effect of lengthening the molecule along the C_3 axis, as evidenced by nonbonded S···S distances. The average S···S distance within a triangular face originating from one terminal cobalt atom is 3.01 (2) Å, while the average S···S cis distance between sulfur atoms on different triangular faces is 3.38 (3) Å. These distances would be equal in a perfect octahedron. In the terminal cobalt(III) coordination sphere, the S–Co$_t$–N "bite" angles are normal, averaging 88.3 (2)°; cf. 88.8 (2)° in $[(en)_2CoL]^{2+}$.[21] However, all S–Co$_t$–S angles are acute (average 84.5 (8)°) and all N–Co$_t$–N angles are obtuse (average 94.6 (6)°), indicating a compression of the S_3 face and concomitant expansion of the N_3 face. This permits a slightly greater Co···Co separation while maintaining optimal Co–S distances. Both of the distortions just described argue against any metal–metal bonding and indicate some repulsion at a Co···Co distance of 2.857 (1) Å. Distortions due to internuclear repulsions have beeen noted for another triply bridged Co(III) binuclear complex, $[(Co(C_8H_{18}N_2S_2))_2NO]^+$, where the Co···Co separation is 2.770 (2) Å.[22]

The sulfur atoms are nearly equally bound to the terminal and central cobalt atoms. Bond distances average 2.238 (7) Å for Co$_t$–S and 2.262 (11) Å for Co$_c$–S. The difference between these two values is small (0.024 (13) Å) and is at the 2σ level of significance, but it is noteworthy that every Co$_c$–S distance is larger than every Co$_t$–S distance (of 12 independent observations for each distance in this structure). Stated another way, the *fac*-S_3 plane is 0.037 Å (average) closer to Co$_t$ than Co$_c$ (1.410 vs. 1.447 Å).

A substantial and fascinating network of hydrogen bonds exists within the lattice. Every amine hydrogen atom is clearly involved in a hydrogen bond to either a chloride or a sulfate oxygen atom. Each sulfate oxygen atom participates in three separate hydrogen bonds, utilizing every available free electron pair in this anion. The average H···O(sulfate) distance is 1.91 (1) Å for 12 entries averaged. The pattern of hydrogen bonding to chloride is most interesting in light of the apparent disorder in the chloride distribution. The atom Cl1, which possesses a site occupancy factor of 1.0 and shows no disorder, is associated with four distinct ammine hydrogen atoms in hydrogen bonding. In contrast, the remaining four chloride sites (Cl2–5) have been assigned occupancy factors of 0.75 and these sites engage the remaining ammine hydrogen atom in bonds at two bonds per site. The requirement for hydrogen bonding throughout the lattice apparently causes three chloride ions to be randomly distributed among these four similar lattice sites. Among the 12 hydrogen bonds to chloride, the average Cl···H distance is 2.31 (6) Å.

The stoichiometry of the synthesis of $[Co(CoL_3)_2]^{3+}$ from CoL_3 requires the generation of the central cobalt atom from excess CoL_3 at some point during the reaction sequence. The central cobalt atom is most reasonably derived from labile cobalt(II) since it is known[8] that under aerobic conditions mixtures of cobalt(II) and CoL_3 readily yield $[Co(CoL_3)_2]^{3+}$. Thus, the major mechanistic point to be resolved in the synthesis of $[Co(CoL_3)_2]^{3+}$ from CoL_3 concerns the origin of Co(II). How does HNO_3 oxidation of CoL_3 yield the labile Co(II) center necessary for the construction of $[Co(CoL_3)_2]^{3+}$?

