A (π-Acetylene)(σ-vinyl) Transition Metal Complex. The Structure of (σ-Dicyanovinyl)(carbonyl)(π-dicyanoacetylene)-bis(triphenylphosphine)iridium(I) $Ir(-C(CN)=CHCN)(CO)(NCC\equiv CCN)(P(C_6H_5)_3)_2$

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Abstract: The structure of (σ-dicyanovinyl)(carbonyl)(π-dicyanoacetylene)bis(triphenylphosphine)iridium(I), $Ir(-C(CN)=CHCN)(CO)(NCC\equiv CCN)(P(C_6H_5)_3)_2$, has been determined from three-dimensional X-ray data collected by counter methods. The pale pink compound crystallizes in space group C_i^1-$P\bar{1}$ of the triclinic system with two molecules in a reduced unit cell of dimensions a = 12.092 (3) Å, b = 15.987 (4) Å, c = 11.575 (4) Å, α = 93.89 (1)°, β = 115.25 (2)°, and γ = 99.75 (1)°. The observed and calculated densities are 1.46 (2) and 1.51 g cm^{-3}, respectively. Full-matrix least-squares refinement gave a final value of the conventional R factor (on F) of 0.038 for the 2652 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of discrete monomers. The coordination geometry about the metal is distorted trigonal bipyramidal if the π-bonding dicyanoacetylene ligand is considered to be monodentate. The triphenylphosphine ligands occupy the apical coordination sites while the dicyanoacetylene, dicyanovinyl, and carbonyl ligands are in the basal plane. The dicyanoacetylene and dicyanovinyl C–C "triple" and "double" bonds are tipped with respect to the basal coordintion plane 3 (1) and 11 (1)°, respectively. Some important bond distances in Å are Ir–P(1), 2.375 (2); Ir–P(2), 2.382 (3); Ir–C(dicyanoacetylene), 2.07 (1), 2.10 (1); Ir–C(dicyanovinyl), 2.09 (1); and Ir–C(carbonyl), 1.89 (2), while the dicyanoacetylene and dicyanovinyl central C–C bonds are equal at 1.29 (2). The bonding of the dicyanoacetylene ligand is similar to that found for other π-bonding acetylenic groups, with a NC–C–C average bond angle of 140 (1)°. The σ-bonding dicyanovinyl C=C bond length and Ir–C=C bond angle of 135 (1)° agree with the values found for other σ-bonding vinyl groups. The dicyanovinyl ligand has the Ir and H atoms trans to each other.

The binding of unsaturated molecules to transition metals has been extensively studied recently because of the importance of these complexes in homogeneous catalysis. In particular, the binding of cyanocarbons has been studied(1) because their transition metal complexes are generally more stable than the analogous hydrocarbon complexes. For example, cyanoacetylenes form more stable metal–carbon complexes than their corresponding acetylenes,(1) presumably because cyano groups effectively remove some of the π-antibonding electron density that accumulates in the ligand as a result of the d_π–p_π bonding of the metal to the unsaturated ligand molecule.

McClure and Baddley have prepared(2) a novel dicyanoacetylene complex by allowing dicyanoacetylene ($NCC\equiv CCN$) to react with the iridium(I)–hydride complex, $IrH(CO)_2(P(C_6H_5)_3)_2$, to give a product, $Ir(-C(CN)=CHCN)(CO)(NCC\equiv CCN)(P(C_6H_5)_3)_2$, which contains the elements of two molecules of dicyanoacetylene per iridium atom. On the basis of spectroscopic and other measurements they conclude that the complex contains a π-bonded dicyanoacetylene ligand and a σ-bonded dicyanovinyl ligand. The complex was presumed to form from the transfer of a hydrogen atom during 1,2-addition of a bound dicyanoacetylene group followed by the addition of a second molecule of dicyanoacetylene. As such, this σ-vinyl-π-acetylene complex can be considered to be a model for intermediates in the linear polymerization of acetylenes as catalyzed homogeneously by transition metal substrates.

The present structural investigation of this complex is the first determination of a σ-vinyl-π-acetylene transition metal complex. A limited number of monomeric acetylenic complexes have had their structures determined,(3–9) one of which,(7) $PtCl(CH_3)[As(CH_3)_3]_2(F_3CC\equiv CCF_3)$, has trigonal-bipyramidal coordination about the metal. There are only five σ-vinyl type complexes whose structures have been determined.(10–14) Our motivation for doing the present structure is not only to provide further comparative data on metal–acetylene and metal–vinyl bonding but also to provide data that will be useful in understanding the attachment of other unsaturated molecules to transition metals in homogeneous catalysis systems.

The present system is, of course, closely related to the compound $Ir(-NCC(CN)CH(CN)_2)(CO)((CN)_2C=C(CN)_2)(P(C_6H_5)_3)_2\cdot{}^1/_2C_6H_6$ formed by the reaction of

