Structure of (Cyano(dicyanomethyl)keteniminato)carbonyl-(tetracyanoethylene)bis(triphenylphosphine)iridium, Ir(C₆N₄H)(CO)((CN)₂C=C(CN)₂)(P(C₆H₅)₃)₂·½C₆H₆

$$\text{Ir}(C_6N_4H)(CO)((CN)_2C{=}C(CN)_2)(P(C_6H_5)_3)_2\cdot{}^1\!/_2C_6H_6$$

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Abstract: A single-crystal X-ray study confirms that the reaction of IrH(CO)₂(PPh₃)₂ (Ph = phenyl) with 2 mol of tetracyanoethylene (TCNE) yields (cyano(dicyanomethyl)keteniminato)carbonyl(tetracyanoethylene)bis(triphenylphosphine)iridium, Ir(C₆N₄H)(CO)(TCNE)(PPh₃)₂. The cyano(dicyanomethyl)keteniminato moiety is formed formally by hydrogen migration from the Ir to a TCNE molecule and subsequent attachment of the resulting group to the Ir through an Ir–N bond. The geometry about iridium is trigonal bipyramidal with the two phosphorus atoms and the olefinic π-bonded TCNE in the equatorial plane while the carbonyl and keteniminato groups occupy axial positions. The average Ir–P and coplanar Ir–C distances are 2.392 (7) and 2.166 (15) Å, respectively. The Ir–N distance is 2.204 (8) Å and the Ir–N–C angle is 161.9 (7)°. The compound crystallizes in space group $P2_1/c$ of the monoclinic system with four molecules of the iridium complex and two molecules of benzene in a cell of dimensions a = 13.012 (7), b = 16.099 (9), c = 21.740 (12) Å, β = 94.33 (2)°. The observed and calculated densities are 1.54 (1) and 1.52 g cm⁻³, respectively. The structure has been refined by least-squares techniques to a final R factor on F of 4.1% based on 3853 observations above background.

The reactions of a number of olefins with the hydrido complexes IrH(CO)(PPh₃)₃,[1] IrH(CO)₂-(PPh₃)₂,[2] and IrH₃(CO)(PPh₃)₂[2] (Ph = phenyl) yield the hydrido π-olefinic complexes IrH(CO)(olefin)(PPh₃)₂ by displacement of triphenylphosphine, carbon monoxide, and hydrogen, respectively. The reaction of tetracyanoethylene (TCNE) with IrH(CO)₂(PPh₃)₂ is more complex and gives a novel product of empirical formula IrH(CO)(TCNE)₂(PPh₃)₂. Infrared spectra[3] are consistent with the attachment of one TCNE through a π-olefinic bond. These spectra are consistent further with the other C₆N₄ unit being coordinated either as an anion radical or in a more novel manner as a cyano(dicyanomethyl)keteniminato moiety formed by hydrogen migration onto the TCNE and formation of an iridium–nitrogen bond.[4]

We have undertaken the present study of this novel product in order to ascertain the type of coordination of the non-π-bonded TCNE moiety and to provide comparative data on metal–olefin attachment, two distinct modes of which turn out to be present. We have shown in a brief report of this work[3] that the compound does indeed contain the keteniminato linkage. Although the existence of the general class of transition metal keteniminato complexes has been established,[5–7] no structural information on this class has been available.

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(2) M. S. Fraser and W. H. Baddley, in preparation.

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(4) M. F. Rettig and R. M. Wing, *Inorg. Chem.*, **8**, 2685 (1969), have given structural and infrared evidence for σ-bonded TCNE in the compound (π-C₅H₅)₂VBr·TCNE. Here TCNE is σ bonded to vanadium through a nitrile nitrogen. Spectroscopic evidence for this type of bonding has also been provided by P. C. Ford, R. D. Foust, Jr., and R. E. Clarke, *ibid.*, **9**, 1933 (1970).

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(7) S. R. Su, J. A. Hanna, and A. Wojcicki, *J. Organometal. Chem.*, **21**, 21 (1970).

Experimental Section

Preparation and Preliminary X-Ray Examination. Crystals were prepared by Miss M. Shirley Fraser and Professor W. H. Baddley by addition of a benzene solution of IrH(CO)₂(PPh₃)₂ to a fourfold excess of TCNE in benzene at room temperature. The bronze-colored crystals analyze for two molecules of tetracyanoethylene per iridium atom. The preparation, proposed reaction path, and spectral data have been discussed previously.[3]

On the basis of oscillation and precession photographs we established that the crystals belong to the monoclinic system. The cell dimensions, obtained with Cu Kα₁ radiation (λ 1.5406 Å) at 25° from refinement of the setting angles of 11 reflections centered on a four-circle diffractometer,[8] are a = 13.012 (7), b = 16.099 (9), c = 21.740 (12) Å, β = 94.33 (2)°. A density of 1.52 g cm⁻³ calculated for four formula units of Ir(C₆N₄H)(CO)(TCNE)-(PPh₃)·½C₆H₆ per unit cell agrees satisfactorily with that of 1.54 (1) g cm⁻³ measured by flotation in aqueous zinc chloride. Precession photographs of the 0kl, 1kl, h0l and h1l nets show systematic absences 0k0 for k odd and h0l for l odd that are characteristic of the space group C_{2h}^5-$P2_1/c$.

Collection and Reduction of Intensity Data. Intensities were collected with Cu Kα radiation from a crystal of hexagonal prismatic habit of approximate dimensions 0.3 mm along a^* (the prism axis) and 0.2 mm diameter. Diffractometer data were collected on a Picker four-circle instrument in a manner previously described.[9] A unique data set collected out to 2θ (Cu Kα) = 100° yielded 4525 independent reflections of which 3853 obeyed the condition $F_o^2 > 3\sigma(F_o^2)$ and these are described as being above background. The intensities of four standard reflections were measured periodically; no decay was discerned and no individual measurement differed from the average by more than 2%.