Oxidation of coordinated thiols can occur by one of several pathways, internal electron transfer (IET) being a particularly intriguing and relatively uncommon case.[4] When a thiol is coordinated to a potentially oxidizing center such as Co(III) or Ru(III), 1-equiv *oxidation* of the thiol can lead to net *reduction* of the metal center. This occurs by IET, the metal center providing the second equivalent of oxidizing power necessary to complete the net 2-equiv oxidation of the coordinated thiol.[4] Thus, the observation of $[Co(CoL_3)_2]^{3+}$ as a product strongly implies that the HNO_3 oxidation of CoL_3 proceeds via IET. The major steps of the net process are summarized as

$$CoL_3 + HNO_3 + H^+ \rightarrow CoL_2(NH_2CH_2CH_2S\cdot)^+ + NO_2 + H_2O$$

$$H^+ + CoL_2(NH_2CH_2CH_2S\cdot)^+ \xrightarrow{IET} Co(II) + L + (NH_2CH_2CH_2S-)_2$$

$$Co(II) + 2CoL_3 \rightarrow Co^{II}(CoL_3)_2^{2+}$$

$$Co^{II}(CoL_3)_2^{2+} + HNO_3 + H^+ \rightarrow Co^{III}(CoL_3)_2^{3+} + NO_2 + H_2O$$

Oxidants other than HNO_3 (e.g. Ce(IV) and V(V)) also convert CoL_3 to $[Co(CoL_3)_2]^{3+}$,[11] and even boiling CoL_3 in aerobic aqueous solution affords a small yield of the trimeric product. It appears that $[Co(CoL_3)_2]^{3+}$ is the stable end product of the reactions of several derivatives of the CoL_3 core.[11]

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Supplementary Material Available: Listings of interatomic distances (Table A), bond angles (Table B), hydrogen atom positional parameters (Table C), thermal parameters (Table D), and observed and calculated structure factors (Table E) (53 pages). Ordering information is given on any current masthead page.

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Cationic Iridium(I) and Dihydridoiridium(III) Complexes of Unsaturated Nitriles and Their Catalytic Activities

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We have investigated the catalytic hydrogenation and polymerization of the unsaturated nitrile $CH_2{=}CHCN$ with $M(ClO_4)(CO)(PPh_3)_2$ (M = Rh, Ir)[1] in which the ClO_4 group is so labile[2] that it is readily replaced by $CH_2{=}CHCN$ to give the cationic complex $[M(CH_2{=}CHCN)(CO)(PPh_3)_2]ClO_4$.[1]

We now report the synthesis of new cationic iridium(I) and dihydridoiridium(III) complexes of unsaturated nitriles, $[IrL(CO)(PPh_3)_2]ClO_4$ (**1**) and $[Ir(H)_2L(CO)(PPh_3)_2]ClO_4$ (**2**) (L = *cis*-crotononitrile (*cis*-$CH_3CH{=}CHCN$), *trans*-crotononitrile (*trans*-$CH_3CH{=}CHCN$), allyl cyanide ($CH_2{=}CHCH_2CN$)), and their catalytic activities for hydrogenation and isomerization of L. Complexes **1** and **2** have been prepared according to eq 1 and 2.

$$Ir(ClO_4)(CO)(PPh_3)_2 + L \rightarrow \underset{\mathbf{1}}{[IrL(CO)(PPh_3)_2]ClO_4} \quad (1)$$

$$\mathbf{1} + H_2 \rightarrow \underset{\mathbf{2}}{[Ir(H)_2L(CO)(PPh_3)_2]ClO_4} \quad (2)$$

L = (**a**) *cis*-$CH_3CH{=}CHCN$, (**b**) *trans*-$CH_3CH{=}CHCN$, (**c**) $CH_2{=}CHCH_2CN$

Spectral Data and Structures

Infrared spectral data for **1** and **2** are given in Table I. These clearly suggest that the unsaturated nitriles are coordinated to iridium through the nitrogen, rather than through the π system of the nitrile group. It is well-known that ν_{CN} of a nitrile increases upon coordination through the nitrogen[3,4] and decreases upon