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Table I. Positional and Thermal Parameters for Ir(-C(CN)═CHCN)(CO)(NCC≡CCN)($P(C_6H_5)_3)_2$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	0.22655 (4)[b]	−0.23805 (3)	0.16044 (4)	0.00840 (7)	0.00447 (3)	0.00844 (7)	0.00152 (3)	0.00427 (5)	0.00165 (3)
P(1)	0.0508 (3)	−0.2136 (2)	0.1890 (3)	0.0091 (3)	0.0052 (2)	0.0097 (3)	0.0016 (2)	0.0049 (3)	0.0016 (2)
P(2)	0.4125 (3)	−0.2523 (2)	0.1441 (3)	0.0092 (3)	0.0047 (2)	0.0099 (3)	0.0018 (2)	0.0048 (3)	0.0012 (2)
N(1)	0.2557 (15)	−0.4350 (10)	0.4215 (15)	0.0388 (29)	0.0124 (11)	0.0359 (27)	0.0140 (15)	0.0267 (24)	0.0146 (15)
N(2)	0.4904 (12)	−0.1140 (9)	0.5607 (14)	0.0168 (17)	0.0132 (11)	0.0189 (20)	0.0052 (11)	0.0048 (16)	−0.0018 (12)
N(3)	0.1636 (12)	−0.4882 (8)	0.0761 (14)	0.0183 (17)	0.0053 (7)	0.0289 (24)	0.0004 (9)	0.0091 (16)	−0.0010 (11)
N(4)	−0.0002 (17)	−0.2223 (12)	−0.2329 (14)	0.0351 (29)	0.0145 (14)	0.0170 (20)	0.0092 (16)	0.0118 (19)	0.0024 (12)
O	0.2076 (8)	−0.0863 (6)	0.0164 (9)	0.0188 (13)	0.0075 (6)	0.0197 (14)	0.0045 (7)	0.0111 (11)	0.0065 (7)
C(1)	0.2670 (14)	−0.3720 (11)	0.3777 (14)	0.0197 (21)	0.0094 (10)	0.0181 (20)	0.0074 (12)	0.0123 (18)	0.0059 (13)
C(2)	0.2788 (12)	−0.2968 (10)	0.3244 (11)	0.0146 (16)	0.0062 (8)	0.0114 (15)	0.0046 (10)	0.0080 (14)	0.0051 (11)
C(3)	0.3322 (12)	−0.2162 (10)	0.3621 (12)	0.0110 (15)	0.0074 (9)	0.0099 (17)	0.0038 (10)	0.0053 (14)	0.0019 (10)
C(4)	0.4160 (14)	−0.1615 (10)	0.4718 (14)	0.0122 (17)	0.0101 (10)	0.0108 (17)	0.0036 (11)	0.0025 (14)	−0.0011 (11)
C(5)	0.1390 (13)	−0.4276 (11)	0.0434 (14)	0.0136 (18)	0.0052 (9)	0.0195 (21)	−0.0004 (11)	0.0064 (15)	−0.0009 (12)
C(6)	0.1178 (11)	−0.3405 (10)	0.0112 (12)	0.0077 (13)	0.0118 (13)	0.0054 (14)	0.0006 (10)	0.0012 (12)	−0.0013 (10)
C(7)	0.0376 (17)	−0.3479 (11)	−0.1084 (21)	0.0187 (24)	0.0097 (12)	0.0232 (32)	0.0022 (13)	0.0126 (25)	0.0011 (15)
C(8)	0.0140 (17)	−0.2800 (15)	−0.1728 (20)	0.0198 (25)	0.0123 (17)	0.0219 (31)	0.0042 (17)	0.0108 (23)	0.0007 (17)
C(9)	0.2156 (11)	−0.1446 (9)	0.0678 (12)	0.0120 (15)	0.0067 (8)	0.0137 (16)	0.0029 (9)	0.0078 (13)	0.0032 (9)
H	−0.0119[c]	−0.4087	−0.1634						

[a] The form of the 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] The numbers given here are estimated standard deviations in the least significant figures. [c] This hydrogen atom is attached to C(7) and is at an idealized sp² position with a C–H distance of 1.0 Å and B = 7.0 Å² (the approximate isotropic thermal parameter of C(7)).

2 mol of tetracyanoethylene with $IrH(CO)_2(P(C_6H_5)_3)_2$ in which a cis, not trans, hydrogen transfer occurs to give a keteniminato as well as a π-bonded tetracyanoethylene (TCNE) ligand.[15]

Collection and Reduction of Intensity Data

Clear, pale pink crystals of Ir(–C(CN)═CHCN)(CO)(C_4N_2)-($PPh_3)_2$ were generously supplied by Professor W. H. Baddley. Preliminary Weissenberg and precession photography of the *hk*0, *hkl*, 0*kl*, and *h*0*l* nets showed that the crystals belong to the triclinic system, consistent with space groups $C_1{}^1$-$P1$ or $C_i{}^1$-$P1$. A crystal of approximate dimensions 0.080 × 0.084 × 0.260 mm was chosen for subsequent data collection. Six of the seven faces were identified from optical goniometry as belonging to the forms $\{\bar{1}10\}$, $\{10\bar{1}\}$, and {011}. The seventh face was (010). Cell parameters were determined at 21° from a least-squares refinement of 12 strong high-order reflections centered on a Picker four-circle automated diffractometer[16] using Cu $K\alpha_1$ radiation (λ 1.54056 Å). For the reduced cell they are a = 12.092 (3) Å, b = 15.987 (4) Å, c = 11.575 (4) Å, α = 93.89 (1)°, β = 115.25 (2)°, and γ = 99.75 (1)°. The density calculated for two formula weights per unit cell is 1.51 g cm^{-3} and is in fair agreement with that of 1.46 (2) g cm^{-3} measured by flotation in aqueous $ZnCl_2$.

The mosaicity of the crystal was examined by means of the narrow-source, open-counter, ω-scan technique. The peak width at half-height for a typical strong reflection was found to be 0.07°, which is acceptably low.[17] The intensity data were collected as previously described.[16] The crystal was mounted on the diffractometer such that the spindle axis was approximately collinear with the long dimension of the crystal.

For data collection Cu Kα radiation was used and the beam was prefiltered through 1.0 mil of nickel foil. The intensities were measured by the θ–2θ technique with a 1 deg min^{-1} scan speed. The takeoff angle was set at 1.7°, a value for which the intensity of a reflection was about 80% of the maximum value as a function of takeoff angle. A receiving aperture with windows completely open (6.4 × 6.4 mm) was positioned 32 cm from the crystal directly in front of the counter. A symmetric scan range of ±0.8° in 2θ from the calculated positions of $K\alpha_1$ and $K\alpha_2$ was employed for all reflections. Background counts were measured at each end of the scan for preset times of 10 sec for reflections with $2\theta < 60°$ and 20 sec for all higher order reflections. Attenuators were inserted automatically if the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan; the attenuators used were Cu foils whose thickness had been chosen to give attenuator factors of approximately 2.3. The pulse height analyzer was set for approximately a 90% window centered on the Cu $K\alpha_1$ peak.

The intensities of six standard reflections were measured every 100 reflections. They showed an average deviation from their average intensity of about ±2.7σ. Intensity data were collected for the unique *hkl* planes up to 2θ(Cu $K\alpha_1$) = 88°. Past this angle there were few reflections above background. The data were processed as previously described.[16] The value of p was chosen as 0.05. Of the 3016 reflections observed, 184 had values for F^2 which were less than their standard deviation on F^2. The linear absorption coefficient for the compound for Cu $K\bar{\alpha}$ radiation is 75.5 cm^{-1}. The data were corrected for absorption.[18] The maximum–minimum transmission factors were 0.643 and 0.441, respectively.

