set yielded the positions of the remaining nonhydrogen atoms. A difference map computed after full-matrix isotropic refinement showed electron density in a region where no atoms were expected. This was interpreted as a disordered methanol molecule and fitted isotropically with one oxygen and two disordered carbon atoms. Several cycles of blocked least-squares refinement were then undertaken in which the atomic coordinates were refined in one matrix and the anisotropic temperature factors and the scale factor in another. The methanol parameters were not refined. A subsequent difference map then revealed the six methyl hydrogens. The other hydrogen atom positions were calculated by using a C–H bond length of 1.0 Å; all positions showed appreciable electron density. The hydrogen atoms were given isotropic temperature factors 1.0 Å^2 larger than the isotropic temperature factors of the atoms to which they were bonded. The final refinement of the 334 parameters, not including the parameters for the methanol or hydrogen atoms, was performed with the same two matrices by using all 4703 reflections with $I > \sigma(I)$. The final R index was 0.066. The only features above 0.7 e/Å^3 on a late difference map were near the copper atoms.

In the above model, one of the two copper atoms (Cu2) exhibited an unusually elongated thermal ellipsoid. A difference Fourier map in the plane of the two largest principal axes suggested disorder; several more cycles of refinement were run in which the anisotropic copper was replaced by two isotropic copper atoms and a population factor. This second model has the same number of parameters as the first. It converged as well to an R of 0.065. The final goodness of fit, $\sum w(k^2F_o^2 - F_c^2)^2/(n-p)$, where n is the number of observations and p the number of parameters, was 1.48. Another difference map in the same plane indicated that this model was indeed slightly better in representing the observed electron density. A final difference Fourier map of the entire asymmetric unit was essentially featureless.

Acknowledgment. We gratefully appreciate assistance from T. J. Smith and financial assistance from the National Science Foundation (Grant No. CHE 76-82124).

Registry No. $Cu^{II}Cu^{I}L(ClO_4)\cdot 0.5CH_3OH$, 72882-14-5.

Supplementary Material Available: Listings of observed and calculated structure factors and hydrogen atom parameters (30 pages). Ordering information is given on any current masthead page.

(21) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368. Main, P.; Woolfson, M. M.; Lessinger, L.; Germain, G.; Declerq, J. D. "Multan 74, a System of Computing Programmes for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data"; University of York, York, England, and Laboratoire de Chimie Physique et de Cristallographic, Louvain-la-Neuve, Belgium, Dec 1974.

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Structure of Bis(triphenylphosphine)(tetrachlorodiazocyclopentadiene)chloroiridium(I) Toluene Solvate, $IrCl(N_2C_5Cl_4)(P(C_6H_5)_3)_2\cdot C_7H_8$

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The structure of bis(triphenylphosphine)(tetrachlorodiazocyclopentadiene)chloroiridium(I) toluene solvate, $IrCl(N_2C_5Cl_4)(PPh_3)_2\cdot C_7H_8$, has been determined crystallographically and consists of discrete molecules of the neutral diazo complex and solvent. The complex crystallizes from toluene–hexane in the monoclinic space group C_{2h}^5-$P2_1/c$ with four formula units in a unit cell of dimensions a = 12.136 (4) Å, b = 24.276 (15) Å, c = 17.849 (7) Å, β = 121.13 (2)°, ρ_{obsd} = 1.56 (3) g/cm^3, and ρ_{calcd} = 1.584 g/cm^3. The structure was solved by Patterson methods. Least-squares refinement has led to a final value of the conventional R index of 0.048 based on 5704 reflections. This complex of iridium(I) possesses square-planar geometry with trans phosphine ligands, P(1)–Ir–P(2) = 176.46 (7)°; the neutral diazo ligand $N_2C_5Cl_4$ is trans to Cl(1), Cl(1)–Ir–N(1) = 172.72 (19)°, and possesses the singly bent geometry Ir–N(1)–N(2) = 174.6 (6)° and N(1)–N(2)–C(1) = 141.2 (7)°. The substituted cyclopentadiene ring displays regular planar geometry with average C–C distances of 1.39 (2) Å and angles of 108.1 (16)°. Some important molecular parameters are Ir–N(1) = 1.824 (6) Å, N(1)–N(2) = 1.163 (7) Å, N(2)–C(1) = 1.347 (9) Å, Ir–Cl(1) = 2.297 (2) Å, Ir–P(1) = 2.338 (2) Å, and Ir–P(2) = 2.350 (2) Å.