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Table I. Infrared (Nujol), Electronic (CH_2Cl_2), and ^1H NMR ($CDCl_3$) Spectral Data for $[IrL(CO)(PPh_3)_2]ClO_4$ (**1**) and $[Ir(H)_2L(CO)(PPh_3)_2]ClO_4$ (**2**) (L = (a) *cis*-$CH_3CH{=}CHCN$, (b) *trans*-$CH_3CH{=}CHCN$, (c) $CH_2{=}CHCH_2CN$)

	IR abs, cm^{-1}				
compd	ν_{CN}[a]	$\nu_{C=C}$[b]	ν_{CO}[c]	ν_{Ir-H}[d]	ρ_{Ir-H}[e]
cis-$CH_3CH{=}CHCN$	2224	1628			
trans-$CH_3CH{=}CHCN$	2227	1638			
$CH_2{=}CHCH_2CN$	2251	1646			
1a	2263	1617	2021		
1b	2273	1626	2020		
1c	2303	1644	2015		
2a	2273	1620	2037	2168, 2234	885
2b	2281	1630	2035	2137, 2234	882, 863
2c	2297	1631	2033	2138, 2233	876, 857

compd	electronic abs,[f] nm
1a	471 (860), 410 (3390), 349 (4400)
1b	473 (850), 412 (3220), 349 (4190)
1c	475 (890), 414 (4060), 350 (4440)

compd	^1H NMR,[g] ppm
cis-$CH_3CH{=}CHCN$	1.90 (dd, CH_3), 5.18 (dq, CH_3C*H*), 6.35 (dq, CHCN)
trans-$CH_3CH{=}CHCN$	1.81 (dd, CH_3), 5.25 (dq, CH_3C*H*), 6.60 (dq, CHCN)
$CH_2{=}CHCH_2CN$	2.92 (m, CH_2CN), 5.20 (m, C*H*$_2$=C*H*)
1a	1.14 (dd, CH_3), 5.05 (dq, CH_3C*H*), 6.69 (dq, CHCN)
1b	1.77 (dd, CH_3), 4.95 (dq, CH_3C*H*), 5.88 (dq, CHCN)
1c	3.00 (m, CH_2CN), 4.90 (m, C*H*$_2$=CH)
2a	1.28 (dd, CH_3), 5.17 (dq, CH_3C*H*), 6.56 (dq, CHCN), −8.26 (dt, Ir H_A),[h] −18.0 (dt, Ir H_B)[i]
2b	1.80 (dd, CH_3), 5.10 (dq, CH_3C*H*), 6.02 (dq, CHCN), −8.37 (dt, Ir H_A),[j] −18.2 (dt, H_B)[k]
2c	2.99 (m, CH_2CN), 4.91 (m, C*H*$_2$=C*H*), −8.40 (dt, Ir H_A),[l] −18.2 (dt, Ir H_B)[m]

[a] Weak. [b] Weak–medium. [c] Very strong. [d] Medium–strong. [e] Medium. [f] Under nitrogen at 25 °C. Extinction coefficients are given in parentheses. [g] Under nitrogen at 25 °C at 60 MHz for **1** and 80 MHz for **2**. Chemical shifts are relative to Me_4Si, and coupling constants are in Hertz. A multiplet due to phenyl protons appears at 7.0–7.5 ppm for all **1** and **2**. [h] $J(P, H_A) = 16.5$, $J(H_A,H_B) = 3.9$ Hz. [i] $J(P,H_B) = 13.6$, $J(H_A,H_B) = 3.9$ Hz. [j] $J(P,H_A) = 16.2$, $J(H_A,H_B) = 4.0$ Hz. [k] $J(P,H_B) = 13.6$, $J(H_A,H_B) = 4.0$ Hz. [l] $J(P,H_A) = 16.3$, $J(H_A,H_B) = 3.8$ Hz. [m] $J(P,H_B) = 13.7$, $J(H_A,H_B) = 3.8$ Hz.

coordination through the π system of the nitrile group.[4,5] A slight decrease in $\nu_{C=C}$ of L upon coordination (Table I) also supports the nitrogen-bonded L in **1** and **2**. A strong and broad band at ca. 1100 cm^{-1} observed for all complexes **1** and **2** is attributable to the tetrahedral (C_{4v}) anion ClO_4^-,[2a] which supports that **1** and **2** are 1:1 electrolytes as confirmed by the conductance measurements (see Experimental Section).