The data were collected by the θ–2θ scan technique at a scan rate of 1°/min from −0.65° from Kα₁ maximum to +0.75° from Kα₂ maximum. Stationary-crystal, stationary-counter background counts were taken for 10 sec at each end of the 2θ scan range. The diffracted beams were filtered through 1.0-mil Ni foil. The counter was placed 31 cm from the crystal and was preceded by an aperture of 4.0 mm by 5.0 mm. The pulse-height analyzer was adjusted to receive approximately 90% of the diffracted radiation. The takeoff angle was 1.5°. The diffracted beams were attenuated by Cu foil when necessary to prevent coincidence losses. The data were processed in the manner described previously[8,9] to yield values of F_o^2 and $\sigma(F_o^2)$. A value of 0.03 for p was used in the estimation of standard deviations.

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(9) R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

Table I. Positional, Thermal, and Group Parameters

Atom	x	y	z	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	0.16080 (3)^b	0.04932 (2)	−0.32557 (2)	45.2 (3)	26.4 (2)	13.4 (1)	1.7 (2)	1.7 (1)	−0.8 (1)
P(1)	0.1106 (2)	−0.0578 (2)	−0.2573 (1)	51 (2)	32 (1)	16 (1)	2 (1)	4 (1)	2 (1)
P(2)	0.3135 (2)	0.3813 (1)	0.2146 (1)	46 (2)	31 (1)	16 (1)	1 (1)	1 (1)	3 (1)
C	0.0891 (7)	0.3682 (6)	0.2121 (4)	68 (8)	41 (5)	8 (2)	8 (5)	1 (3)	6 (3)
O	0.0483 (5)	0.3157 (4)	0.2343 (3)	84 (6)	42 (4)	24 (2)	−1 (4)	11 (3)	10 (2)
N(1)	−0.2419 (5)	0.0418 (5)	0.3640 (3)	68 (6)	31 (4)	12 (2)	−2 (4)	4 (3)	−4 (2)
N(2)	−0.0524 (6)	0.4047 (5)	−0.0308 (3)	82 (7)	44 (4)	13 (2)	−3 (5)	0 (3)	−2 (3)
N(3)	0.2554 (7)	0.0637 (6)	0.5018 (4)	88 (8)	81 (6)	21 (3)	−5 (6)	12 (4)	6 (3)
N(4)	0.0693 (8)	0.2444 (6)	0.0805 (5)	132 (10)	34 (5)	51 (4)	−3 (6)	−24 (5)	4 (4)
N(5)	−0.1332 (8)	0.4112 (6)	0.1171 (4)	82 (8)	56 (5)	29 (3)	−11 (5)	6 (4)	6 (3)
N(6)	−0.3348 (7)	0.3068 (6)	0.3513 (4)	106 (9)	48 (5)	34 (3)	21 (6)	8 (4)	4 (3)
N(7)	−0.1822 (9)	0.3190 (7)	0.5182 (5)	141 (12)	76 (7)	45 (4)	−26 (8)	−1 (5)	−24 (4)
N(8)	−0.4639 (9)	0.3118 (7)	0.0246 (5)	112 (10)	104 (8)	31 (3)	3 (7)	27 (5)	−5 (4)
C(1)	0.0458 (7)	0.4610 (5)	0.0968 (4)	48 (7)	20 (4)	27 (3)	−5 (4)	12 (3)	9 (3)
C(2)	0.1287 (7)	0.3975 (5)	0.0840 (4)	52 (7)	21 (4)	25 (3)	2 (4)	3 (4)	2 (3)
C(3)	−0.0499 (7)	0.0364 (6)	0.4367 (4)	52 (7)	50 (6)	11 (2)	−1 (5)	−4 (3)	8 (3)
C(4)	−0.0535 (9)	0.4337 (6)	0.1070 (5)	81 (10)	25 (5)	23 (3)	−9 (5)	5 (4)	2 (3)
C(5)	0.1992 (8)	0.4188 (6)	0.0379 (4)	58 (8)	43 (5)	13 (2)	9 (5)	−1 (4)	−5 (3)
C(6)	0.0956 (8)	0.3122 (7)	0.0800 (4)	80 (9)	38 (6)	18 (3)	7 (6)	−8 (4)	−1 (3)
C(7)	−0.2910 (7)	0.1772 (6)	0.4154 (4)	61 (7)	31 (5)	15 (2)	10 (5)	5 (3)	−2 (3)
C(8)	−0.2628 (7)	0.1034 (6)	0.3876 (4)	44 (7)	45 (6)	12 (2)	−4 (5)	−4 (3)	7 (3)
C(9)	−0.3177 (8)	0.2463 (7)	0.3788 (5)	70 (8)	36 (5)	23 (3)	14 (6)	10 (4)	−2 (3)
C(10)	−0.2807 (8)	0.1844 (6)	0.4849 (4)	69 (8)	49 (6)	22 (3)	9 (5)	7 (4)	3 (3)
C(11)	−0.3834 (10)	0.3127 (7)	0.0085 (5)	95 (11)	60 (6)	19 (3)	−2 (7)	12 (5)	−3 (3)
C(12)	−0.2219 (9)	0.2400 (8)	0.0053 (5)	94 (10)	58 (7)	19 (3)	1 (7)	−2 (4)	5 (4)
H	−0.2434^c	0.1368	0.5031						

Group^d	x_c	y_c	z_c	δ	ϵ	η
A	0.2913 (3)	0.6765 (3)	0.2990 (2)	0.808 (4)	−2.811 (4)	−2.823 (4)
B	−0.0263 (3)	0.4984 (3)	0.3520 (2)	2.329 (5)	2.481 (3)	−1.744 (5)
C	−0.0291 (3)	0.6787 (2)	0.1529 (2)	−0.966 (4)	2.949 (4)	0.697 (4)
D	0.3067 (3)	0.2004 (3)	0.1515 (2)	−1.092 (5)	2.306 (4)	2.463 (6)
E	0.5285 (4)	0.4634 (3)	0.1842 (2)	−1.933 (11)	−1.959 (4)	0.817 (11)
F	0.3344 (3)	0.3340 (3)	0.3578 (2)	0.750 (4)	−2.897 (4)	−1.460 (4)
S	0.5	0	0	−0.768 (18)	2.056 (9)	1.506 (18)

^{a} The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^{b} Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. ^{c} This hydrogen atom is attached to C(10) and is at an idealized tetrahedral position with a C–H distance of 0.98 Å and $B = 5.5$ Å^2. ^{d} x_c, y_c, and z_c are the fractional coordinates of the ring center; δ, ϵ, and η (in radians) have been defined in R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965). Groups A–F are phenyl rings; group S is the benzene molecule of crystallization.