During the past 10 years, there has been a growing interest in the synthesis and structures of transition-metal compounds containing the aryldiazo ligand, N_2R^+.[1,2] Aryldiazo complexes have been reported for all the members of the Cr, Mn, Fe, Co, and Ni triads with the exception of Ni and Tc.[3–5] Part of the interest in aryldiazo and other diazo ligands has been generated by their close relationship to dinitrogen and nitrosyl ligands. Aryldiazo ligands, like nitrosyl ligands, have been found to adopt varying modes of attachment to transition metals,[5,6] and such variations may be used as a sensitive probe of the metal center and its reaction chemistry.[7–9] In spite of the fact that

(1) Albini, A.; Kisch, H. *Top. Curr. Chem.* **1976**, *65*, 105–45.
(2) Sutton, D. *Chem. Soc. Rev.* **1975**, *4*, 443–70.
(3) Haymore, B. L.; Ibers, J. A.; Meek, D. W. *Inorg. Chem.* **1975**, *14*, 541–6. Haymore, B. L. *J. Organomet. Chem.* **1977**, *137*, C11–5.
(4) Bowden, W. L.; Little, W. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 5084–5. Dart, J. W.; Lloyd, M. K.; Mason, R.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2039–45. Garner, A. W. B.; Mays, M. J. *J. Organomet. Chem.* **1974**, *67*, 153–60. N. G. Connelly, Demidowicz, Z. *Ibid.* **1974**, *73*, C31–2. Brownlee, G. S.; Carty, P.; Cash, D. N.; Walker, A. *Inorg. Chem.* **1975**, *14*, 323–7. Haymore, B. L.; Ibers, J. A. *Ibid.* **1975**, *14*, 2784–95.
(5) (a) Cowie, M.; Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7608–17. (b) Carroll, J. A.; Cobbledick, R. E.; Einstein, F. W. B.; Farrell, N.; Sutton, D.; Vogel, P. L. *Inorg. Chem.* **1977**, *16*, 2462–9. Rattray, A. D.; Sutton, D. *Inorg. Chim. Acta* **1978**, *27*, L85–6.
(6) (a) Avitabile, G.; Ganis, P.; Nemiroff, M. *Acta Crystallogr., Sect. B* **1971**, *27*, 725–31. (b) Gaughan, A. P., Jr.; Haymore, B. L.; Ibers, J. A.; Meyers, W. H.; Nappier, T. E.; Meek, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 6859–61.
(7) Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2713–22. Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 176–7.
(8) Cowie, M.; Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2617–23. Haymore, B. L.; Ibers, J. A. *Ibid.* **1975**, *14*, 1369–76. Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369–79.
(9) Parshall, G. W. *J. Am. Chem. Soc.* **1965**, *87*, 2133–6; **1967**, *89*, 1822–6. Ittel, S. D.; Ibers, J. A. *Ibid.* **1974**, *96*, 4804–9. Ittel, S. D.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 636–40.

0020-1669/80/1319-1231$01.00/0

a number of neutral diazo molecules, N_2R, are found in the literature,[10] studies on the coordination and reaction chemistry of these ligands are just beginning to be undertaken.[11] The use of neutral diazo molecules as ligands to form transition-metal–diazo complexes presents a special challenge since loss of dinitrogen from these molecules is very facile.[12] However, on the basis of our recent work on the complexes[13] Ni(diazofluorene)(t-BuNC)$_2$[14] and $RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$,[15] it appears as though the bonding modes and the reaction chemistry of neutral RN_2 species with transition metals will differ considerably from the more heavily studied RN_2^+ species.

In complexes containing either coordinated RN_2^+ or RN_2 ligands the use of infrared ν(NN) stretching frequencies has proved invaluable in predicting the geometries of these ligands.[16] The complex $IrCl(N_2C_5Cl_4)(PPh_3)_2$,[17] prepared by the reaction of $IrCl(N_2)(PPh_3)_2$ with $N_2C_5Cl_4$, shows a very weak infrared ν(NN) stretching frequency at approximately 1858 cm^{-1}. However, this complex shows a strong band in the resonance Raman spectrum at 1872 cm^{-1}. Since this value of ν(NN) lies in the region expected for the "singly bent" geometry,[16] and thus represents a new coordination geometry for neutral diazo complexes, we decided to determine the structure of the compound $IrCl(N_2C_5Cl_4)(PPh_3)_2$. A preliminary report of this work has been published.[17]

Experimental Section

Crystal Preparation. The title compound was prepared by addition of the diazo species $N_2C_5Cl_4$[18] in chloroform solution to a chloroform solution of $IrCl(N_2)(PPh_3)_2$[19] at 0 °C. After addition of the ligand, the solution became dark green and was stirred at 0 °C overnight. The solvent was removed under vacuum, and the dark green solid was dissolved in a minimum amount of toluene. Crystallization from toluene–hexane gave the final product as dark green, slightly air-sensitive prisms, yield 96%. Anal. Calcd for $C_{48}H_{38}Cl_5IrN_2P_2$: C, 53.66; H, 3.54; N, 2.61. Found: C, 52.50; H, 3.41; N, 2.66.