Solution and Refinement of the Structure

A three-dimensional Patterson synthesis[19] revealed the positions of the iridium and the two phosphorus atoms. Assuming space group $P\bar{1}$, we refined the positions of these atoms and obtained the discrepancy factors of 0.23 and 0.31, respectively, where weights

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

$$Rw = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2)^{1/2}$$

were taken as $4F_o{}^2/\sigma^2(F_o{}^2)$. In this and succeeding full-matrix least-squares refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, and only the 2652 reflections having $F_o{}^2 > 3\sigma(F_o{}^2)$ were used. Atomic scattering factors for neutral iridium, phosphorus, oxygen, nitrogen, and carbon atoms were taken from the new tabulation.[20] Hydrogen atom scattering factors were those of Stewart, Davidson, and Simpson.[21] Anomalous dispersion effects were included in the calculation of F_c[22] using the values of $\Delta f'$ and $\Delta f''$ for iridium, phosphorus, nitrogen, and oxygen calculated by Cromer and Liberman.[23]

Further three-dimensional difference Fourier syntheses revealed the positions of the remaining nonhydrogen atoms. All phenyl

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[19] In addition to various local programs, those used in this work include modifications of Johnson's ORTEP thermal ellipsoid program and Zalkin's FORDAP Fourier program. Our local least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program.

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Table II. Group and Derived Parameters

Group	x_c[a]	y_c	z_c	δ	ϵ	η
GP11[b]	0.0888 (5)	−0.0273 (4)	0.3397 (5)	−1.553 (5)	2.897 (5)	2.654 (5)
GP12	−0.1924 (6)	−0.2143 (4)	−0.0744 (6)	0.652 (7)	2.544 (6)	−2.979 (8)
GP13	−0.0297 (5)	−0.3486 (4)	0.3462 (6)	2.786 (8)	2.332 (5)	1.539 (8)
GP21	0.5858 (5)	−0.3385 (4)	0.3784 (5)	−0.745 (5)	−3.037 (5)	0.643 (5)
GP22	0.5828 (4)	−0.0699 (3)	0.1586 (5)	0.573 (8)	−2.142 (4)	−0.433 (8)
GP23	0.3726 (5)	−0.3531 (4)	−0.1248 (6)	−2.497 (6)	−2.897 (5)	−1.234 (6)

	Derived phenyl-group carbon atoms					Derived phenyl-group hydrogen atoms[c]			
Group	Atom	x	y	z	B, Å^2	Atom	x	y	z
GP11	C(1)	0.0751 (7)	−0.1083 (4)	0.2754 (5)	5.0 (2)				
	C(2)	−0.0281 (6)	−0.0844 (5)	0.2824 (8)	6.5 (3)	H(2)	−0.1119	−0.1251	0.2418
	C(3)	−0.0144 (7)	−0.0034 (6)	0.3467 (9)	7.7 (3)	H(3)	−0.0884	0.0141	0.3516
	C(4)	0.1024 (9)	0.0538 (4)	0.4041 (8)	7.7 (3)	H(4)	0.1123	0.1120	0.4501
	C(5)	0.2056 (6)	0.0299 (5)	0.3971 (8)	7.5 (3)	H(5)	0.2893	0.0706	0.4388
	C(6)	0.1919 (6)	−0.0511 (5)	0.3327 (8)	5.6 (3)	H(6)	0.2658	−0.0687	0.3291
GP12	C(1)	−0.0878 (7)	−0.2156 (6)	0.0408 (7)	5.5 (3)				
	C(2)	−0.1832 (10)	−0.2895 (5)	−0.0193 (10)	8.9 (4)	H(2)	−0.0271	−0.0868	0.0301
	C(3)	−0.2879 (8)	−0.2881 (6)	−0.1345 (10)	12.1 (5)	H(3)	−0.1775	−0.3428	0.0167
	C(4)	−0.2970 (8)	−0.2129 (8)	−0.1895 (8)	10.2 (5)	H(4)	−0.3559	−0.3390	−0.1811
	C(5)	−0.2016 (10)	−0.1391 (6)	−0.1295 (10)	10.7 (5)	H(5)	−0.3698	−0.2091	−0.2733
	C(6)	−0.0969 (8)	−0.1404 (5)	−0.0143 (9)	7.7 (3)	H(6)	−0.2055	−0.0830	−0.1677
GP13	C(1)	0.0073 (8)	−0.2888 (5)	0.2799 (8)	5.2 (3)				
	C(2)	0.0161 (8)	−0.2619 (4)	0.4015 (8)	6.9 (3)	H(2)	0.0499	−0.2006	0.4434
	C(3)	−0.0209 (9)	−0.3217 (7)	0.4678 (7)	9.0 (4)	H(3)	−0.0145	−0.3039	0.5556
	C(4)	−0.0667 (9)	−0.4083 (6)	0.4126 (10)	9.7 (4)	H(4)	−0.0941	−0.4521	0.4588
	C(5)	−0.0754 (9)	−0.4352 (4)	0.2910 (10)	10.3 (4)	H(5)	−0.1092	−0.2971	0.2498
	C(6)	−0.0385 (9)	−0.3754 (6)	0.2247 (7)	7.6 (3)	H(6)	−0.0447	−0.3937	0.1376
GP21	C(1)	0.5144 (7)	−0.3014 (4)	0.2734 (6)	4.4 (2)				
	C(2)	0.4737 (6)	−0.3874 (4)	0.2798 (6)	5.4 (3)	H(2)	0.3927	−0.4220	0.2083
	C(3)	0.5451 (8)	−0.4245 (4)	0.3847 (8)	6.5 (3)	H(3)	0.5145	−0.4865	0.8376
	C(4)	0.6573 (7)	−0.3757 (6)	0.4833 (7)	7.8 (3)	H(4)	0.7069	−0.4034	0.5578
	C(5)	0.6980 (6)	−0.2897 (5)	0.4770 (7)	8.3 (4)	H(5)	0.7774	−0.2557	0.5485
	C(6)	0.6266 (7)	−0.2526 (4)	0.3720 (8)	6.4 (3)	H(6)	0.6555	−0.1911	0.3692
GP22	C(1)	0.5080 (6)	−0.1488 (4)	0.1516 (7)	4.4 (2)				
	C(2)	0.5786 (7)	−0.1430 (4)	0.0822 (6)	5.2 (3)	H(2)	0.5758	−0.1954	0.0274
	C(3)	0.6534 (7)	−0.0642 (5)	0.0892 (7)	6.6 (3)	H(3)	0.7038	−0.0602	0.0389
	C(4)	0.6575 (7)	0.0090 (4)	0.1655 (8)	7.0 (3)	H(4)	0.7110	0.0654	0.1697
	C(5)	0.5869 (7)	0.0032 (4)	0.2349 (7)	6.5 (3)	H(5)	0.5900	0.0556	0.2890
	C(6)	0.5121 (7)	−0.0757 (5)	0.2280 (7)	5.5 (3)	H(6)	0.4620	−0.0796	0.2775
GP23	C(1)	0.3892 (8)	−0.3119 (5)	−0.0063 (6)	4.9 (2)				
	C(2)	0.3148 (8)	−0.2850 (5)	−0.1213 (8)	6.4 (3)	H(2)	0.2703	−0.2378	−0.1189
	C(3)	0.2982 (8)	−0.3262 (6)	−0.2397 (6)	8.0 (4)	H(3)	0.2415	−0.3082	−0.3223
	C(4)	0.3559 (10)	−0.3943 (6)	−0.2432 (8)	9.1 (4)	H(4)	0.3428	−0.4238	−0.3288
	C(5)	0.4303 (10)	−0.4212 (5)	−0.1283 (11)	10.8 (5)	H(5)	0.4727	−0.4690	−0.1317
	C(6)	0.4470 (8)	−0.3800 (6)	−0.0099 (8)	9.0 (4)	H(6)	0.5014	−0.3986	0.0717