Solution of the Structure. An unsharpened, three-dimensional Patterson function[10] was prepared from the inner 1820 data and interpreted to give the coordinates of the iridium and one phosphorus atom. The remaining nonhydrogen atoms were readily located by the usual combination of Fourier and least-squares methods. In the least-squares calculations the function minimized was $\Sigma w \Delta^2$, where $\Delta = |F_o| - |F_c|$ with $|F_o|$ and $|F_c|$ the observed and calculated structure amplitudes, and where the weights, w, were taken as $4F_o{}^2/\sigma^2(F_o{}^2)$. The atomic scattering factors for all nonhydrogen atoms were taken from the usual tabulation,[11] while those for H were from the calculations of Stewart, *et al.*[12] The anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, were taken from the calculations of Cromer[13] and were included in F_c[14] for the iridium and phosphorus atoms. In preparation for an absorption correction, the data crystal was measured and its faces were identified by optical means. Six of the ten crystal faces belonged to the forms {001} and {011}. The other faces were (̄111), (̄1̄11), (̄101), and (100). Based on a calculated linear absorption coefficient of 66.4 cm^{-1} the transmission factors were found to vary between 0.36 and 0.44.

(10) In addition to various local programs for the CDC 6400, local variations of the following programs were used in this study: GONO9 absorption program of W. C. Hamilton, FORDAP Fourier program of A. Zalkin, ORFFE error function program of W. R. Busing and H. A. Levy, ORTEP plotting program of C. Johnson. NUCLS, the least-squares program used, in its nongroup form resembles the Busing–Levy ORFLS program.
(11) J. A. Ibers, "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.
(12) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(13) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(14) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

The trial structure was refined by a least-squares procedure in which the phenyl rings were constrained to D_{6h} symmetry and treated as rigid groups (C–C = 1.390 Å) with individual isotropic thermal parameters. This initial isotropic refinement, based on the inner 1820 data, converged to values of R_1 and R_2 of 0.078 and 0.114, respectively, where $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2)^{1/2}$.

The hydrogen atom of the dicyanomethylketeniminato group was observed in a difference Fourier synthesis and its position as well as the positions of all 30 phenyl hydrogens were idealized on the assumption that C–H = 0.98 Å. The contributions from these idealized hydrogen atoms were added in a fixed manner to subsequent structure factor calculations.

A difference Fourier synthesis also revealed the presence of solvent benzene in the ratio of one molecule of benzene to two formula units of the iridium complex.

Because of the large number of variables (305) involved when allowance for anisotropic thermal vibration of the 25 nongroup atoms was made, each complete cycle of refinement consisted of two parts. In the first half cycle the iridium, the two phosphorus atoms, and the atoms of the tetracyanoethylene group were refined anisotropically while the solvent molecule and three of the six phenyl rings were refined as rigid groups with individual isotropic thermal parameters on the carbon atoms. In the second half cycle the iridium, the two phosphorus atoms, the atoms of the carbonyl, and keteniminato groups were refined anisotropically while the three remaining phenyl rings were refined as rigid groups with individual isotropic thermal parameters on the carbon atoms. Two complete cycles of refinement for 3853 data obeying the condition $F_o{}^2 > 3\sigma(F_o{}^2)$ reduced the values of R_1 and R_2 to 0.041 and 0.055, respectively, and led to the final parameters given in Table I. The derived positions for the ring carbon atoms as well as the idealized positions of the hydrogen atoms are given in Table II. An