Crystallographic Data. In a drybox crystals were mounted in glass capillaries under an inert atmosphere of dinitrogen. Preliminary film data showed the crystals to belong to the monoclinic system with systematic extinctions ($0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$) consistent with the space group C_{2h}^5-$P2_1/c$. Accurate unit cell dimensions were determined by a least-squares analysis of the angular positions of 12 hand-centered reflections in diverse regions of reciprocal space (in the range $57° \geq 2\theta(CuK\alpha_1) \geq 50°$). See Table I for pertinent crystal information and details of data collection.

Data collection was carried out at room temperature on a Picker four-circle diffractometer. Background counts were measured at both ends of the scan range, with both the counter and the crystal stationary. The intensities of six standard reflections were measured every 100 reflections. These were found to decrease linearly by about 15% during the course of data collection, presumably as a result of crystal decomposition. Intensities for reflections $\pm h,-k,+l$ were measured out to $2\theta = 121°$ by using Cu Kα radiation. A value of $p = 0.04$ was used in the calculation of $\sigma(F_o^2)$.[20] Of the 7255 reflections measured, 5998 were unique, and of these 5704 have $F_o^2 > 3\sigma(F_o^2)$. An absorption correction was applied to the data by using Gaussian integration.[21]

Table I. Summary of Crystal Data and Intensity Collection

compd	$IrCl(N_2C_5Cl_4)(P(C_6H_5)_3)_2 \cdot C_7H_8$
formula	$C_{48}H_{38}Cl_5IrN_2P_2$
fw	1074.26
a	12.136 (4) Å
b	24.276 (15) Å
c	17.849 (7) Å
β	121.13 (2)°
V	4502 Å^3
Z	4
ρ	1.584 (calcd), 1.56 (3) (obsd) g/cm^3
space group	C_{2h}^5-$P2_1/c$
cryst dimens; V	0.32 × 0.36 × 0.70 mm; 0.050 mm^3
cryst shape	prism with bounding planes {100}, {011}, {010}, (103)
temp	21.3 °C
radiation	Cu Kα (λ(Cu Kα_1) = 1.540 562 Å)
μ (Cu Kα)	94.0 cm^{-1}
transmission factors	0.057–0.223
receiving aperature	4.1 mm wide × 3.1 mm high; 33 cm from the crystal
takeoff angle	4.5°
scan speed	2.0° in 2θ/min
scan range	1.0° below Kα_1 to 1.0° above Kα_2
bkgd counting time, total	20 s
2θ limits	5–121°
final no. of variables	222
unique data used	5704 $F_o^2 > 3\sigma(F_o^2)$
error in observn of unit wt	2.27 e
R	0.048
R_w	0.064

Solution and Refinement of the Structure. The iridium, chlorine, and phosphorus atoms were located readily from a sharpened, origin-removed Patterson synthesis. Full-matrix least-squares refinements and difference Fourier syntheses were used to locate all remaining atoms. The functions $\sum w(|F_o| - |F_c|)^2$ was minimized, in which $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights, w, are taken as $4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors were taken from the usual tabulation.[22] Anomalous dispersion terms for Ir, P, and Cl were included in F_c.[23]

Each phenyl group was treated throughout the refinement as a planar rigid body with uniform C–C distances of 1.395 Å and individual isotropic thermal parameters for each carbon atom. The toluene solvate was also treated as a rigid body with a fixed C(methyl)–C(ring) distance of 1.530 Å. Owing to the high thermal parameters of the carbon atoms of the toluene solvate, the occupancy of the entire toluene ring was varied in the final two cycles of least-squares refinement; the final refinement converged to an occupancy of 0.83 (1) for the toluene molecule. However, because the thermal parameters and the occupancy are strongly correlated, we take the toluene solvate to possess full occupancy. The ring carbon atoms of the diazo ligand were refined as individual atoms with anisotropic thermal parameters. All phenyl hydrogen atom positions

(10) Cox, A. P.; Thomas, L. F.; Sheridan, J. *Nature (London)* **1958**, *181*, 1000–1. Lemal, D. M.; Menger, F.; Clark, G. W. *J. Am. Chem. Soc.* **1963**, *85*, 2529–30. Zimmerman, H. E.; Paskovich, D. H. *Ibid.* **1964**, *86*, 2149–60. Obata, N.; Moritani, I. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1975–80. Ansell, G. B. *J. Chem. Soc. B* **1969**, 729–32. Presley, C. T.; Sass, R. L. *Acta Crystallogr., Sect. B*, **1970**, *26*, 1195–1202. Abraham, D. J.; Cochran, T. G.; Rosenstein, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 6279–81. Murahashi, S. I.; Yoshimura, Y.; Yamamoto, Y.; Moritani, I. *Tetrahedron* **1972**, *28*, 1485–96. Hope, H.; Black, K. T. *Acta Crystallogr., Sect. B* **1972**, *28*, 3632–4.
(11) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800–12 and references therein.
(12) Reimer, K. J.; Shaver, A. *J. Organomet. Chem.* **1975**, *93*, 239–52. Reimer, K. J.; Shaver, A. *Inorg. Chem.* **1975**, *14*, 2707–16. Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 599.
(13) Abbreviations: t-BuNC = *tert*-butyl isocyanide; Me = methyl; Ph = phenyl.
(14) Nakamura, A.; Yoshida, T.; Cowie, M.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2108–17.
(15) Schramm, K. D.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3287–93.
(16) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3060–70
(17) Schramm, K. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 2932–3.
(18) Disselnkötter, H. *Angew. Chem.* **1964**, *76*, 431–2.
(19) Collman, J. P.; Hoffman, N. W.; Hosking, J. W. *Inorg. Synth.* **1970**, *12*, 8–11.
(20) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204–10.
(21) The Northwestern absorption program AGNOST includes the Coppens–Leiserowitz–Rabinovich logic for Gaussian integration. In addition to local programs for the CDC 6600 computer, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program, Johnson's ORTEP II thermal ellipsoid plotting program, Busing and Levy's ORFFE error function program, and Dewar's program FAME for generation of normalized structure factors. Our full-matrix, least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program.
(22) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. For hydrogen atoms see: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–86. For the values of $\Delta f'$ and $\Delta f''$ for Ir, P, and Cl, see Cromer, D. T.; Liberman, D. *Ibid.* **1970**, *53*, 1891–8.
(23) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781–2.