[a] x_c, y_c, and z_c are the fractional coordinates of the group center; δ, ϵ, and η (in radians) have been defined previously.[24] [b] GP11, GP12, and GP13 are the three phenyl ring rigid-body groups attached to P(1); GP21, GP22 and GP23 are attached to P(2). [c] Hydrogen atoms were assigned temperature factors equal to those of the carbon atom to which each hydrogen atom is attached.

rings were then treated as rigid groups[24] of D_{6h} symmetry (carbon–carbon atom distances of 1.397 Å) with overall group temperature factors. The nongroup atoms were assigned isotropic temperature factors and three cycles of least-squares refinement converged to give the discrepancy factors R = 0.068 and Rw = 0.074. The positions of the phenyl hydrogen atoms were idealized (carbon–hydrogen atom distances of 1.00 Å and C–C–H bond angles of 120°) and assigned an isotropic temperature factor equal to the isotropic temperature factor of the carbon atom to which the hydrogen atom was attached. The vinyl hydrogen atom position, located with a peak height of 0.75 (1) e Å^{-3} on a difference Fourier map, was also idealized in the same manner. A fixed-atom structure factor calculation was performed for these hydrogen atoms and applied in two final cycles of full-matrix least-squares refinement in which the nongroup atoms were allowed anisotropic temperature factors while the phenyl group atoms had individual isotropic temperature factors. These last two cycles of refinement included an extinction variable since an inspection of the data showed that for strong low-order reflections $|F_o|$ was consistently less than $|F_c|$, indicating secondary extinction effects. In the final cycle no positional parameter shifted by more than 0.86 of its standard deviation. The extinction coefficient refined to a value of 0.5 (1) × 10^{-6} e^{-2}. The final discrepancy factors were R = 0.038 and Rw = 0.052. The error of an observation of unit weight is 1.62 e^{-1}. The successful refinement indicates that the space group choice, $P\bar{1}$, is correct.

A comparison of $\Sigma w(|F_o| - |F_c|)^2$ for various classes of reflections based upon $|F_o|$, Miller indices, and the scattering angle shows no unusual trends. A final difference Fourier synthesis reveals no peak greater than 0.73 (1) e Å^{-3}, which is approximately $^1/_5$ the height of a typical carbon atom in previous difference maps. The highest peaks are in regions associated with the rigid-body phenyl rings. Of the 374 reflections omitted from the refinement for which $F_o^2 < 3\sigma(F_o^2)$, only one had $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$.

The positional and thermal parameters of the nongroup atoms obtained from the last cycle of least-squares refinement are given in Table I along with the associated standard deviations as estimated from the inverse matrix. The group positional and thermal parameters with their estimated standard deviations are given in Table II, together with the rigid body atom positions which are derived from the group parameters. Root-mean-square amplitudes of vibration of the atoms treated anisotropically are given in Table III. Final values of 10$|F_o|$ and 10$|F_c|$ in electrons have been deposited.[25]

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(24) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965); S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, 87, 2581 (1965); S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965).

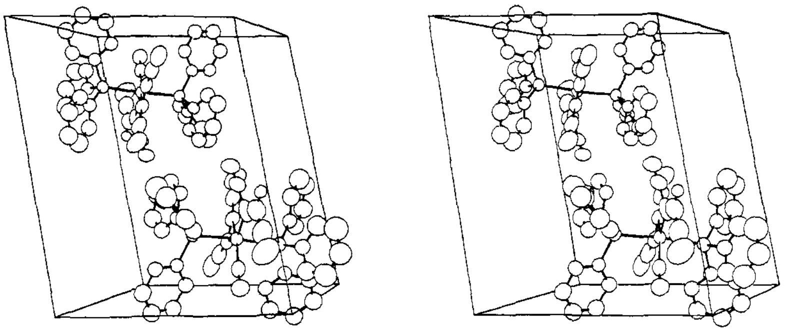

Figure 1. Stereoscopic packing diagram of $\mathrm{Ir(-C(CN){=}CHCN)(CO)(NCC{\equiv}CCN)(P(C_6H_5)_3)_2}$. The view is approximately down z and includes those molecules whose central metal lies within the unit cell. Phenyl hydrogen atoms have been omitted for clarity.

