smaller values of α, consistent with less 3d character than was determined in that study.

Registry No. Table VII 3, 36182-31-7; 6, 36216-34-9.

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Reaction of Sulfur Dicyanide with $IrCl(CO)(PR_3)_2$ and the Structure of Chlorocyano(thiocyanato)-*N*-carbonylbis(triphenylphosphine)iridium(III), $IrCl(CN)(NCS)(CO)(PPh_3)_2$

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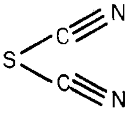
An X-ray structural determination and infrared studies of products of the reactions of sulfur dicyanide with $IrCl(CO)L_2$ ($L = PPh_3$, $PMePh_2$) have shown that $S(CN)_2$ acts as a pseudohalogen in its reactions with these substrates to form *via* trans addition the cyano-*S*-thiocyanato complexes $IrCl(CN)(SCN)(CO)(L)_2$. Recrystallization of these compounds from dichloromethane–methanol is accompanied by isomerization to the *N*-thiocyanato complexes. The complex $IrCl(CN)(NCS)(CO)(PPh_3)_2$ crystallizes with 1 molecule in space group C_i^1-$P\bar{1}$ of the triclinic system in a reduced cell of dimensions $a = 10.141$ (5), $b = 11.222$ (5), $c = 9.381$ (6) Å; $\alpha = 112.21$ (5), $\beta = 95.02$ (5), $\gamma = 64.23$ (4)°; $\lambda(\text{Cu } K\alpha_1)$ 1.54056 Å. The observed and calculated densities are 1.57 (3) and 1.62 g cm^{-3}. Refinement of a model with CO disordered with trans Cl and CN disordered with the NC part of the trans NCS has resulted in a conventional R factor on F of 3.2% for the 1238 counter data having $I > 3\sigma(I)$. Because of the crystallographically imposed center of symmetry, and resultant disorder, bond distances and angles are not of high precision. Important bond distances include Ir–P = 2.418 (3), Ir–Cl = 2.37 (1), Ir–C(of CO) = 1.84 (4), Ir–(C/N) = 1.99 (1), and (C/N)–S = 1.62 Å. The complex is essentially octahedral, and the N–C–S linkage is linear.

Introduction

Sulfur dicyanide, I, is an unstable, reactive molecule that has been known since 1828.[1] However, reactions of $S(CN)_2$



I

with transition metal complexes do not appear to have been previously investigated. In view of our earlier studies of the reactions of cyanocarbons with transition metal complexes where it was found that these strong π acids bond very effectively to electron-rich metal complexes,[2] it was of interest to investigate the reactions of cyanosulfur compounds with metal complexes. We have therefore studied the reactions of $S(CN)_2$ with a number of d^8 and d^{10} noble metal substrates and describe herein the reaction of $S(CN)_2$ with $IrCl(CO)L_2$ ($L = PPh_3$, $PMePh_2$) as well as the results of an X-ray study of one of the products, $IrCl(CN)(NCS)(CO)(PPh_3)_2$, chlorocyano(thiocyanato)-*N*-carbonylbis(triphenylphosphine)iridium(III).

Experimental Section

Materials. The iridium complexes $IrCl(CO)L_2$ were prepared according to literature procedures[3,4] as was sulfur dicyanide.[5] Because of its thermal instability, the $S(CN)_2$ was stored at Dry Ice temperatures under nitrogen. Transfer of materials, reactions, and work-ups were carried out in a nitrogen atmosphere. Sulfur dicyanide has a high vapor pressure and the vapors are quite irritating to the eyes.