Table II. Derived Parameters for Ring Atoms

Ring atom	Carbon			B, Å^2	Hydrogen[a]		
	x	y	z		x	y	z
A$_1$[b]	0.2131 (4)[c]	0.6233 (4)	0.2766 (3)	3.3 (2)			
A$_2$	0.3156 (5)	0.6010 (3)	0.2727 (3)	4.0 (2)	0.333[d]	0.548	0.255
A$_3$	0.3938 (3)	0.6542 (4)	0.2952 (3)	4.6 (2)	0.466	0.639	0.292
A$_4$	0.3694 (4)	0.7297 (4)	0.3215 (3)	5.2 (2)	0.425	0.768	0.337
A$_5$	0.2669 (5)	0.7520 (3)	0.3254 (3)	5.3 (2)	0.250	0.806	0.344
A$_6$	0.1887 (4)	0.6988 (4)	0.3029 (3)	4.5 (2)	0.117	0.715	0.306
B$_1$	0.0334 (5)	0.5234 (5)	0.3049 (2)	3.4 (2)			
B$_2$	0.0568 (5)	0.5515 (5)	0.3648 (3)	5.0 (2)	0.116	0.589	0.374
B$_3$	−0.0030 (5)	0.5264 (4)	0.4119 (2)	5.7 (3)	0.014	0.546	0.454
B$_4$	−0.0860 (6)	0.4733 (5)	0.3990 (3)	6.0 (3)	−0.128	0.456	0.432
B$_5$	−0.1094 (5)	0.4452 (5)	0.3391 (3)	4.9 (2)	−0.168	0.408	0.330
B$_6$	−0.0496 (4)	0.4703 (3)	0.2920 (2)	4.0 (2)	−0.066	0.451	0.250
C$_1$	0.0284 (4)	0.6303 (4)	0.1957 (2)	3.1 (2)			
C$_2$	−0.0752 (4)	0.6128 (3)	0.1815 (3)	4.0 (2)	−0.108	0.567	0.202
C$_3$	−0.1328 (3)	0.6612 (4)	0.1386 (3)	5.0 (2)	−0.206	0.649	0.128
C$_4$	−0.0867 (5)	0.7271 (4)	0.1100 (3)	5.0 (2)	−0.127	0.761	0.079
C$_5$	0.0170 (5)	0.7447 (3)	0.1242 (3)	4.6 (2)	0.050	0.790	0.103
C$_6$	0.0746 (3)	0.6963 (4)	0.1671 (3)	3.9 (2)	0.148	0.708	0.177
D$_1$	0.3125 (8)	0.2786 (3)	0.1787 (3)	3.2 (2)			
D$_2$	0.2544 (5)	0.2164 (4)	0.2037 (2)	4.4 (2)	0.218	0.227	0.240
D$_3$	0.2486 (6)	0.1382 (4)	0.1765 (3)	5.2 (2)	0.208	0.094	0.194
D$_4$	0.3009 (8)	0.1222 (3)	0.1243 (3)	5.6 (3)	0.297	0.067	0.105
D$_5$	0.3590 (5)	0.1844 (4)	0.0993 (2)	4.9 (2)	0.396	0.173	0.062
D$_6$	0.3648 (6)	0.2626 (4)	0.1265 (3)	4.0 (2)	0.406	0.306	0.109
E$_1$	0.4349 (7)	0.4288 (12)	0.1976 (3)	3.6 (2)			
E$_2$	0.4488 (5)	0.4561 (8)	0.1382 (2)	4.2 (2)	0.393	0.451	0.106
E$_3$	0.5424 (7)	0.4907 (6)	0.1248 (2)	6.0 (3)	0.552	0.510	0.083
E$_4$	0.6220 (7)	0.4980 (12)	0.1708 (4)	6.7 (3)	0.688	0.522	0.162
E$_5$	0.6081 (5)	0.4707 (9)	0.2303 (3)	6.8 (3)	0.664	0.475	0.263
E$_6$	0.5145 (6)	0.4361 (5)	0.2437 (2)	4.9 (2)	0.504	0.416	0.286
F$_1$	0.3255 (5)	0.3558 (4)	0.2958 (2)	3.6 (2)			
F$_2$	0.3914 (5)	0.2918 (4)	0.3161 (3)	5.4 (2)	0.432	0.262	0.287
F$_3$	0.4003 (6)	0.2700 (4)	0.3782 (3)	6.5 (3)	0.447	0.226	0.393
F$_4$	0.3433 (6)	0.3122 (5)	0.4198 (2)	6.3 (3)	0.350	0.298	0.464
F$_5$	0.2775 (5)	0.3762 (4)	0.3995 (3)	6.2 (3)	0.237	0.406	0.428
F$_6$	0.2686 (5)	0.3980 (4)	0.3374 (3)	4.2 (2)	0.221	0.442	0.323
S$_1$[e]	0.5707 (7)	0.0510 (4)	0.0329 (3)	9.1 (4)	0.623	0.090	0.051
S$_3$	0.4346 (6)	−0.0506 (4)	0.0312 (3)	8.8 (4)	0.393	−0.084	0.058
S$_5$	0.4947 (6)	−0.0004 (4)	−0.0641 (3)	9.0 (4)	0.484	−0.006	−0.109

[a] All hydrogen atoms have $B = 5.5$ Å^2. [b] Ring atoms are numbered sequentially with carbon atoms A$_1$, B$_1$, etc., attached to P. [c] The estimated standard deviations are derived from those of the group parameters. [d] Hydrogen atom A$_2$ is attached to carbon A$_2$, hydrogen A$_3$ to carbon A$_3$, etc. [e] The solvent benzene molecule lies on an inversion center.

analysis of $|F_o|$ and $|F_c|$ as a function of scattering angle, magnitude of $|F_o|$, and Miller indices revealed no unexpected trends and provided no evidence for extinction effects. The error in an observation of unit weight is 2.51 and thus the weighting scheme appears to be a reasonable one. The final values of the structure amplitudes are tabulated as $10|F_o|$ and $10|F_c|$ (in electrons) for those reflections used in the refinement.[15] The maximum density on a final difference Fourier synthesis is 0.58 electron/Å^3, approximately 10% of the height of a carbon atom in this structure.

Discussion

The formulation of the present compound as a keteniminato complex is based on the detection of the H atom attached to C(10) in a difference Fourier map and on the general disposition of the bonds about C(10). Thus on the basis of this structure determination the compound may be named (cyano(dicyanomethyl)-keteniminato)carbonyl(tetracyanoethylene)bis(triphenylphosphine)iridium. The formal structure and numbering system for the atoms in the inner coordination sphere about Ir are given in Figure 1. The vibrational thermal ellipsoids for these atoms are also dis-