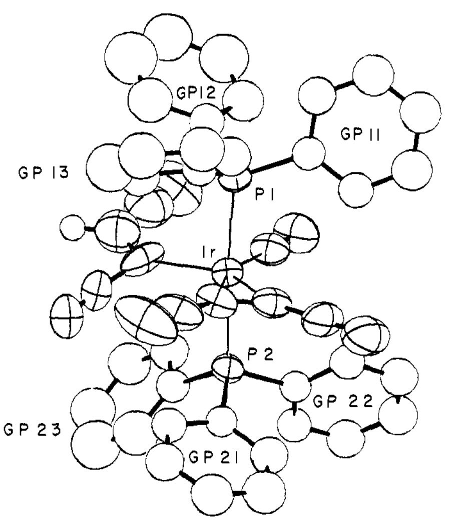

Figure 2. Perspective view of the asymmetric unit. The 50% probability vibrational ellipsoids are shown. Phenyl hydrogen atoms are not shown.

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

Atom	Min	Intermediate	Max
Ir	0.200 (1)	0.219 (1)	0.238 (1)
P(1)	0.212 (4)	0.232 (4)	0.254 (4)
P(2)	0.217 (4)	0.232 (4)	0.242 (4)
N(1)	0.248 (19)	0.339 (16)	0.538 (18)
N(2)	0.296 (16)	0.307 (16)	0.445 (16)
N(3)	0.247 (18)	0.335 (16)	0.414 (17)
N(4)	0.290 (18)	0.377 (20)	0.481 (20)
O	0.231 (13)	0.305 (11)	0.367 (11)
C(1)	0.255 (18)	0.261 (21)	0.389 (18)
C(2)	0.176 (24)	0.248 (16)	0.322 (18)
C(3)	0.221 (18)	0.232 (17)	0.309 (18)
C(4)	0.229 (20)	0.271 (17)	0.379 (17)
C(5)	0.231 (22)	0.306 (20)	0.345 (19)
C(6)	0.162 (24)	0.238 (17)	0.396 (20)
C(7)	0.285 (19)	0.338 (21)	0.376 (22)
C(8)	0.303 (21)	0.349 (23)	0.401 (26)
C(9)	0.223 (18)	0.247 (17)	0.302 (16)

Description of the Structure

The crystal structure of $\mathrm{Ir(-C(CN){=}CHCN)(CO)(NCC{\equiv}CCN)(PPh_3)_2}$ consists of the packing of discrete molecules. A stereoscopic packing diagram is given in Figure 1, while a perspective view of a single molecule, the asymmetric unit, is given in Figure 2. The closest intermolecular contacts are between each nitrogen atom of the asymmetric unit and four different phenyl hydrogen atoms of four different adjacent symmetry-related molecules. The nitrogen to idealized hydrogen atom contact distances are 2.60, 2.52, 2.63, and 2.62 Å for N(1) through N(4), respectively, values which are just slightly less than the N–H van der Waals sum of the radii of 2.7 Å.[26] There are no other unusual intermolecular contacts.

The coordination polyhedron about the iridium atom can be described as distorted trigonal bypyramidal if the π-dicyanoacetylene ligand is considered to be monodentate. The two triphenylphosphine ligands occupy the apical coordination sites, while the carbonyl, dicyanoacetylene, and dicyanovinyl ligands occupy the trigonal plane. The distortions from trigonal-bipyramidal geometry appear to result from the minimization of interaction between the bulky ligands. The apical triphenylphosphine groups bend away from the bulky dicyano groups in the trigonal plane, closing down the P(1)–Ir–P(2) angle to 175.4 (1)°. The two dicyano groups in the trigonal plane minimize their spatial interaction mainly by closing down the C(6)–Ir–C(9) angle from an expected value of about 120 to 101.2 (6)°. There are no unusual close nonbonded contacts between the groups in the trigonal-coordination plane.

Selected bond distances and angles are presented in Figures 3 and 4 as well as in Table IV. Various dihedral angles and vector to plane-normal angles are given in Table V. Table VI contains calculated least-squares planes through various atoms.

The dicyanoacetylene ligand lies in the trigonal plane with the acetylenic C(2)–C(3) bond tilted 3 (1)° with respect to the least-squares plane defined by the coordinating atoms of the trigonal plane. The acetylenic carbon atoms are equidistant from the iridium atom at an average value of 2.09 (1) Å. The dicyanoacetylene group itself is bent; the average C≡C—CN bond angle is 139.5 (13)°. This feature along with the long carbon–carbon central bond will be discussed later. With respect to its own best least-squares plane, the dicyanoacetylene group is slightly boat shaped. The minor

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(25) Tables of the structure factors 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, by referring to code number JACS-73-1095. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(26) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p 189.

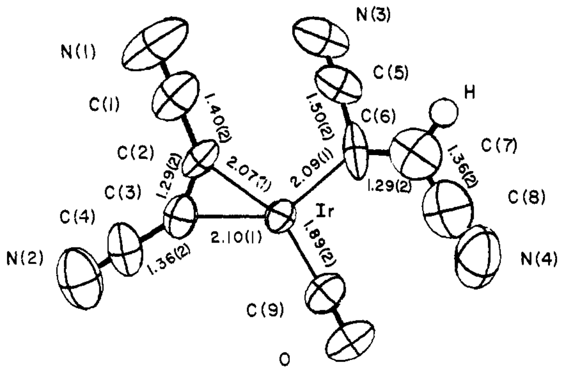

Figure 3. Atom labeling scheme and selected bond distances in the trigonal plane.