Reactions of Sulfur Dicyanide with $IrCl(CO)L_2$. (A) Chlorocarbonylbis(triphenylphosphine)iridium(I) (0.39 g, 0.5 mmol) was dissolved in 30 ml of benzene and to the solution was added 0.4 g (5 mmol) of sulfur dicyanide at room temperature. As the clear mixture was stirred, it began after a few minutes to take on a cloudy appearance as a precipitate slowly formed. After 0.5 hr the off-white solid was collected on a filter. This product was recrystallized from dichloromethane–methanol as colorless octagonal prisms, mp >300°. *Anal.* Calcd for $C_{39}H_{30}ClIrN_2OP_2S$: C, 54.19; H, 3.50; N, 3.24; P, 7.17; S, 3.70. Found: C, 53.88; H, 3.57; N, 3.27; P, 7.19; S, 4.15. The X-ray analysis described below provides unambiguous proof that this recrystallized product is not the result of direct addition of $S(CN)_2$ to $IrCl(CO)(PPh_3)_2$, but rather that oxidative addition has occurred to form $IrCl(CN)(NCS)(CO)(PPh_3)_2$. Since mechanistically the N-bonded isomer is surprising, the preparation was repeated and both the initial product and that obtained upon recrystallization from various solvent mixtures were characterized by infrared techniques. Ir (Nujol): 2155 w (CN of Ir–CN), 2135 m (CN of Ir–SCN), 2080 vs (CO), and 440, 420 m (SCN bend). The higher value of the C–N stretching frequency, along with its sharpness (as contrasted to the lower frequency and broadness of the C–N stretch in the isomer described below), the absence of an absorption in the 760–880-cm^{-1} range which is characteristic of M–NCS bonding, and the bending frequencies in the 400–440-cm^{-1} range (which are characteristic of M–SCN bonding as contrasted to bending frequencies in the 450–490-cm^{-1} range for *N*-thiocyanates), is suggestive of an *S*-thiocyanate structure. As noted above, recrystallization of the initial *S*-bonded product from dichloromethane–methanol gives a compound which from the X-ray study is known to be the N-bonded form. Infrared data are consistent with an *N*-thiocyanato structure. Ir (Nujol): 2155 w (CN of Ir–CN), 2115 vs, br (CN of Ir–NCS), 2075 vs (CO), 875 m (CS), and 455 m (NCS bend). Both this N-bonded isomer and the S-bonded form show a strong infrared absorption at 310 cm^{-1} which is ascribed to the iridium–chlorine stretching frequency. The Raman spectra of both isomers also show a band at 310 cm^{-1}.

No isomerization occurred when the initial S-bonded form was recrystallized from a dichloromethane–tetrahydrofuran mixture; an analytically pure form of the S isomer was obtained in this manner.

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(1) M. Lassaigne, *Ann. Chim. Phys.*, **39**, 197 (1828).

(2) W. H. Baddley, *Inorg. Chim. Acta Rev.*, **2**, 7 (1968).

(3) K. Vrieze, J. P. Collman, C. T. Sears, and M. Kubota, *Inorg. Syn.*, **11**, 101 (1968).

(4) J. P. Collman and C. T. Sears, *Inorg. Chem.*, **7**, 27 (1968).

(5) D. A. Long and D. Steele, *Spectrochim. Acta*, **19**, 1731 (1963).

Table I. Final Atomic Parameters for $IrCl(CN)(NCS)(CO)(PPh_3)_2$

Atom	x	y	z	β_{11}[a] or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	0	0	0	0.00848 (11)	0.00895 (11)	0.01048 (13)	−0.00312 (7)	0.00132 (7)	0.00248 (8)
S	0.1787 (8)	0.3295 (7)	0.0273 (8)	0.0320 (13)	0.0190 (10)	0.0248 (12)	−0.0165 (10)	−0.0048 (10)	0.0097 (9)
P	−0.1671 (2)	0.1915 (2)	0.2202 (3)	0.0099 (4)	0.0089 (3)	0.0114 (4)	−0.0031 (3)	0.0020 (3)	0.0028 (3)
Cl	−0.1813 (9)	0.0655 (7)	−0.1692 (10)	0.0168 (12)	0.0110 (9)	0.0117 (12)	−0.0027 (7)	−0.0025 (11)	0.0044 (9)
$(C/N)_1$[b]	0.0759 (9)	0.1334 (10)	−0.0106 (9)	0.0110 (13)	0.0096 (13)	0.0108 (14)	−0.0021 (11)	0.0029 (10)	0.0034 (11)
$(C/N)_2$[b]	0.1151 (10)	0.2130 (10)	−0.0046 (10)	0.0159 (15)	0.0085 (13)	0.0169 (17)	−0.0075 (12)	0.0025 (12)	0.0041 (12)
C	0.154 (5)	−0.043 (4)	0.120 (5)	8.6 (1.5)					
O	0.220 (2)	−0.077 (2)	0.229 (3)	6.1 (7)					

Group	x_c[c]	y_c	z_c	δ	ϵ	η
R1	−0.3560 (5)	0.5017 (5)	0.2071 (5)	2.027 (9)	−1.974 (4)	−0.130 (9)
R2	−0.0165 (5)	0.2917 (4)	0.5275 (6)	−0.746 (5)	2.629 (4)	1.454 (5)
R3	−0.4013 (5)	0.0914 (5)	0.2765 (5)	0.888 (4)	2.591 (5)	3.075 (5)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; the isotropic B is in Å². [b] $(C/N)_1$ corresponds to the position of the C atom of the CN group or the N atom of the NCS group; $(C/N)_2$ corresponds to the N atom of the CN group or the C atom of the NCS group. [c] The group parameters have been defined in previous papers (*e.g.*, ref 6).