Electronic absorption spectra of **1** show three bands in the visible region (Table I), while no absorption bands are observed for **2**. These results are in agreement with spectral data previously reported for the related four-coordinated planar iridium(I)[6] and six-coordinated dihydridoiridium(III) complexes.[7]

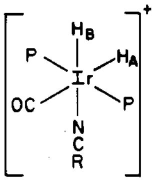
The chemical shifts of the protons of the unsaturated nitriles in **1** and **2** are given in Table I. These shifts are only slightly different from those of the free unsaturated nitriles. Practically no changes in coupling constants have been observed for the unsaturated nitriles upon coordination to $Ir(CO)(PPh_3)_2$ and $Ir(H)_2(CO)(PPh_3)_2$.

Table II. Hydrogenation and Isomerization of Unsaturated Nitriles (L) with $[IrL(CO)(PPh_3)_2]ClO_4$ (**1**) and $[Ir(H)_2L(CO)(PPh_3)_2]ClO_4$ (**2**) (L = (a) *cis*-$CH_3CH{=}CHCN$, (b) *trans*-$CH_3CH{=}CHCN$, (c) $CH_2{=}CHCH_2CN$) [100 °C for 24 h under $P_{N_2} = 1$ atm; 0.1 mmol of Ir Complex Used in All Experiments]

	amt of products, mmol			
reaction syst	*cis*-$CH_4CH{=}CHCN$	*trans*-$CH_3CH{=}CHCN$	$CH_2{=}CHCH_2CN$	$CH_3CH_2CH_2CN$
2a, H_2[a]	27			10
2b, H_2[b]		27		10
2c, H_2[c]	3	3	5	26
2a, N_2[a]	37			
2b, N_2[b]		37		
2c, N_2[c]	11	11	15	
1a, N_2[a]	37			
1b, N_2[b]		37		
1c, N_2[c]	7	7	23	
H_2 or N_2[a,d]	37			
H_2 or N_2[b,d]		37		
H_2 or N_2[c,d]	1	1	35	

[a] In *cis*-$CH_3CH{=}CHCN$ (3.0 mL, 37 mmol). [b] In *trans*-$CH_3CH{=}CHCN$ (3.0 mL, 37 mmol). [c] In $CH_2{=}CHCH_2CN$ (3.0 mL, 37 mmol). [d] In the absence of Ir complex.

The coupling constants between hydride and trans phosphorus are relatively large (53–154 Hz) compared with those between hydride and cis phosphorus (10–20 Hz).[8] The relatively small coupling constants (13.6–16.5 Hz) observed for **2** (Table I) indicate that both hydrides are cis to both phosphorus atoms. The large difference in the chemical shifts of the hydrides observed for **2** implies that the two hydrides are trans to different groups, respectively. Accordingly, the two hydrides are cis to each other and trans to CO and nitrogen (unsaturated nitrile), respectively. For the series of related hydridoiridium(III) complexes, it is well-known that the chemical shift of a hydride depends on the trans donor atom.[8,9] The shielding at the hydride trans to nitrogen (CH_3CN) is higher (−17 to −20 ppm relative to Me_4Si)[8d,9a] than that at the hydride trans to carbon (CO, $C_6H_{11}NC$) (−7 to −11 ppm).[8c,9b] Accordingly, the signals at ca. −8 ppm observed for **2** (Table I) are due to the hydride (H_A) trans to CO and those at ca. −18 ppm to the hydride (H_B) trans to the nitrogen of the unsaturated nitrile. See I.