Table IV. Selected Bond Distances and Angles

Distance, Å		Angle, deg	
Ir-P(1)	2.375 (3)	P(1)-Ir-P(2)	175.4 (1)
Ir-P(2)	2.382 (3)	P(1)-Ir-C(2)	88.4 (3)
Ir-C(2)	2.074 (11)	P(1)-Ir-C(3)	88.8 (3)
Ir-C(3)	2.097 (12)	P(1)-Ir-C(6)	92.5 (3)
Ir-C(6)	2.085 (13)	P(1)-Ir-C(9)	88.7 (3)
Ir-C(9)	1.888 (15)	P(2)-Ir-C(2)	91.1 (3)
C(9)-O	1.135 (13)	P(2)-Ir-C(3)	88.0 (3)
N(1)-C(1)	1.171 (17)	P(2)-Ir-C(6)	92.1 (3)
N(2)-C(4)	1.148 (16)	P(2)-Ir-C(9)	89.9 (3)
N(3)-C(5)	1.105 (17)	C(9)-Ir-C(2)	155.7 (6)
N(4)-C(8)	1.184 (23)	C(9)-Ir-C(3)	119.7 (6)
C(1)-C(2)	1.402 (20)	C(9)-Ir-C(6)	101.2 (6)
C(2)-C(3)	1.291 (16)	C(2)-Ir-C(3)	36.1 (4)
C(3)-C(4)	1.363 (18)	C(2)-Ir-C(6)	103.0 (6)
C(5)-C(6)	1.502 (20)	C(3)-Ir-C(6)	139.1 (6)
C(6)-C(7)	1.290 (20)		
C(7)-C(8)	1.361 (24)	Ir-C(9)-O	176.5 (11)
P(1)-C(1)(GP11)	1.810 (7)	Ir-C(2)-C(3)	72.9 (7)
P(1)-C(1)(GP12)	1.809 (7)	Ir-C(3)-C(2)	71.0 (7)
P(1)-C(1)(GP13)	1.805 (10)	Ir-C(6)-C(7)	135.2 (14)
P(2)-C(1)(GP21)	1.813 (7)	Ir-C(6)-C(5)	115.3 (9)
P(2)-C(1)(GP22)	1.813 (9)		
P(2)-C(1)(GP23)	1.825 (7)	Ir-P(1)-C(1)(GP11)	114.1 (3)
		Ir-P(1)-C(1)(GP12)	114.9 (4)
		Ir-P(1)-C(1)(GP13)	112.3 (3)
		Ir-P(2)-C(1)(GP21)	113.0 (3)
Nonbonded distances		Ir-P(2)-C(1)(GP22)	112.3 (3)
		Ir-P(2)-C(1)(GP23)	115.7 (3)
Intramolecular		N(1)-C(1)-C(2)	179.2 (17)
Ir-C(7)	3.13 (2)	C(1)-C(2)-C(3)	139.2 (13)
N(4)-H(2)(GP21)	2.51	C(2)-C(3)-C(4)	139.8 (13)
		C(3)-C(4)-N(2)	176.3 (16)
Intermolecular		N(3)-C(5)-C(6)	174.0 (16)
		C(5)-C(6)-C(7)	109.5 (14)
N(1)-H(4)(GP23)[a]	2.60	C(6)-C(7)-C(8)	123.6 (17)
N(2)-H(5)(GP22)[b]	2.52	C(7)-C(8)-N(4)	174.7 (20)
N(3)-H(5)(GP11)[c]	2.63		
N(4)-H(3)(GP13)[d]	2.62		

[a] The symmetry operation for the second atom is $x, y, z + 1$. [b] $-x, -y, 1 - z$. [c] $1 - x, -y, 1 - z$. [d] $x, y, z - 1$.

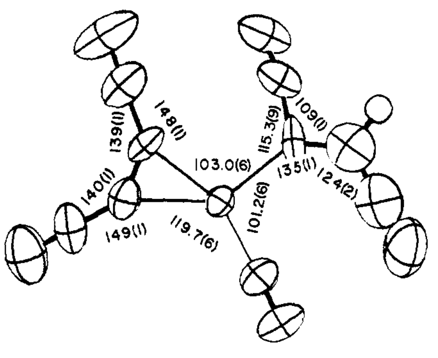

Figure 4. Selected bond angles in the trigonal plane.

Table V. Vector–Plane-Normal and Dihedral Angles (deg)

Vector-plane-normal angles[a]	
C(2)-C(3) Ir, C(2), C(3), C(6), C(9)	87 (1)
C(6)-C(7) Ir, C(2), C(3), C(6), C(9)	79 (1)
N(1)-C(1) C(1), C(2), C(3)	89 (1)
N(2)-C(4) C(4), C(3), C(2)	87 (1)
N(3)-C(5) C(5), C(6), C(7)	88 (2)
N(4)-C(8) C(8), C(7), C(6)	85 (2)
Dihedral angles[b]	
C(1), C(2), C(3) C(4), C(3), C(2)	9 (1)
C(5), C(6), C(7) C(8), C(7), C(6)	11 (1)
C(5), C(6), C(7) Ir, C(2), C(3), C(6), C(9)	19 (1)

[a] Let the two groups of atoms be A(1)-A(2) and B(1)-B(2)-B(3). Form the vector V(1) from A(1) to A(2). Form the vector V(2) from B(1) to B(2). Form vector V(3) from B(1) to B(3). Then the normal to the plane of B(1)-B(2)-B(3) is parallel to V(1) × V(3). The vector-plane-normal angle is defined as the angle between V(1) and the normal to the plane. [b] Let the two groups of atoms be A(1)-A(2)-A(3) and B(1)-B(2)-B(3). Form the normals to these planes as in (*a*). Then the dihedral angle is defined as the angle between the two normals.

buckling of this boat shape at atoms C(4) and N(2) is probably caused by the closest intermolecular contact found in this structure, which is 2.5 Å between N(2) and H(5) of phenyl group 21.

The dicyanovinyl group, nominally considered to be σ bonded to the iridium atom through the sp^2 C(6) atom, has the same coordinating Ir-C bond length as those in the π-bonded dicyanoacetylene group. The vinyl C(6)=C(7) formal double bond is surprisingly short at 1.29 (2) Å, interestingly the same value as for the central C(2)≡C(3) bond in the acetylene ligand. These bonding effects will be discussed later. Also of note is that the 1,2-addition process which produces the dicyanovinyl group occurs trans.

The dicyanovinyl group lies more nearly in its best least-squares plane than does the dicyanoacetylene group, but both groups have the same boat shape. However, the 11 (1)° tilt of the vinyl group C(6)-C(7) vector with respect to the coordination plane is much larger than the 3 (1)° tilt of the acetylene C(2)-C(3) vector to that same plane.

There is considerable distortion of bond distance and angle values from expected values in the dicyanovinyl group, presumably a result of the binding of atom C(6) to the iridium atom. The bond angles about atom C(6) vary considerably from the value of 120° expected for sp^2 hybridization. The C(5)-C(6) bond distance of 1.50 (2) Å approaches a normal C-C single bond distance of 1.54 Å,[27] but the comparable C(7)-C(8) bond is 7σ shorter at 1.36 (2) Å. The cyano group adjacent to the normal single bond has a triple bond that is 4σ

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(27) "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. **11** (1958); *ibid.*, No. **18** (1965).