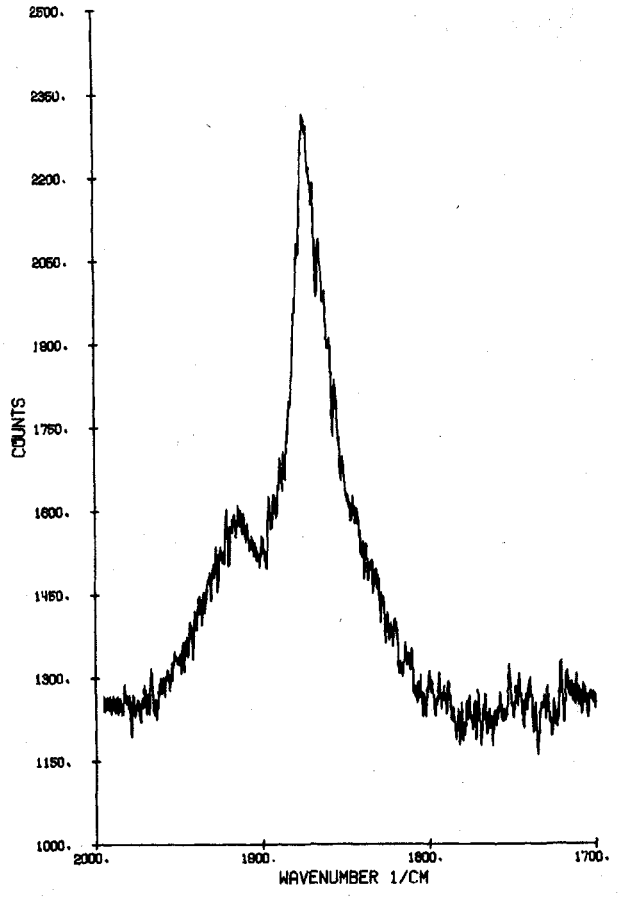


Figure 1. Resonance Raman spectrum of $IrCl(N_2C_5Cl_4)(PPh_3)_2$ using 4579-Å Ar^+ excitation.

were idealized; the C–H distance was assumed to be 0.95 Å with normal C–C–H bond angles. The isotropic thermal parameter of a hydrogen atom was assumed to be 1.0 $Å^2$ larger than the thermal parameter of the carbon atom to which it is attached. All hydrogen atoms were included as fixed contributions in the final anisotropic refinements.

The final agreement indices, based on 5704 significant observations and 222 variables, are $R = 0.048$ and $R_w = 0.064$. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices shows no unusual trends other than slightly higher error values at lower 2θ values. This trend is indicative of an inadequate description of the toluene solvate. The highest peak in the difference Fourier map of 1.2 (1) e $Å^{-3}$ is located near carbon atoms C(34) and C(35) and is about 20% of the height of a typical carbon atom in this structure.

The final positional and thermal parameters of atoms and groups appear in Tables II and III, the idealized positions of the hydrogen atoms in Table IV,[24] and the root-mean-square amplitudes of vibration in Table V.[24] A listing of the observed and calculated structure amplitudes is available.[24]

Resonance Raman Spectroscopy. The resonance Raman spectrum (Figure 1) of the title complex was recorded on a 0.85-m Spex 1401 double-monochromator spectrometer with photon-counting detection.[25] A light-stabilized Spectra Physics 164 Ar^+ laser was employed; the spectrum was taken at room temperature with 4579-Å excitation by utilizing the 180° backscattering geometry and spinning samples. To avoid excessive decomposition, we employed a power of 20 mW, with 10 mW at the sample.