played in this figure and the root-mean-square amplitudes of vibration are presented in Table III. These
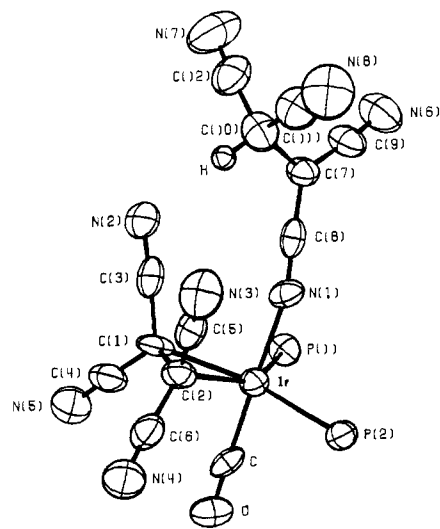
Figure 1. A drawing of the inner coordination sphere about Ir in Ir(C$_6$N$_4$H)(CO)(TCNE)(PPh$_3$)$_2$. The 50% probability vibrational ellipsoids are shown.
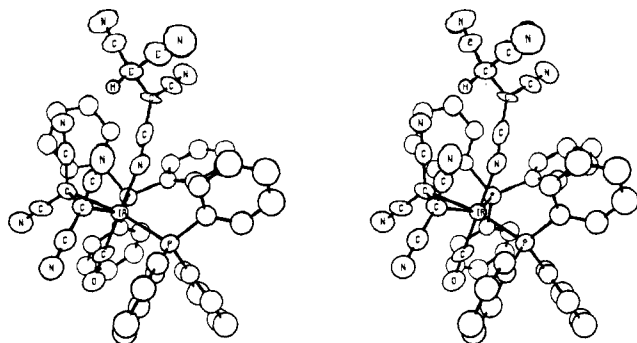
Figure 2. A stereoscopic drawing of the isolated molecule.

Figure 3. A stereoscopic drawing of four molecules of Ir(C$_6$N$_4$H)-(CO)(TCNE)(PPh$_3$)$_2$ whose central metal atoms all lie within the same unit cell. Solvent benzene molecules are located at $^1/_2$, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$. View is perpendicular to [010].

vibrational data appear to be reasonable, with the cyano nitrogen atoms exhibiting the greatest thermal motion. A stereoscopic drawing of the isolated molecule is shown in Figure 2. From the positional parameters in

Table III. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Inter	Max
Ir	0.1771 (8)	0.1856 (8)	0.1985 (7)
P(1)	0.191 (4)	0.203 (4)	0.215 (4)
P(2)	0.184 (4)	0.199 (4)	0.212 (4)
C	0.123 (20)	0.224 (14)	0.256 (14)
O	0.188 (11)	0.258 (9)	0.281 (9)
N(1)	0.157 (14)	0.208 (12)	0.241 (11)
N(2)	0.176 (14)	0.240 (12)	0.267 (11)
N(3)	0.205 (14)	0.280 (12)	0.329 (13)
N(4)	0.209 (14)	0.278 (13)	0.406 (14)
N(5)	0.230 (14)	0.269 (13)	0.294 (13)
N(6)	0.223 (14)	0.278 (13)	0.324 (12)
N(7)	0.229 (16)	0.356 (15)	0.388 (15)
N(8)	0.219 (15)	0.340 (14)	0.370 (14)
C(1)	0.126 (21)	0.203 (15)	0.271 (13)
C(2)	0.162 (17)	0.210 (14)	0.243 (13)
C(3)	0.146 (18)	0.216 (14)	0.266 (16)
C(4)	0.172 (18)	0.235 (14)	0.267 (15)
C(5)	0.164 (17)	0.208 (15)	0.258 (14)
C(6)	0.192 (15)	0.219 (17)	0.282 (14)
C(7)	0.170 (17)	0.198 (15)	0.242 (13)
C(8)	0.147 (17)	0.196 (15)	0.256 (16)
C(9)	0.181 (17)	0.236 (16)	0.265 (14)
C(10)	0.217 (15)	0.229 (15)	0.270 (15)
C(11)	0.198 (17)	0.279 (16)	0.292 (16)
C(12)	0.207 (17)	0.280 (16)	0.286 (16)

Table I and the correlation matrix, the relevant interatomic distances, bond angles, and their standard deviations were calculated and are presented in Table IV.[16]

The crystal structure consists of individual monomeric molecules, each of which is one asymmetric unit. The stereo drawing of four complete molecules in a unit cell (Figure 3) represents a view perpendicular to [010]. There are no unusually close intermolecular contacts.

The geometry about iridium is trigonal bipyramidal if TCNE is considered a monodentate ligand. The two phosphorus atoms and the π-bonded TCNE lie in the equatorial plane, while the carbonyl and the keteniminato groups occupy axial positions (see Figure 1). The Ir–N distance of 2.024 (8) Å appears to be that of a

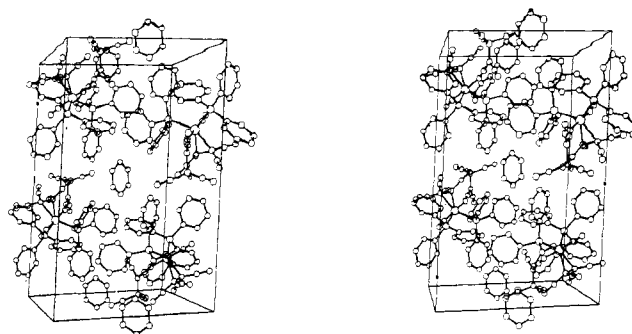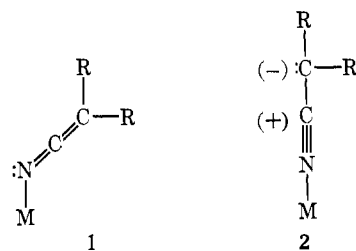(16) Certain bond distance errors do not contain correlation effects because of blocking of the matrix.

normal single bond. Thus the bond is slightly longer than that of 1.97 Å in IrCl(NO)(CO)(PPh$_3$)$_2$$^+$,[17] where the bond is formulated as single. The Ir–N bond length also is near to Pt–amine bonds of 2.05 (4) Å in cis- and trans-dichlorodiamineplatinum(II)[18] and of 2.057 (6) Å in cis-dichlorobis(ethylenediamine)platinum(IV) chloride.[19]

Previously, there existed little information concerning the characteristics ot the keteniminato–transition metal bond. In the light of valence-bond theory the M–N–C bond angle may be indicative of the relative contributions of the structures