Anal. Found: C, 53.88; H, 3.33; N, 3.04. From a chloroform–methanol mixture the N-bonded form was obtained on recrystallization of the S form whereas a mixture of the S and N forms was obtained on recrystallization of the S form from dichloromethane–ethanol. Refluxing the S form in either benzene, tetrahydrofuran, or chloroform for 1 hr did not result in isomerization nor did heating a solid sample of the S form to 150° on a melting point block.

(B) Reaction of $S(CN)_2$ with $IrCl(CO)(PMePh_2)_2$ was carried out as described above for $IrCl(CO)(PPh_3)_2$. The initial material obtained was the S isomer, mp 135–138°. Ir (Nujol): 2145 w (CN of Ir–CN), 2119 m (CN of Ir–SCN), 2069 vs (CO), and 315 m (Ir–Cl). *Anal.* Calcd for $C_{29}H_{26}ClIrN_2OP_2S$: C, 47.00; H, 3.50; N, 3.78. Found: C, 46.47; H, 3.52; N, 3.56. The ^1H nmr spectrum in $CDCl_3$ includes a triplet at τ 7.50. Recrystallization of the complex from dichloromethane–methanol gave the N-bonded isomer, $IrCl(CN)(NCS)(CO)(PMePh_2)_2$, mp 95–98°. *Anal.* Found: C, 46.88; H, 3.50; N, 3.63. Ir (Nujol): 2147 w (CN of Ir–CN), 2115 vs (CN of Ir–NCS), 2086 vs (CO), 852 m (CS), and 315 m (Ir–Cl). The ^1H nmr spectrum in $CDCl_3$ includes a triplet at τ 7.55.

Crystallographic Details. The crystals, on the basis of extensive film work, belong to the triclinic system and have reduced cell dimensions a = 10.141 (5), b = 11.222 (5), c = 9.381 (6) Å; α = 112.21 (5), β = 95.02 (5), γ = 64.23 (4)°. These dimensions were obtained from the centering angles of 11 reflections, using Cu Kα_1 radiation (λ 1.54056 Å) and a Picker FACS-1 diffractometer. A density of 1.57 (3) g cm^{-3}, obtained by flotation in aqueous $ZnCl_2$, agrees reasonably well with that of 1.62 g cm^{-3} calculated for 1 molecule in a unit cell of volume 886.3 Å³. A crystal of approximate dimensions 0.3 × 0.2 × 0.2 mm was mounted in a general orientation on the diffractometer and intensity data were collected using Cu Kα radiation prefiltered through 1.0-mil Ni foil. Cu Kα, rather than Mo Kα radiation, was used because of the inherently better signal to noise ratio thus obtained with little increase in absorption. A scan rate of 1.0°/min in 2θ from 1.0° below the Kα_1 peak position to 1.0° above the Kα_2 peak position was used, and background counts of 10 sec were collected at each end of the scan range. The takeoff angle was 3.75°; the counter was positioned 32 cm from the crystal and was preceded by an aperture of dimensions 7 × 7 mm. A total of 1660 reflections was collected out to a 2θ limit of 85°. Included in this total are 1238 unique reflections and 422 corresponding Friedel pairs. These latter reflections were collected as an aid in the determination of the space group. Six standards were monitored throughout the course of the data collection, and their constancy indicated no electronic or crystal instabilities. The data were reduced to values of $F_o{}^2$ and $\sigma(F_o{}^2)$ in the usual way,[6] using a p of 0.03. All reflections collected had $I > 3\sigma(I)$, and it is clear that a considerably larger number of data could have been collected. However, the centric habit of the crystal made it likely that the space group is $P\bar{1}$ and that the molecule consequently has an imposed center of symmetry. Thus we anticipated that the reaction product resulted from oxidative addition, and not from the direct addition of $S(CN)_2$ to form a five-coordinate product. We therefore expected the product to be an octahedral Ir(III) complex, with disorder imposed on it in the solid state by imposition of the crystallographic center of symmetry, and we felt that the additional time involved in further data collection was not merited, at least if our suspicions were confirmed. Our expectations were further strengthened when an analysis of the agreement between Friedel pairs indicated an average deviation of 1.9%, well within that expected if Friedel's law was obeyed and the space group is $P\bar{1}$.

