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METAL COMPLEXES OF CYANOCARBONS

XIII*. DICYANOKETENIMINATO COMPLEXES OF SOME NOBLE METALS

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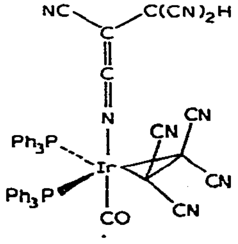
SUMMARY

The preparation and characterization of some percyanocarbon complexes containing the $M-N=C=C(CN)_2$ linkage, where M is rhodium, iridium, palladium, and platinum, are described. From IR and NMR spectral data it is concluded that the dicyanoketeniminato group is a hard ligand which is comparable in its electronic characteristics as a ligand to the *N*-cyanato and *N*-thiocyanato groups.

INTRODUCTION

A novel keteniminato complex of iridium was recently prepared in this laboratory from the reaction of tetracyanoethylene with some hydridoiridium complexes[2]. This complex, (I), is the first example of a keteniminato complex of a noble metal,



(I)

but other compounds containing the $M-N=C=C\langle$ linkage, where M is either a transition metal[3-8] or a main group metal[9-14] have been previously described.

With a view toward learning something of the bonding propensities of a keteniminato ligand toward noble metals, we have prepared some representative examples of rhodium, iridium, palladium, and platinum complexes containing the dicyanoketeniminato moiety, $-N=C=C(CN)_2$. An assessment of the nature of bonding in the $M-N=C=C(CN)_2$ linkage is made from infrared and NMR spectral studies.

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* For Part XII see ref. 1.

EXPERIMENTAL

I. Materials

Potassium tricyanomethanide was prepared from the reaction of potassium cyanide and dibromomalononitrile as described in the literature[15]. Noble metal substrates used as starting materials were also prepared by literature procedures. These include the following: $IrCl(CO)(PPh_3)_2$[16], $IrCl(CO)(AsPh_3)_2$*, $RhCl(CO)(PPh_3)_2$[18], $PtEt(I)(PPh_3)_2$[19], *cis*-$PtCl_2(PPh_3)_2$[20], *trans*-$PtHCl(PPh_3)_2$[21], *trans*-$PtHCl(PEt_3)_2$[22], and $[PdCl(Me_5dien)]PF_6$**,[23]. All other chemicals were reagent-grade materials, and were used without further purification with the exception of tetracyanoethylene, which was sublimed prior to use.

II. Preparation of the complexes

Infrared spectral data are given in Table 1.

A. Dicyanoketeniminato(carbonyl)bis(triphenylphosphine)iridium, $Ir(C_4N_3)CO(PPh_3)_2$. A solution of *trans*-$IrCl(CO)(PPh_3)_2$ (0.78 g, 1 mmole) and potassium tricyanomethanide (2.78 g, 20 mmoles) in 200 ml of acetone was refluxed under nitrogen for 3 h. Solvent was removed under reduced pressure with a rotary evaporator and the residue was extracted with benzene. Addition of hexane to the benzene extract or reduction of the volume of the benzene extract to ca. 10 ml caused small yellow crystals of $Ir(C_4N_3)CO(PPh_3)_2$ to precipitate in quantitative yield. Recrystallization from dichloromethane/hexane gave the pure complex, m.p. 160–165° (dec.). (Found: C, 59.07; H, 3.59; N, 4.78; mol. wt. in $CHCl_3$, 885. $C_{41}H_{30}IrN_3OP_2$ calcd.: C, 58.97;

TABLE 1

INFRARED DATA FOR DICYANOKETENIMINATO COMPLEXES[a]