I

P = PPh_3; R = *cis*-$CH_3CH{=}CH-$, *trans*-$CH_3CH{=}CH-$, $CH_2{=}CHCH_2-$

Catalytic Activities

Complexes **1** and **2** may play important roles in the catalytic hydrogenation and isomerization of the corresponding L. It has been found that **2** catalyzes the hydrogenation of L to produce butyronitrile but no amines and imines. The hydrogenation of an unsaturated nitrile ($CH_2{=}CHCN$) to the saturated nitrile by

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a nitrogen-bonded unsaturated nitrile complex ($RuCl_2(CH_2{=}CHCN)_4$) has been previously reported, where the rearrangement of the nitrogen-bonded $CH_2{=}CHCN$ complex to the olefinic π-system-bonded complex has been suggested as the initial step in the catalytic cycle.[10] Hydrogenation rates are given in Table II.

The hydrogenation of $CH_2{=}CHCH_2CN$ is seen to be faster than that of each $CH_3CH{=}CHCN$ isomer while no difference in the rates of hydrogenation of *cis*- and *trans*-$CH_3CH{=}CHCN$ is observed. It is noticed that **1c** and **2c** in $CH_2{=}CHCH_2CN$ produce a 1:1 mixture of *cis*- and *trans*-$CH_3CH{=}CHCN$ while **1a** (or **1b**) and **2a** (or **2b**) in *cis*-$CH_3CH{=}CHCN$ (or *trans*-$CH_3CH{=}CHCN$) do not produce $CH_2{=}CHCH_2CN$ and *trans*-$CH_3CH{=}CHCN$ (or *cis*-$CH_3CH{=}CHCN$) at all.

The isomerization of $CH_2{=}CHCH_2CN$ to $CH_3CH{=}CHCN$ by **1c** in the absence of hydrogen seems to be unusual. One could find, however, some related reactions; e.g., the dimerization of $CH_2{=}CHCN$ to $NCCH_2CH_2CH{=}CHCN$ is catalyzed by $RuCl_2(PPh_3)_3$ in the absence of hydrogen, presumably t hrough the hydrido β-cyanovinyl complex, $RuH({-}CH{=}CHCN)$.[11]

Experimental Section

Materials. $Ir(ClO_4)(CO)(PPh_3)_2$ was prepared according to the literature method.[2a] All solvents were dried and distilled before use. *cis*- and *trans*-$CH_3CH{=}CHCN$ were separated from a mixture (cis/trans = ca. 3.0, Eastman) by preparative GC using a Carbowax 20M column. $CH_2{=}CHCH_2CN$ (Aldrich) was used as purchased.

Physical Measurements. Infrared and electronic absorption spectra were measured on Shimadzu IR-440 and Shimadzu UV-240. Proton NMR spectra were obtained on Varian 60-MHz (Model EM-360A) (for **1**) and Bruker WP 80-MHz FT-NMR spectrometers (for **2**). Conductance measurements were obtained with Wiss-Tech conductivity meter LBR for the corresponding unsaturated nitrile at 25 °C under nitrogen. Elemental analyses were carried out by Spang Microanalytical Laboratory, Eagle Habor, MI.

Preparation. Standard vacuum line and Schlenk-type glassware were used in handling metal complexes. The complexes **1a–c** are not soluble in nonpolar solvents (hexane, benzene) and are soluble in polar solvents (chloroform, dichloromethane) while the complexes **2a–c** are only slightly soluble in polar solvents (chloroform, dichloromethane). All complexes of **1** and **2** are stable in the solid state in air and in solution under nitrogen at 25 °C.

[Ir(*cis*-$CH_3CH{=}CHCN$)(CO)(PPh_3)$_2$]ClO_4 (1a). Addition of *cis*-$CH_3CH{=}CHCN$ (1 drop, ca. 0.3 mmol) into the benzene solution (10 mL) of $Ir(ClO_4)(CO)(PPh_3)_2$ (0.12 g, 0.15 mmol) under nitrogen at 25 °C immediately resulted in precipitation of light yellow microcrystals that were collected by filtration, washed with benzene (10 mL), and dried under vacuum; yield 0.12 g (90% based on **1a**). Anal. Calcd for $IrC_{41}H_{35}O_5NP_2Cl$: C, 54.04; H, 3.87; N, 1.54; Cl, 3.90; P, 6.80. Found: C, 54.29; H, 3.95; N, 1.41; Cl, 3.95; P, 6.71. $\Lambda_M = 110\ \Omega^{-1}\ cm^2\ mol^{-1}$ ([Ir] = 5.0×10^{-5} M in *cis*-$CH_3CH{=}CHCN$).