Table VI. Weighted Least-Squares Planes

	Atoms defining plane	Distance (A) from plane
a	Ir	0.0001 (4)
	C(2)	−0.039 (11)
	C(3)	0.025 (11)
	C(6)	0.003 (12)
	C(9)	−0.025 (11)
b	N(1)	0.652 (15)
	C(1)	0.111 (15)
	C(2)	−0.548 (12)
	C(3)	−0.267 (12)
	C(4)	0.817 (14)
	N(2)	0.294 (14)
c	N(3)	0.064 (13)
	C(5)	−0.001 (14)
	C(6)	−0.024 (11)
	C(7)	−0.189 (15)
	C(8)	−0.035 (18)
	N(4)	0.200 (18)

Equations of the planes are in the form $Ax + By + Cz - D = 0$ (in triclinic coordinates)

	A	B	C	D
a	11.960	−4.481	−5.658	2.868
b	1.404	−2.024	9.813	4.724
c	11.780	0.184	−6.527	1.276

shorter than the other cyano group of this vinyl ligand. Thus the effect of conjugation within the dicyanovinyl ligand is uneven.

The carbonyl ligand is bound to the iridium atom in a perfectly normal manner. The bond distances and angles found in this structure lie more or less in the middle of the range of values for the C–O bond distance and metal–C–O angle found in a survey of 17 second- and third-row transition metal carbonyl complexes.

As previously mentioned, the triphenylphosphine ligands bend away slightly from the two dicyano ligands in the basal plane and the only close intramolecular contact is between N(3) and H(2) of phenyl group 21 (2.5 Å). In addition, the phenyl rings are bent in a direction away from the iridium atom. This is shown by the average Ir–P–C(1) (phenyl group) angle of 113.8 (4)°, slightly larger than the tetrahedral value expected. However there are no unusual close intramolecular contacts between the phenyl rings. A comparison of the bond angle and distance values as well as the Ir–P distances with 15 similar iridium(I) complexes that contain the triphenylphosphine ligand shows that the values found in the present complex are completely normal, falling in the middle of the ranges of previously reported values.[28-31]

Discussion

The nature of the bonding of acetylene complexes has been discussed in recent reviews,[14,32] and the results of this structural study support the arguments presented there. Acetylene–metal bonding and geometry can be described using a modified Dewar–Chatt–Duncanson model[33] or a model based upon the superposition of electronic ground-state and low-lying excited-state geometries.[32] Both bonding descriptions predict that the stronger the metal–acetylene bonding, the lower the bond order will be, resulting in a longer C≡C bond. Electron-withdrawing groups on the acetylene should help stabilize the bonding by removing π-antibonding electron density from the C≡C bond. Both bonding models also predict that an increase of electron density in the C≡C π-antibonding orbital of a coordinated acetylene leads to a cis-bent structure.[32-34]

Table VII summarizes the known structures of monomeric complexes with coordinated acetylenes. As can be seen, there seems to be a correlation between the C≡C bond length and the R—C≡C bond angle. The trend observed is consistent with the above bonding arguments. As the back-bonding of electron density from the metal to the antibonding π orbitals on the acetylene increases, the C≡C bond length increases and the R—C≡C angle value decreases. Further comparisons between the complexes listed in Table VII are difficult to make because of the lack of similarity between the various species and the large standard deviations associated with their parameters.

Table VII. Geometry of Uncoordinated and Nonbridging Coordinated Acetylenes

Acetylene	C≡C distance, Å	R—C≡C angle, deg	Ref
Uncoordinated RC≡CR	1.202 (5)[a]	180	27
$PtCl_2[(CH_3)_3CC{\equiv}CC(CH_3)_3]$-(*p*-toluidine)	2.24 (2)	162, 165 (1)	3
$Nb(\pi\text{-}C_5H_5)(CO)$-$(C_6H_5C{\equiv}CC_6H_5)$-$[\pi\text{-}C_4(C_6H_5)_4]$	1.26 (4)	142 (3)	4
$Ni(C_6H_5C{\equiv}CC_6H_5)$-$[(CH_3)_3CN{\equiv}C]_2$	1.28 (2)	149 (1)	5
$Ir(-C(CN){=}CHCN)(CO)$-$(NCC{\equiv}CCN)(P(C_6H_5)_3)_2$	1.29 (2)	140 (1)	This work
$W(C_6H_5C{\equiv}CC_6H_5)_3(CO)$	1.30	140	6
$PtCl(CH_3)[As(CH_3)_3]_2$-$(F_3CC{\equiv}CCF_3)$	1.32 (4)	135, 150 (4)	7
$Pt(C_6H_5C{\equiv}CC_6H_5)$-$[P(C_6H_5)_3]_2$	1.32 (9)	140	8
$Nb(\pi\text{-}C_5H_5)(CO)$-$(C_6H_5C{\equiv}CC_6H_5)_2$	1.35 (2)	138 (4)	9
Uncoordinated $\underset{R}{>}C{=}C\underset{R}{<}$	1.339 (2)	117.3 (3)	27

[a] An early X-ray structure determination (R. B. Hannan and R. L. Collins, *Acta Crystallogr.*, **6**, 350 (1953)) of dicyanoacetylene gives C≡C, 1.19 Å, and (NC)—C≡C, 180°.

A comparison of the dicyanoacetylene group of this study with other ethylenic cyano groups in similar structures, $IrH(CO)$(*trans*-$H(NC)C{=}C(CN)H)(P(C_6H_5)_3)_2$,[35] $IrBr(CO)((NC)_2C{=}C(CN)_2)(P(C_6H_5)_3)_2$,[36] and $Ir(C_6N_4H)(CO)((NC)_2C{=}C(CN)_2)(P(C_6H_5)_3)_2$,[15] yields some interesting information. All of the above complexes, as well as the C_2F_4 complex of $IrI(CO)(P(C_6H_5)_3)_2$,[37] have trigonal-bipyramidal coordination ge-

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(28) B. A. Frenz and J. A. Ibers, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.*, in press, Table VIII and references cited therein.

(29) J. Clemens, M. Green, M.-C. Kuo, C. J. Fritchie, Jr., J. T. Mague, and F. G. A. Stone, *J. Chem. Soc. D*, 53 (1972).

(30) M. S. Weininger, I. F. Taylor, Jr., and E. L. Amma, *ibid.*, 1172 (1971).