Compound	*ν(C≡N)*	*ν(C≡O)*
$Ir(C_4N_3)CO(PPh_3)_2$[b]	2230 w, 2192 m, 2174 s	2005 s
$Ir(C_4N_3)CO(AsPh_3)_2$	2230 w, 2188 m, 2175 s	2000 s
$Ir(C_4N_3)CO(TCNE)(PPh_3)_2$	2225 m, 2220 sh, 2200 m, 2172 s	2074 s
$Ir(C_4N_3)CO(FUMN)(PPh_3)_2$[c]	2223 w, 2220 m, 2192 m, 2172 s	2057 s
$Ir(C_4N_3)CO(SO_2)(PPh_3)_2$	2232 w, 2190 m, 2179 s	2042 s
$Rh(C_4N_3)CO(PPh_3)_2$	2227 w, 2190 m, 2174 s	2017 s
$Rh(C_4N_3)CO(TCNE)(PPh_3)_2$	2242 w, 2225 m, 2223 m, 2186 s	2082 s
$Pt(C_2H_5)(C_4N_3)(PPh_3)_2$	2230 w, 2180 sh, 2174 s	
$PtCl(C_4N_3)(PPh_3)_2$	2235 w, 2190 sh, 2180 s	
$PtH(C_4N_3)(PPh_3)_2$	2225 w, 2175 s	
$PtH(C_4N_3)(PEt_3)_2$	2220 w[d], 2185 m[d], 2175 s[d]	
$[Pd(C_4N_3)(Me_5dien)]PF_6$	2240 w, 2195 m, 2190 s	

[a] Recorded in nujol mulls and given in cm^{-1}. Abbreviations are: s, strong; m, medium; w, weak; sh, shoulder; br, broad; sp, sharp. [b] In $CHCl_3$ absorptions are: 2234 w, 2190 m, 2173 s, and 1993 s. [c] FUMN is fumaronitrile. [d] Benzene solution.

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* Prepared from $Na_3IrCl_6 \cdot 12\ H_2O$ by a procedure analogous to that used for $IrCl(CO)(PPh_3)_2$ in ref. 17.

** Me_5dien is 1,1,4,7,7-pentamethyldiethylenetriamine.

H, 3.62; N, 5.03%; mol.wt., 834.) The compound is soluble in benzene, chloroform, dichloromethane, carbon disulfide, and slightly soluble in ethanol.

B. Dicyanoketeniminato(carbonyl)bis(triphenylarsine)iridium, $Ir(C_4N_3)CO(AsPh_3)_2$. The compound $IrCl(CO)(AsPh_3)_2$ (0.4 g, 0.4 mmole) and $K(C_4N_3)$ (0.6 g, 5 mmoles) were dissolved in 100 ml of dichloromethane/acetone (1/1) and stirred at room temperature for 2 h. Solvent was removed and the residue was extracted with benzene. Evaporation of the benzene and recrystallization of the residue from benzene/methanol gave a quantitative yield of $Ir(C_4N_3)CO(AsPh_3)_2$, m.p. 210–215° (dec.). (Found: C, 53.20; H, 3.39; N, 4.32. $C_{41}H_{30}As_2IrN_3O$ calcd.: C, 53.55; H, 3.28; N, 4.55%.)

C. Attempted preparation of dicyanoketeniminato(carbonyl)bis(methyldiphenylphosphine)iridium, $Ir(C_4N_3)CO(PMePh_2)_2$. To a solution of $Ir(C_4N_3)CO(PPh_3)_2$ (0.3 g, 0.36 mmole) in benzene (25 ml) was added 0.5 ml of methyldiphenylphosphine. The solution was stirred for $\frac{1}{2}$ h under nitrogen and hexane was added. A solid separated but the material became oily as it was collected on a filter. An elemental analysis was not obtained. Infrared and NMR data (see Results and Discussion) are consistent with the material being *cis*-$Ir(C_4N_3)CO(PMePh_2)_2$.

D. Dicyanoketeniminato(carbonyl)(tetracyanoethylene)bis(triphenylphosphine)iridium, $Ir(C_4N_3)CO(TCNE)(PPh_3)_2$. To a benzene solution (5 ml) of $Ir(C_4N_3)CO(PPh_3)_2$ (0.2 g, 0.24 mmole) was added tetracyanoethylene (0.128 g, 1.0 mmole) at room temperature. A pale yellow solid separated, and this was collected (0.2 g, 85%) and washed well with benzene to give $Ir(C_4N_3)CO(TCNE)(PPh_3)_2$, m.p. 200–208° (dec.). (Found: C, 58.67; H, 2.93; N, 10.05. $C_{47}H_{30}IrN_7OP_2$ calcd.: C, 58.60; H, 3.14, N, 10.18%.)

E. Dicyanoketeniminato(carbonyl)fumaronitrilebis(triphenylphosphine)iridium, $Ir(C_4N_3)CO(C_4H_2N_2)(PPh_3)_2$. This compound was prepared as described above in (*D*) except that heptane was used to precipitate the complex, which was obtained as an impure white solid, m.p. 120–125° (dec.), that dissociates in solution. Recrystallization from dichloromethane/methanol containing fumaronitrile gave the complex as white needles. (Found: C, 58.27; H, 3.68; N, 7.43. $C_{45}H_{32}IrN_5OP_2$ calcd.: C, 59.18; H, 3.53; N, 7.67%.)