The structure was solved by routine procedures. Details on quantities minimized, definitions of R factors, sources of real and anomalous scattering factors, sources of programs, etc. have been given previously.[6] A least-squares calculation with Ir placed at the origin led to an R factor of 40% and to a difference Fourier synthesis on which the positions of all the other nonhydrogen atoms were found. At this point it was clear that the compound is $IrCl(CN)(NCS)(CO)(PPh_3)_2$, but whether or not the molecule is disordered as a consequence of crystallizing in space group $P\bar{1}$, rather than $P1$, could not be determined. An absorption correction was next applied to the data. The crystal is an octagonal prism, with end faces $\{100\}$ and the faces around the girdle being $\{001\}$, $\{01\bar{2}\}$, $\{01\bar{1}\}$, and $\{010\}$. The crystal had a computed volume of 0.00865 mm³ and the resultant transmission factors, based on a μ of 89.4 cm^{-1}, ranged from 0.16 to 0.35, and averaged 0.28. A reanalysis of the Friedel pairs now showed an average agreement of 1.6%. This fact, coupled with the ability to find the phenyl hydrogen atoms on a subsequent difference Fourier map, strongly suggests that the crystal indeed has imposed symmetry $\bar{1}$. All subsequent refinements were carried out in space group $P\bar{1}$. As a result of the imposed symmetry, it was assumed that the CN and NCS groups are disordered as are the Cl and CO portions of the molecule.

The model refined involved rigid groups for the phenyl rings, each C atom being assigned an individual isotropic thermal parameter, and complete anisotropic motion for the other nonhydrogen atoms except for the C and O atom of the half CO group which were assigned variable isotropic thermal parameters. This refinement converged to an R of 4.8%. At this point the contributions to F_c of the phenyl hydrogen atoms were added in a fixed manner and the refinement was continued to convergence. The final values of R and R_w are 3.2 and 4.5%, respectively, and the error in an observation of unit weight is 2.76 e for the 96 variables and 1238 observations. A final difference Fourier synthesis showed a maximum density of 0.86 e/Å³, about 10% of the height of a C atom in this structure. An error analysis of $\Sigma w \cdot (|F_o| - |F_c|)^2$ showed no unusual trends. Final atomic parameters are given in Table I. The fractional coordinates of the C atoms of the phenyl group are given in Table II. Values of $10|F_o|$ and $10|F_c|$ (in electrons) are given in Table III.[7]

Analyses and Instrumentation. Elemental analyses were carried out by Mr. R. Seab, Department of Chemistry, Louisiana State University, and Galbraith Laboratories, Knoxville, Tenn. Infrared spectra in the 4000–200-cm^{-1} region were measured in Nujol on a Perkin-Elmer 621 grating infrared spectrophotometer and Raman spectra were obtained with powdered samples on a JEOL JRS-S1 laser Raman spectrophotometer with an argon laser. The ^1H nmr spectra were measured in $CDCl_3$ on a Perkin-Elmer R12B spectrometer at 60 MHz.

Results and Discussion

On the basis of an X-ray structure determination and subsequent infrared studies of the initial and recrystallized products, we have found that $S(CN)_2$ acts as a pseudohalogen in its reactions with $IrCl(CO)L_2$ ($L = PPh_3, PMePh_2$) to form through oxidative addition the six-coordinate complexes chlorocyano(thiocyanato)-*S*-carbonylbis(triphenylphosphine)iridium(III) and the methyldiphenylphosphine analog. Re-

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(6) See, for example, D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 10, 1479 (1971).