[Ir(*trans*-$CH_3CH{=}CHCN$)(CO)(PPh_3)$_2$]ClO_4 (1b) and [Ir($CH_2{=}CHCH_2CN$)(CO)(PPh_3)$_2$]ClO_4 (1c). These compounds were prepared in the same manner described for **1a**, gave satisfactory elemental analyses, and showed molar conductance values close to that of **1a**.

[Ir(H)$_2$(*cis*-$CH_3CH{=}CHCN$)(CO)(PPh_3)$_2$]ClO_4 (2a). A 10-mL CH_2Cl_2 solution of **1a** (0.1 g, 0.11 mmol) was stirred under the atmospheric pressure of hydrogen at 25 °C. The yellow solution became a white-beige suspension within 30 min. Addition of hexane (25 mL) precipitated more white-beige solid that was collected by filtration, washed with benzene (10 mL), and dried under vacuum; yield 0.99 g (90% based on **2a**). Anal. Calcd for $IrC_{41}H_{37}O_5NP_2Cl$: C, 53.93; H, 4.08; N, 1.53; Cl, 3.88; P, 6.78. Found: C, 54.10; H, 4.12; N, 1.49; Cl, 3.98; P, 6.69. $\Lambda_M = 115\ \Omega^{-1}\ cm^2\ mol^{-1}$ ([Ir] = 5.0×10^{-5} M in *cis*-$CH_3CH{=}CHCN$).

[Ir(H)$_2$(*trans*-$CH_3CH{=}CHCN$)(CO)(PPh_3)$_2$]ClO_4 (2b) and [Ir(H)$_2$($CH_2{=}CHCH_2CN$)(PPh_3)$_2$]ClO_4 (2c). These compounds were prepared in the same manner as described for **2a**, gave satisfactory elemental analyses, and showed molar conductance values close to those of **1a** and **2a**.

Catalytic Reactions. In all experiments, the following procedure was used with 0.1 mmol (0.91 g) of **1** (or **2**) and 37 mmol (3.0 mL) of the corresponding unsaturated nitrile.

Reactions under Hydrogen. The iridium complex in the corresponding unsaturated nitrile was placed in a bomb reactor (Parr 1341; volume 360 mL) that was then immediately flushed with hydrogen before the cap of the reactor was applied. Hydrogen was introduced into the reactor until the pressure reached 3 atm at 25 °C. The reactor was then placed in an oven maintained at 100 °C for 24 h. The hydrogen pressure in the reactor at 100 °C should initially be higher than 3 atm but may be lower than 3 atm at the later stage. The reactor was cooled to 25 °C at which temperature no catalytic reactions occur. The reactor was opened under nitrogen, and the solution was analyzed by ^1H NMR. Addition of hexane into the reactor resulted in precipitation of a beige-white solid that was identified as **2** (85% yield).

Reactions under Nitrogen. These experiments were carried out in the same manner described above except that the pressure (P_{N_2}) in the reactor at room temperature was 1 atm.

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Registry No. **1a**, 95045-47-9; **1b**, 95120-09-5; **1c**, 95069-29-7; **2a**, 95045-49-1; **2b**, 95120-11-9; **2c**, 95045-51-5; $Ir(ClO_4)(CO)(PPh_3)_2$, 55821-24-4; *trans*-$CH_3CH{=}CHCN$, 627-26-9; *cis*-$CH_3CH{=}CHCN$, 1190-76-7; $CH_2{=}CHCH_2CN$, 109-75-1.

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