The angle in question, Ir–N(1)–C(8), of 161.9 (7)° is nearer 180° than 120°, which suggests that the zwitterion 2 is the more important form. The nitrogen atom, N(1), is part of a planar system consisting of N(1), C(7), C(8), C(9), C(10), and N(6) (see Table V), and this plane is inclined 68.1° to the plane formed by Ir, P(1), and P(2). The N(1)–C(8) distance of 1.158 (11) Å is typical of a C≡N bond and does not differ significantly from the average (1.144 (25) Å) of the remaining C≡N bond distances. The C(7)–C(8) distance of 1.394 (13) Å and the N(1)–C(8)–C(7) bond angle of 178.3 (10)° are also typical. The C(7)–C(10) bond distance at 1.511 (12) Å is that of an ordinary carbon–carbon single bond and does not differ significantly from the analogous C(1)–C(2) distance (1.526 (12) Å) in the π-bonded TCNE. The angles about C(7) average 120°, while those around C(10) are typical of a tetrahedral carbon atom.

Table VI presents a comparison of structural data on three cyano-substituted ethylene complexes of iridium: I, IrH(CO)(FUMN)(P(C$_6$H$_5$)$_3$)$_2$[20] (FUMN = fumaro-

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Table IV. Distances (Å) and Angles (Deg)

─────Bond Distances─────			─────Bond Angles─────	
Ir–P(1)	2.397 (2)		P(1)–Ir–P(2)	111.6 (1)
Ir–P(2)	2.387 (2)	2.392 (7)[a]	P(1)–Ir–C(1)	102.8 (2)
			P(1)–Ir–C(2)	143.8 (2)
Ir–C(1)	2.176 (10)		P(1)–Ir–C	94.2 (3)
Ir–C(2)	2.155 (9)	2.166 (15)	P(1)–Ir–N(1)	84.8 (2)
			P(2)–Ir–C(1)	145.5 (2)
Ir–C	1.849 (10)		P(2)–Ir–C(2)	104.3 (2)
Ir–N(1)	2.024 (8)		P(2)–Ir–C	86.4 (3)
			P(2)–Ir–N(1)	92.5 (2)
P(1)–C(A₁)	1.813 (6)		C(1)–Ir–C(2)	41.3 (3)
P(1)–C(B₁)	1.830 (6)		C(1)–Ir–N(1)	88.6 (3)
P(1)–C(C₁)	1.840 (6)		C(2)–Ir–N(1)	89.1 (3)
P(2)–C(D₁)	1.828 (5)	1.823 (12)	C–Ir–N(1)	178.1 (3)
P(2)–C(E₁)	1.818 (12)		Ir–P(1)–C(A₁)	116.3 (2)
P(2)–C(F₁)	1.808 (4)		Ir–P(1)–C(B₁)	115.5 (3)
			Ir–P(1)–C(C₁)	106.7 (2)
C–O	1.126 (10)		Ir–P(2)–C(D₁)	106.8 (3)
C(1)–C(2)	1.526 (12)		Ir–P(2)–C(E₁)	116.2 (5)
			Ir–P(2)–C(F₁)	118.1 (2)
C(1)–C(3)	1.418 (13)		Ir–C–O	177.2 (8)
C(1)–C(4)	1.398 (14)		Ir–N(1)–C(8)	161.9 (7)
C(2)–C(5)	1.450 (13)	1.426 (18)	Ir–C(1)–C(3)	114.4 (6)
C(2)–C(6)	1.440 (14)		Ir–C(1)–C(4)	116.3 (7)
			C(2)–C(1)–C(3)	115.2 (8)
C(3)–N(2)	1.186 (11)		C(2)–C(1)–C(4)	119.5 (8)
C(4)–N(5)	1.135 (12)		C(3)–C(1)–C(4)	114.9 (8)
C(5)–N(3)	1.148 (11)		Ir–C(2)–C(5)	116.7 (6)
C(6)–N(4)	1.145 (12)	1.144 (25)	Ir–C(2)–C(6)	118.0 (7)
C(9)–N(6)	1.155 (12)		C(1)–C(2)–C(5)	117.4 (8)
C(11)–N(8)	1.130 (13)		C(1)–C(2)–C(6)	115.9 (8)
C(12)–N(7)	1.106 (13)		C(5)–C(2)–C(6)	112.7 (8)
C(8)–N(1)	1.158 (11)		C(1)–C(3)–N(2)	174.2 (9)
			C(1)–C(4)–N(5)	177.9 (11)
C(7)–C(8)	1.394 (13)		C(2)–C(5)–N(3)	179.2 (10)
C(7)–C(9)	1.397 (13)		C(2)–C(6)–N(4)	176.1 (12)
C(7)–C(10)	1.511 (12)		C(7)–C(8)–N(1)	178.3 (10)
C(10)–C(11)	1.467 (14)		C(7)–C(9)–N(6)	175.0 (12)
C(10)–C(12)	1.488 (15)		C(10)–C(11)–N(8)	177.4 (13)
			C(10)–C(12)–N(7)	175.8 (14)
			C(8)–C(7)–C(9)	119.6 (8)
			C(8)–C(7)–C(10)	119.5 (8)
			C(9)–C(7)–C(10)	120.5 (8)
			C(7)–C(10)–C(11)	109.7 (8)
			C(7)–C(10)–C(12)	111.4 (8)
			C(11)–C(10)–C(12)	109.3 (9)
			C(A₁)–P(1)–C(B₁)	107.7 (3)
			C(A₁)–P(1)–C(C₁)	103.6 (3)
			C(B₁)–P(1)–C(C₁)	105.9 (3)
			C(D₁)–P(2)–C(E₁)	105.8 (6)
			C(D₁)–P(2)–C(F₁)	102.0 (3)
			C(E₁)–P(2)–C(F₁)	106.4 (3)