The UV–visible spectrum of the complex is shown in Figure 2. The 4000-Å band in this spectrum is probably a Ir–L charge-transfer band since use of the 4579-Å excitation line did result in a Raman band at 1872 cm^{-1} which we assign to ν(NN). When the 5145-Å excitation line was used, no Raman band at 1872 cm^{-1} was observed.

(24) Supplementary material.
(25) Shriver, D. F.; Dunn, J. B. R. *Appl. Spectrosc.* **1974**, *28*, 319–23.

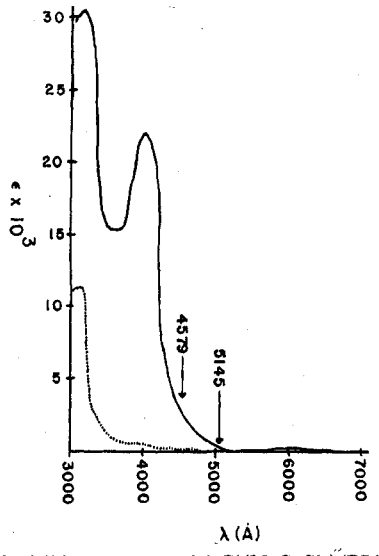


Figure 2. UV–visible spectrum of $IrCl(N_2C_5Cl_4)(PPh_3)_2$ (—) and $N_2C_5Cl_4$ (···) in toluene solution.

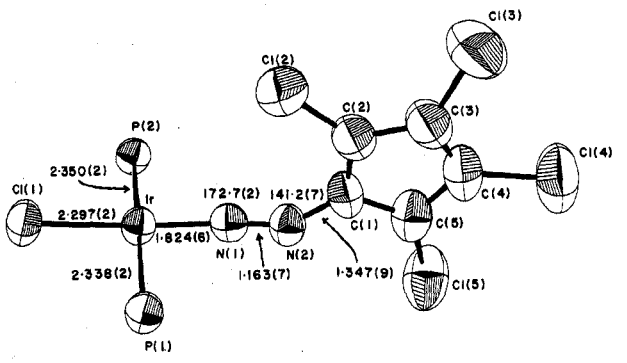


Figure 3. The coordination sphere with some bond distances and angles for $IrCl(N_2C_5Cl_4)(PPh_3)_2$. Vibrational ellipsoids are drawn at the 50% probability level.

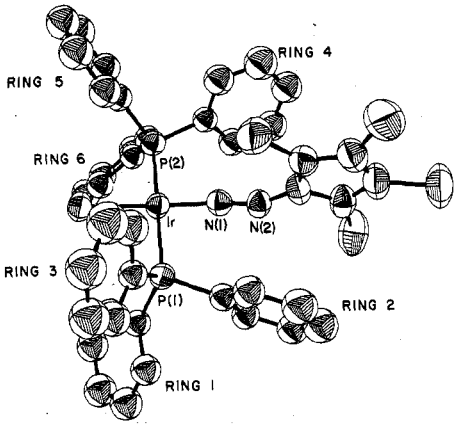


Figure 4. Drawing of an individual molecule of $IrCl(N_2C_5Cl_4)(PPh_3)_2$. Vibrational ellipsoids are drawn at the 50% probability level. The H atoms have been omitted for the sake of clarity.

Results and Discussion

The crystal structure of $IrCl(N_2C_5Cl_4)(PPh_3)_2 \cdot C_7H_8$ consists of the packing of four molecules of the iridium complex and four toluene molecules in the unit cell. The labeling scheme for this complex, together with some bond distances and angles, is shown in Figures 3 and 4. A stereodrawing of the unit cell is shown in Figure 5. There are no significant intermolecular contacts, the shortest being H(22)–H(35) = 2.50 Å, H(55)–H2C(77) = 2.48 Å, and H(72)–H3C(77) = 2.23 Å.

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $IrCl[N_2C_5Cl_4][P(C_6H_5)_3]_2 \cdot C_7H_8$