Table II. Positional and Thermal Parameters for the Ring Carbon Atoms

Atom	x	y	z	B, Å^2
R1C1	−0.2729 (6)	0.3653 (5)	0.2072 (7)	3.6 (2)
R1C2	−0.2678 (7)	0.3920 (6)	0.0751 (6)	5.4 (2)
R1C3	−0.3509 (8)	0.5283 (7)	0.0750 (7)	7.0 (3)
R1C4	−0.4391 (7)	0.6381 (5)	0.2070 (8)	6.4 (3)
R1C5	−0.4442 (7)	0.6114 (6)	0.3391 (7)	6.3 (3)
R1C6	−0.3611 (7)	0.4750 (7)	0.3392 (6)	5.3 (2)
R2C1	−0.0802 (7)	0.2405 (7)	0.3951 (6)	3.8 (2)
R2C2	−0.1267 (7)	0.2521 (8)	0.5369 (8)	6.0 (2)
R2C3	−0.0631 (8)	0.3034 (8)	0.6693 (6)	8.1 (3)
R2C4	0.0471 (8)	0.3430 (8)	0.6600 (7)	7.3 (3)
R2C5	0.0936 (7)	0.3314 (8)	0.5182 (8)	6.3 (3)
R2C6	0.0300 (7)	0.2802 (7)	0.3858 (6)	5.0 (2)
R3C1	−0.3009 (7)	0.1391 (7)	0.2577 (8)	4.3 (2)
R3C2	−0.2636 (6)	0.0434 (7)	0.3311 (8)	5.7 (2)
R3C3	−0.3640 (8)	−0.0043 (7)	0.3500 (8)	7.0 (3)
R3C4	−0.5018 (7)	0.0437 (8)	0.2954 (9)	7.2 (3)
R3C5	−0.5391 (6)	0.1395 (8)	0.2219 (9)	7.3 (3)
R3C6	−0.4387 (7)	0.1872 (7)	0.2031 (8)	5.7 (2)

Table IV. Bond Distances (Å) and Angles (deg) in IrCl(CN)(NCS)(CO)(PPh$_3$)$_2$

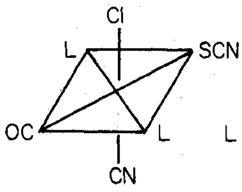
Ir-P	2.418 (3)	P-Ir-P	180
Ir-Cl	2.37 (1)	P-Ir-Cl	89.7 (2), 90.3 (2)
Ir-C	1.84 (4)	P-Ir-(C/N)$_1$	89.0 (2), 91.0 (2)
Ir-(C/N)$_1$	1.99 (1)	P-Ir-C	92 (1), 88 (1)
(C/N)$_2$-S	1.62 (1)	Cl-Ir-(C/N)$_1$	91.1 (3), 88.9 (3)
(C/N)$_1$-(C/N)$_2$	1.11 (1)	Cl-Ir-C	173 (1)
C-O	1.27 (4)	C-Ir-(C/N)$_1$	82 (1), 98 (1)
H···H(min)	2.40	Ir-(C/N)$_1$-(C/N)$_2$	175 (1)
		(C/N)$_1$-(C/N)$_2$-S	172 (1)
		Ir-C-O	156 (3)

crystallization of IrCl(CN)(SCN)(CO)(PPh$_3$)$_2$ at room temperature from dichloromethane-methanol or chloroform-methanol mixtures is accompanied by isomerization to the N-bonded form, but no isomerization is noted when the compound is recrystallized from dichloromethane-tetrahydrofuran. Dissolution of the S isomer in either benzene, chloroform, or tetrahydrofuran, followed by refluxing of the solutions for 1 hr, did not lead to linkage isomerization. Also, a solid sample of the S isomer was heated to 150° without any linkage isomerization occurring. It would be expected that the N isomer would be the thermodynamically stable form in a tervalent iridium complex containing π-acid ligands, and the failure of the S isomer to isomerize under the thermal conditions mentioned above is consistent with the great kinetic inertness of Ir(III) complexes. The ease with which isomerization occurs when methanol is present is unusual, and the isomerization behavior of these and related complexes prepared from the reaction of S(CN)$_2$ with noble metal substrates is being further studied.

The compound IrCl(CN)(NCS)(CO)(PPh$_3$)$_2$ is essentially octahedral as the distances and angles given in Table IV indicate. Because of the disorder imposed by the crystallographic center of symmetry the errors on most of the bond distances are larger than would be expected in view of the excellence of the agreement between $|F_o|$ and $|F_c|$. In particular, the refinement of the half carbonyl group in the presence of the half Cl atom is difficult, and this probably accounts for the apparent Ir-C-O angle of 156 (3)°. With the exception of this bond angle, the other molecular dimensions given in Table IV are those expected for an octahedral Ir(III) complex.