F. Dicyanoketeniminato(carbonyl)(sulfur dioxide)bis(triphenylphosphine)iridium, $Ir(C_4N_3)CO(SO_2)(PPh_3)_2$. Sulfur dioxide was bubbled through a benzene solution (2 ml) of $Ir(C_4N_3)CO(PPh_3)_2$ (0.1 g, 0.12 mmole) at room temperature and a green color appeared. After 1 h hexane was added and lime-green crystals separated, m.p. 100–105° (dec.). The green compound reverts to starting materials in solution. (Found: C, 54.31; H, 3.50; N, 4.38. $C_{41}H_{30}IrN_3O_3P_2S$ calcd.: C, 54.76; H, 3.36; N, 4.67%.)

G. Dicyanoketeniminato(carbonyl)bis(triphenylphosphine)rhodium, $Rh(C_4N_3)CO(PPh_3)_2$. This compound was prepared by the same procedure used for the iridium analog as described above in (*A*). (Found: C, 65.18; H, 4.01; N, 5.43; mol.wt. in chloroform, 850. $C_{41}H_{30}N_3OP_2Rh$ calcd.: C, 66.03; H, 4.06; N, 5.64%; mol.wt., 745.)

H. Attempted preparation of dicyanoketeniminato(carbonyl)tetracyanoethylenebis(triphenylphosphine)rhodium, $Rh(C_4N_3)CO(TCNE)(PPh_3)_2$. Tetracyanoethylene (0.128 g, 1 mmole) was added to a benzene solution (5 ml) of $Rh(C_4N_3)CO(PPh_3)_2$ (0.1 g, 0.15 mmole) and the mixture was stirred at room temperature for 1 h. Since no precipitation had occurred, heptane was added and a golden-yellow crystalline solid separated, m.p. 130–135° (dec.). In solution the complex dissociated. An analytically pure sample was not obtained. Infrared data (Table 1) suggest a formulation analogous to $Ir(C_4N_3)CO(TCNE)(PPh_3)_2$.

I. Dicyanoketeniminato(1,1,4,7,7-pentamethyldiethylenetriamine)palladium(II) hexafluorophosphate, $[Pd(C_4N_3)(Me_5dien)]PF_6$. A mixture of $[PdCl(Me_5dien)]PF_6$ (1 g, 2.2 mmoles) and $K(C_4N_3)$ (1 g, 7.7 mmoles) in 100 ml of acetone was stirred at room temperature for 3 h. The solvent was evaporated and the residue was extracted with methanol. Addition of water to the methanol extract caused the complex to precipitate quantitatively as pale yellow plates, m.p. 240–245° (dec.). (Found: C, 30.20; H, 4.55; N, 16.01. $C_{13}H_{23}F_6N_6PdP$ calcd.: C, 30.38; H, 4.32; N, 16.36%.)

J. Dicyanoketeniminato(ethyl)bis(triphenylphosphine)platinum(II), $Pt(C_4N_3)(C_2H_5)(PPh_3)_2$. A mixture of $Pt(C_2H_5)I(PPh_3)_2$ (0.2 g, 0.23 mmole) and $K(C_4N_3)$ (1.3 g, 10 mmoles) was refluxed in 50 ml of 1/1 acetone/benzene for 1 h. The mixture was taken to dryness and the residue was washed well with water. Recrystallization of the residue from acetone/benzene gave the complex as a cream-colored powder, m.p. 200–210° (dec.). (Found: C, 60.65; H, 4.06; N, 4.35; mol.wt. in chloroform, 915. $C_{42}H_{35}N_3P_2Pt$ calcd.: C, 60.12; H, 4.12; N, 5.01%; mol.wt., 838.)