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
IR	0.048700(27)	0.218400(13)	-0.243960(19)	91.76(34)	21.76(7)	45.22(17)	-3.27(11)	34.91(18)	-3.70(8)
P(1)	-0.12416(17)	0.244397(82)	-0.22865(12)	97.2(17)	22.49(39)	47.22(85)	-2.37(68)	37.3(10)	-3.91(47)
P(2)	0.22106(17)	0.197478(86)	-0.26375(12)	98.7(18)	23.10(38)	51.54(93)	0.18(68)	40.1(11)	-1.17(49)
CL(1)	0.18210(18)	0.266653(91)	-0.11615(12)	109.0(18)	32.33(49)	52.55(91)	-6.69(74)	32.4(11)	-10.85(53)
CL(2)	-0.03801(25)	0.05311(12)	-0.24544(17)	192.2(34)	30.61(55)	83.6(15)	1.6(11)	34.3(18)	6.34(71)
CL(3)	-0.23831(31)	-0.05470(11)	-0.36037(25)	233.2(43)	25.25(55)	171.1(30)	-9.7(12)	92.5(30)	4.1(10)
CL(4)	-0.43368(28)	-0.01332(13)	-0.56656(22)	204.6(36)	43.24(77)	125.5(22)	-42.6(14)	78.6(24)	-37.3(11)
CL(5)	-0.35890(30)	0.11929(13)	-0.58674(16)	243.8(41)	50.55(85)	56.4(12)	-36.8(15)	46.9(18)	-5.47(80)
N(1)	-0.05754(56)	0.17333(24)	-0.33481(38)	112.9(64)	21.3(12)	50.7(31)	-1.3(23)	45.0(39)	-2.5(16)
N(2)	-0.13334(57)	0.14697(26)	-0.39332(40)	112.8(65)	24.1(14)	51.7(31)	-7.4(25)	43.0(39)	-6.7(18)
C(1)	-0.18530(74)	0.09616(33)	-0.41213(51)	130.4(87)	22.3(16)	60.9(42)	-12.1(31)	51.3(52)	-10.2(22)
C(2)	-0.15522(79)	0.05163(36)	-0.35376(58)	129.0(93)	24.2(19)	73.1(51)	-5.5(33)	52.8(57)	-5.9(25)
C(3)	-0.23403(91)	0.00928(36)	-0.39734(66)	166.(11)	23.2(18)	81.7(58)	-8.6(37)	64.3(69)	-6.1(26)
C(4)	-0.31489(89)	0.02657(41)	-0.46550(71)	154.(11)	31.7(24)	95.2(67)	-24.2(43)	70.7(74)	-22.1(32)
C(5)	-0.28548(81)	0.08002(38)	-0.49471(53)	147.(10)	29.4(21)	57.8(44)	-15.8(37)	55.2(56)	-11.2(24)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $\exp[-(B11h^2+B22k^2+B33l^2+2B12hk+2B13hl+2B23kl)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS $\times 10^4$.

Table III. Derived Parameters for the Rigid-Group Atoms of $IrCl[N_2C_5Cl_4][P(C_6H_5)_3]_2 \cdot C_7H_8$

ATOM	X	Y	Z	B, $Å^2$	ATOM	X	Y	Z	B, $Å^2$
C(11)	-0.16221(49)	0.31748(16)	-0.24568(33)	4.91(14)	C(45)	0.05720(53)	0.11793(26)	-0.49807(25)	7.54(22)
C(12)	-0.07365(40)	0.35448(23)	-0.24486(36)	5.91(17)	C(46)	0.09730(52)	0.15850(18)	-0.43378(34)	6.07(17)
C(13)	-0.10141(54)	0.41070(21)	-0.25592(41)	7.56(22)	C(51)	0.36501(44)	0.17235(22)	-0.16777(31)	5.34(16)
C(14)	-0.21773(62)	0.42991(16)	-0.26781(42)	8.04(24)	C(52)	0.48126(57)	0.17328(24)	-0.16600(34)	6.70(20)
C(15)	-0.30629(46)	0.39291(24)	-0.26862(41)	7.39(22)	C(53)	0.59327(44)	0.15368(28)	-0.09276(43)	8.38(25)
C(16)	-0.27853(45)	0.33670(21)	-0.25756(37)	6.28(18)	C(54)	0.58904(50)	0.13315(27)	-0.02130(35)	7.96(24)
C(21)	-0.27625(40)	0.21272(20)	-0.30859(28)	4.80(14)	C(55)	0.47279(64)	0.13222(27)	-0.02307(33)	8.07(24)
C(22)	-0.34245(49)	0.23372(18)	-0.39356(32)	5.28(16)	C(56)	0.36078(48)	0.15182(26)	-0.09630(40)	7.11(21)
C(23)	-0.45602(49)	0.20866(23)	-0.45748(25)	6.31(19)	C(61)	0.27581(51)	0.25608(19)	-0.29888(35)	4.99(14)
C(24)	-0.50340(44)	0.16259(24)	-0.43643(34)	7.63(23)	C(62)	0.27922(56)	0.30757(23)	-0.26303(33)	6.32(18)
C(25)	-0.43720(56)	0.14158(20)	-0.35145(40)	7.62(22)	C(63)	0.31995(61)	0.35372(18)	-0.28879(40)	7.77(22)
C(26)	-0.32362(52)	0.16665(21)	-0.28754(28)	6.19(18)	C(64)	0.35727(60)	0.34839(21)	-0.35040(42)	7.55(21)
C(31)	-0.09934(54)	0.22574(23)	-0.12276(31)	5.01(15)	C(65)	0.35385(60)	0.29690(26)	-0.38625(36)	7.26(22)
C(32)	-0.02102(58)	0.18042(23)	-0.08002(41)	7.36(21)	C(66)	0.31312(57)	0.25075(19)	-0.36049(36)	6.59(19)
C(33)	-0.00412(63)	0.16272(23)	-0.00038(42)	9.19(28)	C(71)	-0.3007(11)	-0.00278(44)	-0.03266(74)	15.39(64)
C(34)	-0.06553(69)	0.19033(30)	0.03652(33)	8.32(25)	C(72)	-0.42306(94)	0.00118(49)	-0.10745(91)	13.34(60)
C(35)	-0.14384(64)	0.23564(29)	-0.00622(42)	8.59(26)	C(73)	-0.4363(13)	0.00991(57)	-0.18896(77)	14.57(69)
C(36)	-0.16075(53)	0.25335(22)	-0.08586(40)	6.90(20)	C(74)	-0.3272(18)	0.01468(53)	-0.19570(90)	17.84(73)
C(41)	0.17948(49)	0.14487(20)	-0.34593(30)	4.86(14)	C(75)	-0.2049(14)	0.01072(61)	-0.1209(12)	22.74(94)
C(42)	0.22157(50)	0.09069(23)	-0.32237(28)	6.84(20)	C(76)	-0.19163(92)	0.00199(61)	-0.03942(96)	20.59(87)
C(43)	0.18147(62)	0.05013(17)	-0.38666(42)	8.56(25)	C(77)	-0.2862(21)	-0.01236(76)	0.05672(68)	26.7(10)
C(44)	0.09929(62)	0.06375(22)	-0.47451(36)	7.57(22)					