─────Dihedral Angles[b]─────	
C(1)–C(3)–C(4) C(5)–C(2)–C(6)	67.4 (12)
C(1)–C(2)–Ir C(1)–C(2)–C(3)	107.8 (8)
C(1)–C(2)–Ir C(1)–C(2)–C(4)	108.9 (9)
Ir–P(1)–P(2) N(1)–C(10)–C(9)	68.1 (2)
Ir–P(1)–P(2) Ir–C(2)–C(1)	5.4 (4)
C(1)–C(2)–Ir C(1)–C(2)–C(5)	110.5 (8)
C(1)–C(2)–Ir C(1)–C(2)–C(6)	112.3 (8)

─────Vector-Plane Normal Angles─────	
C(1)–C(2) Ir–P(2)–P(1)	86.0 (5)
C(1)–C(2) C(1)–C(3)–C(4)	58.7 (12)
C(2)–C(1) C(2)–C(6)–C(5)	53.9 (11)

[a] These are average quantities. The estimated standard deviation in parentheses is the larger of an individual deviation or of the standard deviation of a single observation as calculated from the mean. [b] The dihedral angle between two planes is defined as the angle between the normals to these planes each of which is defined by a group of three atoms. See ref 22.

nitrile = *trans*-1,2-dicyanoethylene); II, IrBr(CO)-(TCNE)(P(C₆H₅)₃)₂;[21] and III, this study. Worthy of note is the lengthening of the Ir–P and the olefinic carbon–carbon distances with increased electron withdrawal from these bonds in going from I to II or to III. The greater number of cyano groups on II and III probably has the effect of lessening the degree of mul-

tiple bonding which can exist between phosphorus and the central metal. Although the absence of a value for the Ir–C (of CO) bond length in II precludes a direct comparison, it would appear, both on the basis of the Ir–N(1) bond length discussed above and on the basis of the Ir–P distances in II and III, that the ketenim-inato ligand is very similar to the bromide ligand in its bonding characteristics. Just why the Ir–C (of CO) bond length is abnormally long in I is not clear to us.

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Table V. Weighted Least-Squares Planes

Plane equation: $Ax + By + Cz - D = 0$, with x, y, z in monoclinic coordinates

Plane no.	A	B	C	D
1	12.501	4.451	-1.028	3.225
2	9.920	3.089	12.147	-2.207
3	-0.825	-8.743	18.255	-6.507
4	7.758	-10.664	-10.813	4.243
5	-0.577	-8.894	18.117	-7.662
6	9.444	3.996	12.718	-3.672

Deviations from the planes, Å

	1	2	3	4	5	6
Ir		-0.0001 (4)	-0.0002 (3)	-0.0009 (4)		
P(1)		0.000 (2)		0.013 (2)		
P(2)			0.000 (2)	0.010 (2)		
C		0.000 (8)	0.024 (8)			
O		0.029 (7)	0.006 (7)			
N(1)	-0.012 (7)	0.056 (7)	0.028 (7)			
N(2)					-0.021 (7)	
N(3)						0.001 (9)
N(4)						0.011 (10)
N(5)					0.012 (9)	
N(6)	-0.044 (10)					
N(7)						
N(8)						
C(1)				0.057 (8)	-0.017 (9)	
C(2)				0.161 (9)		0.006 (9)
C(3)					0.045 (8)	
C(4)					-0.018 (10)	
C(5)						-0.001 (9)
C(6)						-0.016 (9)
C(7)	0.051 (9)					
C(8)	-0.002 (8)					
C(9)	0.039 (10)					
C(10)	-0.038 (10)					

Table VI. Comparison of Structural Data[a] (Average Values)

	I	II	III
Ir–C[e]	2.110 (9)	2.148 (11)[b]	2.166 (15)[b]
Ir–P	2.317 (3)	2.400 (3)[b]	2.392 (7)[b]
Ir–CO	1.98 (2)		1.849 (10)
C–C	1.431 (20)	1.506 (15)	1.526 (12)
∠C–Ir–C[f]	39.7 (5)	41.0 (4)	41.3 (3)
∠P–Ir–P	114.1 (1)	110.4 (1)	111.6 (1)
∠Ir–C–O	178.7 (24)		177.2 (8)
∠C–C–CN	117.5 (12)	117.6 (19)[b]	117.0 (19)[b]
∠(C–C–CN)– (C–C–Ir)[c]	111.8 (8)	111.7 (31)[b]	109.6 (20)[b]
α[d]		70.4 (13)	67.4 (12)

[a] I = IrH(CO)FUMN(PPh₃)₂ (FUMN = *trans*-1,2-dicyanoethene);[20] II = IrBr(CO)(TCNE)(PPh₃)₂ (TCNE = tetracyanoethylene);[21] III, present work (reference is to the π-bonded TCNE). [b] These are average quantities. The estimated standard deviation in parentheses is the larger of an individual standard deviation or of the standard deviation of a single observation as calculated from the mean. [c] This is the dihedral angle between the planes defined by the two sets of three atoms. [d] α is defined in the text. [e] Bonds in ångströms. [f] Angles in degrees.