K. Chloro(dicyanoketeniminato)bis(triphenylphosphine)platinum(II), $PtCl(C_4N_3)(PPh_3)_2$. A mixture of *cis*-$PtCl_2(PPh_3)_2$ (0.3 g, 0.38 mmole) and $K(C_4N_3)$ (10 mmoles) in 100 ml of 1/1 acetone benzene was refluxed for 1 h. Solvent was removed under reduced pressure and the residue was washed well with water. Recrystallization of the residue from chloroform/hexane gave the complex as an off-white powder, m.p. 240–245° (dec.). (Found: C, 57.11; H, 3.68; N, 5.04. $C_{40}H_{30}ClN_3P_2Pt$ calcd.: C, 56.82; H, 3.58; N, 4.97%.)

L. Hydrido(dicyanoketeniminato)bis(triphenylphosphine)platinum(II), $PtH(C_4N_3)(PPh_3)_2$. Potassium tricyanomethanide (0.8 g, 6.2 mmoles) and *trans*-$PtHCl(PPh_3)_2$ (0.43 g, 0.57 mmole) were dissolved in 50 ml of acetone and the mixture was refluxed for 10 min. The acetone was evaporated and the residue was washed well with water. Recrystallization of the pale yellow residue from chloroform/hexane gave *trans*-$PtH(C_4N_3)(PPh_3)_2$ as cream-colored microcrystals, m.p. 190–195° (dec.). (Found: C, 58.92; H, 4.89; N, 5.06; mol.wt. in chloroform, 792. $C_{40}H_{41}N_3P_2Pt$ calcd.: C, 58.51; H, 5.04; N, 5.12%; mol.wt., 820.)

M. Attempted preparation of hydrido(dicyanoketeniminato)bis(triethylphosphine)platinum(II), $PtH(C_4N_3)(PEt_3)_2$. A solution of *trans*-$PtHCl(PEt_3)_2$ (0.5 g, 1.1 mmoles) and $K(C_4N_3)$ (0.7 g, 5.5 mmoles) in 30 ml of acetone was refluxed for 15 min. The acetone was evaporated and the residue was extracted with benzene. Addition of hexane to the benzene extract caused white crystals to precipitate, but an oily product was obtained on the filter which was not analyzed. Infrared and NMR data (Tables 1 and 2) for this oily solid are consistent with it being *trans*-$PtH(C_4N_3)(PEt_3)_2$.

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 with a Beckman IR-7 spectrophotometer in Nujol or hexachlorobutadiene mulls, and chloroform or benzene solutions.

TABLE 2

INFRARED AND ^{1}H MAGNETIC RESONANCE DATA FOR COMPLEXES OF THE TYPE[a] H–Pt$(PEt_3)_2$–X

X	*ν(Pt–H) (cm^{-1})*	*τ(Pt–H)*
CN	2041	17.8
$SnCl_3$	2105	19.2
I	2156	22.6
Br	2178	25.5
Cl	2183	26.8
N=C=C$(CN)_2$	[b]	27.6
NCO	2229	27.7
NO_3	2242	33.6

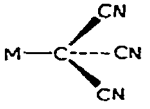
[a] Data are taken from refs. 29, 30, and 31 except for –N=C=C$(CN)_2$. [b] Not observed; see text.

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

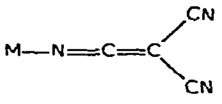
Proton magnetic resonance spectra were measured with a Varian HA-100 instrument using TMS as an internal standard in benzene solution.

RESULTS AND DISCUSSION

A number of new complexes containing the percyanocarbon anion C_4N_3 covalently bonded to palladium, platinum, rhodium, and iridium have been prepared (see Table 1) from the metathetical reactions of potassium tricyanomethanide with various halogen-substituted substrates of these metals. Two structural forms, (II) and/or (III) might be anticipated for complexes containing the C_4N_3 unit. Two and three infrared-active absorptions are expected for (II) (C_{3v}) and (III) (C_{2v}) respectively in the ν(C≡N) region. Infrared data of Table 1 are consistent with metal–nitrogen bonding as in (III) since each compound, with the single exception of PtH$(C_4N_3)(PPh_3)$ which shows only two bands, exhibits three absorptions both in the solid state and in solution in the 2150–2250 cm^{-1} region due to the C_4N_3 moiety. In the case of *trans*-PtH$(C_4N_3)(PPh_3)$ the bonding mode is also believed to be via a nitrogen atom since the NMR spectrum in the high-field region shows a broad signal for the hydrogen attached to platinum.