RIGID GROUP PARAMETERS

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
RING1	-0.18997(37)	0.37370(16)	-0.25674(22)	1.7709(35)	-2.6880(36)	3.1230(38)
RING2	-0.36982(34)	0.18765(15)	-0.37251(24)	-3.0221(46)	-2.3169(34)	2.6722(49)
RING3	-0.08243(39)	0.20803(17)	-0.04312(28)	0.6868(44)	-2.8162(36)	-1.4726(40)
RING4	0.13938(34)	0.10431(16)	-0.41022(26)	0.6651(40)	2.6176(35)	0.8358(40)
RING5	0.47702(40)	0.15275(16)	-0.09453(27)	1.9653(67)	-3.1666(36)	-0.8821(64)
RING6	0.31654(34)	0.30224(17)	-0.32464(25)	-2.8916(61)	2.2039(33)	1.0557(60)
RING7	-0.3140(10)	0.00595(33)	-0.11419(76)	-1.5626(88)	3.0430(81)	1.4175(62)

[A] X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA (RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511 (1965).

The complex itself exhibits normal square-planar geometry with trans phosphine ligands and a singly bent diazo ligand. The bond angles about the iridium atom are very close to 90°: N(1)–Ir–P(1) = 90.07 (18)°, N(1)–Ir–P(2) = 90.68 (18)°, Cl(1)–Ir–P(1) = 88.26 (7)°, and Cl(1)–Ir–P(2) = 91.42 (7)°. The Ir, P(1), P(2), Cl(1), and N(1) atoms lie approximately in a plane; the distances of these atoms from the least-squares plane are 0.0023 (3), −0.068 (2), −0.072 (2), 0.022 (2), and 0.211 (6) Å, respectively.

The metal–ligand distances (Table VI) are normal. Thus the Ir–P distances of 2.344 (9) Å in $IrCl(N_2C_3Cl_4)(PPh_3)_2$ (I) are very similar to those of 2.338 (5) Å in $IrCl(CO)(P(o\text{-tolyl})_3)_2$ (II),[26] 2.327 (6) Å in *trans*-$Ir(C_6H_5)(CO)(PPh_3)_2$ (III),[26] 2.315 (3) Å in $IrCl(C_2H_4)(PPh_3)_2$ (IV),[26] and 2.358

(26) Restivo, R. J.; Ferguson, G.; Kelly, T. L.; Senoff, C. V. *J. Organomet. Chem.* **1975**, *90*, 101–9.
(27) Haymore, B. L., personal communication.

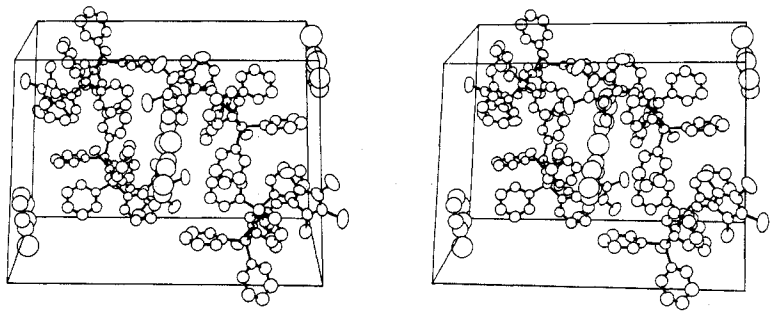


Figure 5. Stereoview of a unit cell of $IrCl(N_2C_5Cl_4)(PPh_3)_2 \cdot C_7H_8$. The x axis is pointing toward the top of the page, the y axis is horizontal to the right, and the z axis is perpendicular to the paper pointing away from the reader. Vibrational ellipsoids are drawn at the 20% probability level.