Although the overall geometry of the complex has been established, it is important to note that we have refined a particular model, namely, that with CN trans to NCS and CO trans to Cl. The nature of the disorder and the relative scattering powers of the various atoms are such that we cannot eliminate the possibility that the structure is in fact a second isomer with CO trans to NCS and CN trans to Cl. This second isomer seems less likely, however, on the basis of the far-infrared data (*vide infra*).

Nine geometrical isomers are possible for complexes of the type Mabcde$_2$ such as these new linkage isomers are. Structures for the nine *S*-thiocyanato isomers are given by **1-9** (L = PPh$_3$, PMePh$_2$).



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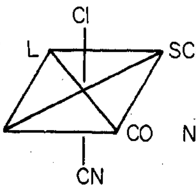

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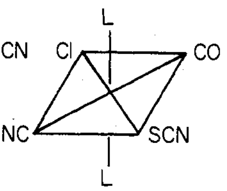

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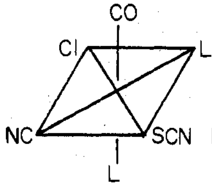

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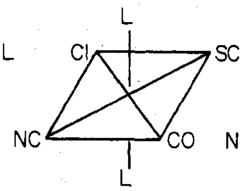

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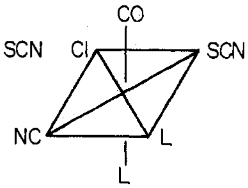

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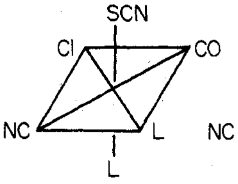

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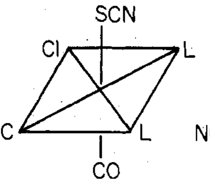

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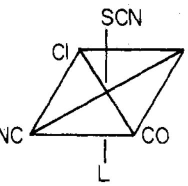

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The structure of the compound recrystallized from CH$_2$Cl$_2$-methanol, the N-bonded isomer, has been found from the X-ray results to be analogous to **5**. Formally, a trans addition of the addend has occurred and the tertiary phosphines have retained the mutually trans configuration as exists in IrCl(CO)(PPh$_3$)$_2$. In view of the current interest in the mechanism of oxidative addition reactions,[8] with particular reference to the variety of stereochemical modes of addition that have been reported, it is of interest to know the geometrical disposition of the six ligands around iridium in the initially isolated complex, *i.e.*, presumably the kinetic product. Several of the nine possible isomers may be eliminated on the basis of laser Raman and infrared spectral data in the 200-500-cm^{-1} range. Iridium-chlorine stretching frequencies are quite useful in assigning stereochemistries because they are sensitive to the type of ligands trans to them but very little affected by the nature of the cis ligands.[9,10] For example, with respect to the sensitivity to the trans ligand, $\nu_{\text{Ir-Cl}}$ values in the range 320-303 cm^{-1} have been reported for chloride trans to chloride and values in the ranges 278-262 and

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(7) Table III, a listing of structure amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-229.

(8) See R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970), and references contained therein.

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249-246 cm^{-1} are known for iridium(III) complexes having chloride, trans phosphines, and hydrides, respectively. The general order of decreasing $\nu_{\text{Ir-Cl}}$ values according to the nature of the trans ligand has been given as follows:[10] $Cl > Br > I \sim CO > CH_3 \sim PR_3 \sim AsR_3 > H$. Both $IrCl(CN)(SCN)(CO)(PPh_3)_2$ and $IrCl(CN)(NCS)(CO)(PPh_3)_2$ show strong absorptions at 310 cm^{-1} in both their infrared and Raman spectra which are assigned as $\nu_{\text{Ir-Cl}}$. Structures **6-8** can be eliminated for $Ir(CN)(SCN)(CO)(PPh_3)_2$ because with Cl trans to triphenylphosphine a $\nu_{\text{Ir-Cl}}$ at *ca.* 260-280 cm^{-1} would be expected. It is also reasonable to suppose that a CN and an H would have similar effect on a trans Ir-Cl bond, and hence structures **1** and **2** with Cl trans to CN may be eliminated. We are not aware of data for $\nu_{\text{Ir-Cl}}$ values with chloride trans to *S*-thiocyanate, but do know that at least 20 Ir(III) complexes with chloride trans to carbon monoxide[9-12] exhibit iridium-chlorine stretching frequencies in the narrow 300-310-cm^{-1} range. It seems likely then that the initially isolated *S*-thiocyanate linkage isomer has either the structure **5** or **9**, which corresponds to either a trans or a cis mode of addition, respectively.