(31) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 10, 1479 (1971).

(32) L. D. Pettit and D. S. Barnes, *Fortschr. Chem. Forsch.*, 28, 85 (1972), and references cited therein.

(33) J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, **91**, 7005 (1969).

(34) A. C. Blizzard and D. P. Santry, *ibid.*, **90**, 5749 (1968).

(35) L. Manojlović-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, **47**, 84 (1969); K. W. Muir and J. A. Ibers, *J. Organometal. Chem.*, **18**, 175 (1969).

(36) J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968).

(37) N. E. Kime, Doctoral Dissertation, Northwestern University, 1968.

ometry with the triphenylphosphine groups cis to each other rather than the trans arrangement found in diffraction studies of all other five-coordinate additional complexes of the parent complex, $IrX(CO)(P(C_6H_5)_3)_2$ (X = H or halogen). It was concluded[35] from appropriate molecular models that steric considerations preclude the placing of a bulky substituted olefin in the basal plane of a trigonal bipyramid that has apical trans triphenylphosphines. The dicyanoacetylene ligand is much less bulky than cyano substituted olefin ligands and can be located in the basal plane without suffering from abnormal close contacts, as mentioned earlier. There appears to be no trans influence from the triphenylphosphine groups; the average Ir–P (trans) distance for the present dicyanoacetylene complex of 2.379 (3) Å falls in the middle of the range of the three percyanoethylene Ir–P(cis) distances of 2.317 (3),[35] 2.400 (3),[36] and 2.392 (7) Å.[15] Probably the most important factor influencing these distances is the π-bonding strengths of the other coordinating ligands. There is a range of π-bonding strength present in these complexes, as indicated by the length of the central multiple C–C bond which correlates with the strength of the metal-unsaturated ligand bond, as we discussed previously. The central $C{\equiv}C$ bond distances given in Table VII range from values close to a normal triple bond (1.24 Å) to a normal double bond (1.35 Å). The range of similar central ethylenic $C{=}C$ bond distances range from values close to a normal double bond (1.41 Å)[35] to a normal single bond (1.53 Å).[15]

It is also interesting to compare the π-dicyanoacetylene group and the σ-dicyanovinyl group with the solid-state structure of pure dicyanoacetylene.[38] As can be seen in Table VIII, all bond distance values of the π-acetylene and σ-vinyl groups are within 3σ of the free dicyanoacetylene (DCNA) values except for the $C{\equiv}C$ bond values (which are the same for the π-acetylene and σ-vinyl groups) and the C–C* of the σ-vinyl group. With one exception, all comparable vinyl and acetylene group bond distances are within 3σ of each other. The Ir–C (vinyl or acetylene) distances are also the same. Hence the π-acetylene and σ-vinyl groups are remarkably similar, differing only in the bond angles about the carbon atom (C*) attached to the iridium atom. Churchill indicates[39] that there is a contraction relative to metal–C(sp^2) single bonds for metal–C(σ-vinyl) bonds of about 0.1 Å, indicating an increase in the M–C(σ-vinyl) bond order of about 1.15–1.25. This is explained by a drift of electrons from the metal atom into the ligand group. How this might affect the $C{=}C$ bond in the vinyl group is unknown. Table IX gives some structural data for all known σ-vinyl ligands bonded to transition metals. The number of data is small, the nature of the complexes is diverse, and the standard deviations of the numbers are large so that no conclusions can be drawn.

Table VIII. Bond Distances (Å) of the π-Acetylene and σ-Vinyl Groups[a]

	$N{\equiv}C$	C—C*	$C^*{\equiv}C$	C—C	$C{\equiv}N$
Free DCNA	1.14	1.37	1.19		
π-Acetylene	1.17 (2)	1.40 (2)	1.29 (2)	1.36 (2)	1.15 (2)
σ-Vinyl	1.11 (2)	1.50 (2)	1.29 (2)	1.36 (1)	1.18 (2)

[a] Asterisk signifies carbon bound to metal in σ-vinyl group.

Table IX. Geometry of σ-Vinyl Ligand Groups

	$C{\equiv}C$ distance, Å	$M{-}C{=}C$ angle, deg	Ref
$(C_6H_5C_2COOCH_3)_3COFe(CO)_2$	1.26 (3)	?	10
(*cis*-$HFC{=}CF)Mn(CO)_5$	1.28 (4)	130	11
$Ir({-}C(CN){=}CHCN)(CO)(NCC{\equiv}CCN)(P(C_6H_5)_3)_2$	1.29 (2)	135 (1)	This work
$(\pi\text{-}C_5H_5)Fe(CO)_2C_4H_5SO_2$	1.31 (1)	129.1 (7)	12
(BAE)[a] $Co(CH{=}CH_2)(H_2O)$	1.33 (2)	127.2 (9)	13
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2C_4H_4$	1.340 (7)[b]	131.8 (4)	14

[a] BAE = *N,N'*-ethylenebis(acetylacetone iminato). [b] Bridging vinyl group.

The addition of metal hydrides to olefinic or acetylenic molecules leads often to stereospecifically monohydrogenated ligands. The mechanism for the formation of the present complex, $Ir({-}C(CN){=}CHCN)(NCC{\equiv}CCN)(CO)(P(C_6H_5)_3)_2$, has not been investigated, but the 1,2 addition across a dicyanoacetylene triple bond to give the σ-dicyanovinyl ligand occurs exclusively trans in the material isolated as crystals. Stereospecific trans addition of metal hydrides to acetylenes has been explained[40] as occurring when the source of the hydrogen is exo, a further molecule of metal hydride or a solvent molecule. By contrast, cis addition has been suggested[41,42] to occur through intramolecular addition processes, those in which the hydrogen atom is attached to the same metal that is interacting with the ligand. Pale pink crystals of Ir(*trans*-$C(CN){=}CHCN)(NCC{\equiv}CCN)(CO)(P(C_6H_5)_3)_2$ were obtained after adding methanol to an intense greenish black solution of dicyanoacetylene and starting material, $IrH(CO)_2(P(C_6H_5)_3)_2$. It is conceivable that the source of the exo hydrogen atom is methanol. In view of the interest in this type of compound as an intermediate in the polymerization of acetylenes, there is clearly a need for additional mechanistic as well as structural data.

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