(II)

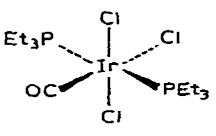


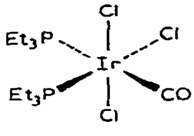
(III)

Reactions of two of the new keteniminato complexes M(C_4N_3)CO$(PPh_3)_2$ (M=Rh, Ir) with some Lewis acids have been studied to see if a reactivity analogous to that of Vaska's compound would be observed. With the strong π-acid tetracyanoethylene (TCNE), 1/1 adducts were obtained. In the case of the iridium complex, the compound is quite stable both in the solid state and in solution, but while the rhodium complex appears to be stable indefinitely in the solid state, there is reversible dissociation into $Rh(C_4N_3)CO(PPh_3)_2$ and TCNE in solution. Fumaronitrile (FUMN), oxygen, and sulfur dioxide are weaker π-acids than TCNE and as expected were found to be less reactive toward $M(C_4N_3)CO(PPh_3)_2$. With FUMN and $Ir(C_4N_3)CO(PPh_3)_2$ a 1/1 adduct, which dissociated in solution, was isolated but with the same olefin and $Rh(C_4N_3)CO(PPh_3)_2$ a reaction did not occur. Sulfur dioxide behaved like fumaronitrile. A bright green crystalline solid, which dissociates in solution, was isolated from reaction with the iridium substrate but with $Rh(C_4N_3)CO(PPh_3)_2$ no reaction occurred. Molecular oxygen is known to react in solution with the complexes $IrX(CO)(PPh_3)_2$ ($X = Cl, Br, I, N_3$) to form oxygenated species[24], but reaction does not occur with the isothiocyanato-complex $Ir(NCS)CO(PPh_3)_2$. Behavior of the new dicyanoketeniminato complex $Ir(C_4N_3)CO(PPh_3)_2$ toward O_2 is similar to that of $Ir(NCS)CO(PPh_3)_2$ *i.e.* there is no reaction.

Attempts were made to prepare a dicyanoketeniminato–iridium complex containing molecular nitrogen. However, neither the reaction of $K(C_4N_3)$ with $IrCl(N_2)(PPh_3)_2$ nor the reaction of benzoyl azide with $Ir(C_4N_3)CO(PPh_3)_2$ gave the desired product.

The well-known complexes of the type $IrX(CO)(PR_3)_2$ exhibit carbonyl stretching frequencies in the narrow range 1950–1970 cm^{-1} for $X = Cl, Br, I, N_3$, NCO, and NCS. The $\nu(C{\equiv}O)$ is almost independent not only of the X group but also of the nature of the R group as has been pointed out[25]. We were therefore surprised to find a value of 2000 cm^{-1} for $\nu(C{\equiv}O)$ in the dicyanoketeniminato complex $Ir(C_4N_3)CO(PPh_3)_2$ (Table 1). One explanation for the abnormally high value might be that the dicyanoketeniminato ligand is a very strong π-acceptor. If it is in a position *trans* to CO then a shift of $\nu(C{\equiv}O)$ to a higher frequency is explicable in terms of a competition between CO and C_4N_3 for iridium *d* electrons. However, an alternative explanation might be based on a *cis* configuration for the complex rather than a *trans* one as is believed to be applicable for most complexes of the type $IrX(CO)(PR_3)_2$. We believe that this new dicyanoketeniminato complex has a *cis* structure, and base our belief, in part, on the criterion suggested by Kemmitt and Bland[26] who noted a correlation between the arrangement of triphenylphosphine groups around a metal atom and the relative intensities of two infrared bands in the 1570–1590 cm^{-1} region of the spectrum in some square planar complexes of platinum, rhodium, and iridium. They found for a *cis* stereochemistry that the higher energy band was more intense than the lower energy band whereas in *trans* complexes the relative intensities were reversed. Using this criterion then, the complexes $Ir(C_4N_3)CO(PPh_3)_2$, $Rh(C_4N_3)CO(PPh_3)_2$, $Pt(C_2H_5)(C_4N_3)(PPh_3)_2$, and $PtCl(C_4N_3)(PPh_3)_2$ have *cis* configurations whereas the square complex $PtH(C_4N_3)(PPh_3)_2$ has by the same criterion a *trans* configuration. A *trans* configuration for the latter complex is confirmed by the high-field NMR spectrum in which a broad triplet is observed for the H bound to platinum. The solubility of $Ir(C_4N_3)CO(PPh_3)_2$ was not great enough to obtain a good ^{31}P NMR spectrum. In order to apply the NMR criterion of virtual coupling as a means of ascertaining stereochemistry in tertiary phosphine complexes, the triphenylphosphine complex $Ir(C_4N_3)CO(PPh_3)_2$ was allowed to react with an excess of methyldiphenylphosphine. An oily solid believed to be $Ir(C_4N_3)CO(PMePh_2)_2$ on the basis of its infrared spectrum [benzene, 2234 m, $\nu(C{\equiv}N)$, 2220 m, $\nu(C{\equiv}N)$, 2174 s, $\nu(C{\equiv}N)$, and 2000 vs $\nu(C{\equiv}O)$] was obtained. The NMR spectrum of this material is consistent with a *cis* configuration in that the methyl signal appears as a doublet [τ 8.12, J(P–H) 12 Hz], rather than as a triplet which would be expected for a *trans*-configuration with virtual coupling. On the basis of these infrared and NMR data then, it seems likely that the triphenylphosphine complex $Ir(C_4N_3)CO(PPh_3)_2$ has a *cis* configuration. By analogy it is expected that ν(C≡O) would be higher in a *cis* than in a *trans* geometry, *cf.*, (IV) and (V) where the carbonyl frequencies are 2031 and 2073 cm^{-1} respectively[27].