The structural characteristics of the π-bonded TCNE moiety are consistent with those detailed for several complexes in an earlier paper concerning the structure of Ni(TCNE)(t-buNC)₂[22] (t-buNC = *tert*-butyl isocyanide). There is the expected lengthening of the ole-

finic C(1)–C(2) bond on attachment to the metal. Back-donation from the metal orbitals into the π* antibonding orbitals of the ligand probably accounts for this lengthening in olefins π-bonded to transition metals.[23,24] There appears to be little effect of coordination on the remaining TCNE carbon–carbon and carbon–nitrogen bonds. Also, in keeping with the results obtained for Ni(TCNE)(t-buNC)₂[22] is the marked deviation from planarity of the π-bonded TCNE. The dihedral angle, α, between the planes formed by C(3)–C(1)–C(4) and C(5)–C(2)–C(6) (α is defined as the angle between the normals to these planes) is 67.4 (12)° and is consistent with the trend of increasing central C–C bond distance with an increase in the dihedral angle, α, as discussed earlier.[22]

In Table V are given the equations of the weighted least-squares planes through several groups of atoms together with the displacements of these atoms from their respective planes. The strictly planar groups include the C(CN)₂ fragments of the π-bonded TCNE and the system which includes N(1), C(7), C(8), C(9), C(10), and N(6). The distortions of the iridium and four basal atoms from coplanarity are smaller here than in Ni(TCNE)(t-buNC)₂, although again there is a slight tendency in the direction of a tetragonal-pyramidal geometry, with the iridium atom on one side of the least-squares plane and P(1), P(2), C(1), and C(2) on the other (Table V). The

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"twist angle," the angle between the Ir–P(1)–P(2) and Ir–C(1)–C(2) planes, is 5.4 (4)°, a value typical of trigonal-bipyramidal structures containing olefins π-bonded to metals.[20]

# Preparation and Properties of Some Cationic Complexes of Rhodium(I) and Rhodium(III)

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Abstract: Cationic complexes of the type $[Rh(diene)L_2]^+$ (diene = 1,5-cyclooctadiene (COD) or norbornadiene (NBD), L = tertiary phosphine or arsine ligand) have been prepared by several routes. These complexes serve as useful intermediates for the synthesis of many other cationic rhodium(I) and rhodium(III) species. Treatment of $[Rh(COD)\{P(C_6H_5)_3\}_2]^+$ with basic phosphines, L, leads to the isolation of the cations $[RhL_4]^+$. Under identical conditions using $[Rh(NBD)\{P(C_6H_5)_3\}_2]^+$, however, the five-coordinate species $[Rh(NBD)L_3]^+$ are produced. Treatment of solutions of $[Rh(NBD)\{P(C_6H_5)_3\}_2]^+$ with molecular hydrogen generates $[Rh\{P(C_6H_5)_3\}_2H_2S_2]^+$ (S = solvent) *in situ* with the elimination of norbornane. These solutions react with phosphines to give the cations of the type $[RhL_4H_2]^+$ or, alternatively, with carbon monoxide to yield carbonyl complexes such as $[Rh\{P(C_6H_5)_3\}_2(CO)_3]^+$, $[Rh\{P(C_6H_5)_3\}_2CO(S)]^+$ (S = solvent), or $[Rh\{P(C_6H_5)_3\}_3CO]^+$. Further, treatment of the solution-labile species $[Rh\{P(C_6H_5)_3\}_2(CO)_3]^+$ with dienes leads to the isolation of the five-coordinate complexes $[Rh\{P(C_6H_5)_3\}_2(diene)(CO)]^+$. The infrared and nmr ($^1H$ and ^{31}P) of the complexes are discussed. The use of certain complexes as homogeneous catalysts is also briefly investigated.

It is well known that reactions of the dimeric diene complexes of rhodium(I), $[Rh(diene)Cl]_2$, with uncharged monodentate ligands such as triphenylphosphine lead to bridge cleavage and the formation of monomeric species of the type $Rh(diene)P(C_6H_5)_3Cl$.[1–5] We have recently reported[6] that under the appropriate conditions further reaction can also occur in which chloride ion is displaced from the metal by the neutral ligand to form a cationic four-coordinate rhodium(I) complex, viz.

$$Rh(diene)P(C_6H_5)_3Cl \xrightarrow{P(C_6H_5)_3} [Rh(diene)\{P(C_6H_5)_3\}_2]^+ + Cl^-$$
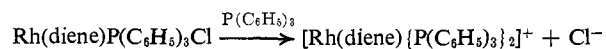
These complexes can be readily isolated from solution by the addition of a suitable precipitating counteranion such as $B(C_6H_5)_4^-$, ClO_4^-, or PF_6^-.

By this route (and, in some cases, by less direct methods) we have prepared a series of cationic diene complexes $[Rh(diene)L_2]^+A^-$, where diene = norbornadiene (NBD) or 1,5-cyclooctadiene (COD); L = tertiary phosphine, phosphite, arsine, or amine; and A = noncoordinating anion. These complexes have some interesting chemical properties. Direct reaction under mild conditions with ligands such as phosphines or carbon monoxide leads to a variety of rhodium(I) complexes, e.g., $[Rh(NBD)\{P(CH_3)_2C_6H_5\}_3]^+$, $[Rh\{P(CH_3)_2C_6H_5\}_4]^+$, and $[Rh\{P(C_6H_5)_3\}_2(CO)_3]^+$. Treat-

ment of solutions of the cationic diene complexes with molecular hydrogen causes reduction of the diene moiety to alkene (and, subsequently, alkane) and species of the type $[RhL_2H_2S_2]^+$ (S = solvent molecule) are produced. These species will react further with phosphines or arsines to yield dihydridorhodium(III) complexes, e.g., $[Rh\{P(CH_3)_3\}_4H_2]^+$, or, alternatively, will react with other dienes to yield rhodium(I)–diene complexes such as $[Rh(1,3\text{-butadiene})\{P(C_6H_5)_3\}_2]^+$. The solvated dihydrido species have also been found to be active catalysts for the homogeneous hydrogenation of a variety of substrates.[6,7] The preparation of the series of catalyst precursors, $[Rh(diene)L_2]^+$, with variation only in the ligand L, has thus enabled a detailed study of the effect of the nature of the ligand L on the catalytic process. The results of this study will be the subject of a subsequent publication.

In this paper the preparations of the cationic species of the type $[Rh(diene)L_2]^+$ and species derived therefrom are described, and the spectroscopic and chemical properties reported. Following our earlier communication of this work,[6] certain of the complexes reported here have been isolated by two other independent research groups.[8–10]

Discussion

The general methods of synthesis and some of the reactions of complexes described in this paper are collected together in the form of flow charts in Figure 1

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