(PPh_3)_2$, $IrH_2Cl(CO)(PPh_3)_2$, $IrHCl(SnCl_3)(CO)(PPh_3)_2$, $IrH_2(SnCl_3)(CO)(PPh_3)_2$, $IrHCl_2(PPh_3)_3$, $IrH_2Cl(PPh_3)_3$, and $IrH_3(PPh_3)_3$ behaved differently toward TCNE. The same iridium-containing product was obtained from reactions of $IrHCl_2(CO)(PPh_3)_2$, $IrH_2Cl(CO)(PPh_3)_2$, $IrHCl(SnCl_3)(CO)(PPh_3)_2$, and $IrH_2(SnCl_3)(CO)(PPh_3)_2$ with TCNE, *viz.*, $IrCl(CO)(TCNE)(PPh_3)_2$ which was previously prepared from the reaction of Vaska's compound with TCNE[15]. In a formal sense these reactions are a combination of reductive-elimination and addition processes, *i.e.* reduction of Ir^{III} to Ir^{I} as HCl, H_2, $SnHCl_3$, or SnH_2Cl_2 is eliminated, with either prior or subsequent addition of TCNE to give a seven-coordinate or five-coordinate complex respectively. Kinetic data for the reaction of *trans*-$PtHCl(PPh_3)_2$ with TCNE were interpreted in terms of an initial addition of

TCNE to the four-coordinate substrate, followed by reductive-elimination of HCl to give $Pt(PPh_3)_2(TCNE)^2$, and a similar mechanism may be operative in the case of these octahedral iridium complexes.

The trihydrido-complex $IrH_3(PPh_3)_3$ in its reaction with TCNE did not conform to either of the two patterns exhibited by the other complexes in this study. The product was neither a keteniminato-complex nor a reductive-elimination product, but rather was the dihydrido(cyano)-complex $IrH_2(CN)(PPh_3)_3$. A way in which this compound could be produced in this reaction is via an initial formation of a 1/1 adduct $IrH_3(TCNE)(PPh_3)_2$. A 1,4-addition would give a keteniminato-complex (V) which, by virtue of a solution instability of the iridium–keteniminato linkage analogous to that in $Ir(C_6H_4N)(CO)(TCNE)(PPh_3)_2$, might decompose to a cyano-complex. The intense red color of the mixture of $IrH_3(PPh_3)_3$ and TCNE, and the infrared absorption in the 2150 cm^{-1} region suggest that a keteniminato-complex was formed as an intermediate.


(V)

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