The initial product of the reaction of $S(CN)_2$ with the methyldiphenylphosphine complex $IrCl(CO)(PMePh_2)_2$, which also is the S-bonded linkage isomer, has mutually trans phosphine groups as deduced from the nmr spectrum which shows a triplet methyl signal that must be a consequence of virtual coupling of two mutually trans phosphorus atoms.

Therefore, $IrCl(CN)(SCN)(CO)(PMePh_2)_2$ has either structure **1**, **3**, or **5**. Structure **5** is the preferred structure since the far-infrared spectrum shows a medium-strength band at 315 cm^{-1} which is assumed to be the iridium-chlorine stretching frequency, and this value is consistent as discussed above with Cl being trans to CO, but is less likely for Cl being trans to CN as in structures **1** and **3**. While it does not follow that the triphenylphosphine complexes will necessarily have the same ligand dispositions as the methyldiphenylphosphine complexes, such nevertheless seems more likely and therefore we believe that $IrCl(CN)(SCN)(CO)(PPh_3)_2$ also has structure **5**, *i.e.*, a structure derived from a trans addition process.

In summary, it seems likely that $S(CN)_2$ reacts with $IrCl(CO)L_2$ ($L = PPh_3, PMePh_2$) *via* a trans mode of oxidative addition to give as the initial products the S isomers and that transformation to the N isomers is facilitated in the recrystallization process when methanol is present. It has been noted previously[8] that trans addition is consistent with orbital symmetry predictions. Finally, the fact that the use of sulfur dicyanide as a thiocyanation reagent in these reactions gives the S-bonded isomers as kinetic products is of some synthetic utility. For example, reaction of $Ir(NCS)(CO)(PPh_3)_2$, which contains N-bonded thiocyanate, with $S(CN)_2$ has provided a means of preparing the novel compound $Ir(NCS)(SCN)(CN)(CO)(PPh_3)_2$ which contains both N-bonded and S-bonded thiocyanate groups.[13]

Registry No. $IrCl(CO)(PPh_3)_2$, 15318-31-7; $IrCl(CO)(PMePh_2)_2$, 15318-32-8; $S(CN)_2$, 627-52-1; $IrCl(CN)(NCS)(CO)(PPh_3)_2$, 36863-03-3; $IrCl(CN)(NCS)(CO)(PMePh_2)_2$, 36863-04-4; $IrCl(CN)(SCN)(CO)(PPh_3)_2$, 36863-05-5; $IrCl(CN)(SCN)(CO)(PMePh_2)_2$, 36863-06-6.

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Transition Metal Hydroborate Complexes. V.[1] Crystal Structure of Tetrahydroboratobis(cyclopentadienyl)titanium(III)

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The structure of $(h^5\text{-}C_5H_5)_2Ti(BH_4)$ has been determined in a single-crystal X-ray diffraction study. The compound crystallizes in space group *Fm*2*m* of the orthorhombic system with $a = 9.336$ (3), $b = 7.991$ (3), $c = 13.467$ (9) Å, and $\rho_{\text{calcd}} = 1.27$ g/cm^3 for $Z = 4$. From 249 independent observed reflections collected by diffractometer, the structure was solved by the usual Patterson and Fourier synthesis methods. Least-squares refinement of all atoms except the cyclopentadienyl ring protons converged at values for $R_1 = 0.030$ and $R_2 = 0.038$. The molecule has crystallographically required *m*2*m* site symmetry with the tetrahydroborate group coordinated to the titanium atom through two bridging hydrogen atoms. The coordination geometry of the titanium atom is quasitetrahedral with an average (ring centroid)-Ti-(ring centroid) angle of 136.7° and a H-Ti-H angle of 60 ± 5°. The refined Ti-H, Ti-B, and average Ti-C distances are 1.75 (8), 2.37 (1), and 2.35 (4) Å, respectively. The carbon atoms of the cyclopentadienyl groups are disordered, the average Ti-(ring centroid) distance being 2.03 Å.

Introduction

The synthesis of tetrahydroboratobis(cyclopentadienyl)titanium(III) was reported by Noth and Hartwimmer,[2] who suggested that the borohydride group contributes two hydrogen atoms to the coordination sphere of the titanium atom. Several discussions[2-5] of the infrared spectrum of this complex revealed the need for definitive structural information. As part of a continuing study of the chemical and geometric

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