(IV)


(V)

The position of a ligand in the *trans* effect series may be correlated with the electronic properties of the ligand[28]. Thus, ligands that are good *trans* activators such as cyanide ion and carbon monoxide are those that form strong σ and/or π-bonds with the metal while ligands that are low in the series such as hydroxide ion and ammonia form weak σ-bonds and no π-bonds. In an effort to gain information about the electronic characteristics of the dicyanoketeniminato group as a ligand, we have tried to determine its position in the *trans* effect series. In complexes of the type *trans* $PtHX(PR_3)_2$ it is known that ν(Pt–H) generally decreases as the position of X becomes higher in the *trans* effect series (Table 2). Unfortunately, in the complexes $PtH(C_4N_3)(PR_3)_2$ (R = Et, Ph) we did not observe a band that could be unequivocally assigned to the platinum–hydrogen stretching vibration, perhaps because it is hidden under one of the several bands in the 2175–2220 region associated with the C_4N_3 ligand*. It has also been observed that the chemical shift of the hydridic hydrogen in *trans*-$PtHX(PEt_3)_2$ complexes decreases from X = NO_3 (τ 33.8) to X = CN (τ 17.8) and that generally, the gradual decrease in τ values for various X ligands correlates with the increasing *trans* effect of X. As shown in Table 2 the hydridic hydrogen chemical shift of the dicyanoketeniminato complex *trans*-$PtH(C_4N_3)(PEt_3)_2$ is observed at τ 27.6. This value is very close to those found for the *N*-cyanato and *N*-thiocyanatocomplexes, τ 27.7 and τ 27.6 respectively[31], and suggests that $-N{=}C{=}C(CN)_2$ is electronically similar in ligand properties to these well known pseudohalides. A fact cited earlier, *i.e.* that $Ir(C_4N_3)CO(PPh_3)_2$ and $Ir(NCS)CO(PPh_3)_2$ fail to react in solution with molecular oxygen whereas the chloro, bromo, etc. complexes to undergo oxygenation, is consistent with the idea that $-N{=}C{=}C(CN)_2$ and $-N{=}C{=}S$ are electronically similar. In a study of some nickel(II) complexes of the C_4N_3 anion, Köhler and coworkers observed from electronic spectral data that C_4N_3 and NCS have similar spectrochemical effects[32].

We conclude by saying that the dicyanoketeniminato ligand, in common with other ligands that are low in the *trans* effect series, may be classified as "hard", and suppose that it is not a good σ-bonder and is a quite poor (or negligible) π-bonder. That the ν(C≡O) values in the dicyanoketeniminato–iridium complexes are abnormally high may be a manifestation not only of a *cis* configuration but also of a

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* The spectra of $PtH(C_4N_3)(PPh_3)_2$ and $PtD(C_4N_3)(PPh_3)_2$ appear to be identical in the 1800–2300 cm^{-1} region.

highly polar iridium–nitrogen bond. Such a bond would be expected to result from the bonding of a hard C_4N_3 ligand to a soft iridium center.

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