Table VI. Selected Distances (Å) and Angles (Deg) in $IrCl(N_2C_5Cl_4)(P(C_6H_5)_3)_2 \cdot C_7H_8$

Bond Distances

Ir-P(1)	2.338 (2)	Ir-P = 2.344 (9)[a]	C(1)-C(2)	1.412 (11)	C-C = 1.391 (30)
Ir-P(2)	2.350 (2)		C(1)-C(5)	1.397 (11)	
Ir-Cl(1)	2.297 (2)		C(2)-C(3)	1.345 (11)	
Ir-N(1)	1.824 (6)		C(3)-C(4)	1.421 (11)	
N(1)-N(2)	1.163 (7)		C(4)-C(5)	1.378 (12)	
N(2)-C(1)	1.347 (9)		P(1)-C(11)	1.819 (5)	P-C = 1.813 (5)
C(2)-Cl(2)	1.709 (9)	C-Cl = 1.710 (16)	P(1)-C(21)	1.820 (4)	
C(3)-Cl(3)	1.699 (10)		P(1)-C(31)	1.811 (6)	
C(4)-Cl(4)	1.733 (9)		P(2)-C(41)	1.809 (5)	
C(5)-Cl(5)	1.699 (9)		P(2)-C(51)	1.807 (5)	
			P(2)-C(61)	1.814 (6)	

Bond Angles

N(1)-Ir-Cl(1)	172.72 (19)		Cl(2)-C(2)-C(1)	124.4 (6)	Cl-C-C = 126.0 (17)
N(1)-Ir-P(1)	90.07 (18)		Cl(2)-C(2)-C(3)	126.7 (8)	
N(1)-Ir-P(2)	90.68 (18)		Cl(3)-C(3)-C(2)	129.0 (8)	
Cl(1)-Ir-P(1)	88.26 (7)		Cl(3)-C(3)-C(4)	123.9 (7)	
Cl(1)-Ir-P(2)	91.42 (7)		Cl(4)-C(4)-C(3)	125.1 (8)	
P(1)-Ir-P(2)	176.46 (7)		Cl(4)-C(4)-C(5)	125.2 (9)	
Ir-N(1)-N(2)	174.6 (6)		Cl(5)-C(5)-C(1)	126.7 (7)	
N(1)-N(2)-C(1)	141.2 (7)		Cl(5)-C(5)-C(4)	127.2 (7)	
N(2)-C(1)-C(2)	127.5 (7)		C(31)-P(1)-C(21)	105.5 (3)	C-P-C = 105.2 (19)
N(2)-C(1)-C(5)	124.1 (8)		C(31)-P(1)-C(11)	108.0 (3)	
C(2)-C(1)-C(5)	108.4 (7)		C(21)-P(1)-C(11)	102.4 (2)	
C(3)-C(2)-C(1)	108.9 (8)		C(51)-P(2)-C(41)	105.0 (3)	
C(2)-C(3)-C(4)	107.0 (8)	C-C-C = 108.0 (15)	C(51)-P(2)-C(61)	104.2 (3)	
C(3)-C(4)-C(5)	109.7 (8)		C(41)-P(2)-C(61)	105.8 (3)	
C(4)-C(5)-C(1)	106.0 (8)				
Ir-P(1)-C(11)	114.2 (2)				
Ir-P(1)-C(21)	113.7 (2)				
Ir-P(1)-C(31)	112.3 (2)				
Ir-P(2)-C(41)	112.2 (2)	Ir-P-C = 113.5 (12)			
Ir-P(2)-C(51)	115.5 (2)				
Ir-P(2)-C(61)	113.3 (2)				

[a] The figure in parentheses following an average value is the larger of that estimated for an individual value from the inverse matrix or on the assumption that the values averaged are from the same population.

Å in $[Ir\,Cl(N_2Ph)(PPh_3)_2][BF_4]$ (V)[27] (see Table VII). While the Ir–Cl bond distances of I and V are comparable, 2.297 (2) and 2.281 Å, respectively, they are significantly shorter than the Ir–Cl bond lengths in II and IV, 2.43 (1) and 2.371 (2) Å. Thus the trans influence of these ligands is $N_2C_5Cl_4 \approx N_2Ph^+ \ll C_2H_4 < CO$. The Ir–N (1.824 (6), 1.794 Å) and the N–N (1.163 (7), 1.159 Å) bond distances of I and V are also very similar.

The tetrachlorodiazocyclopentadiene ligand assumes the singly bent geometry in this complex. Comparisons of the geometries of this ligand are limited as the structure of the free molecule is unknown and the present structure is the first to be reported in which this ligand occurs. The Ir–N(1)–N(2) angle of 174.6 (6)° is very nearly linear, while the N(1)–N(2)–C(1) angle of 141.2 (7)° is much larger than the expected value of 120° for an sp^2-hybridized nitrogen atom. The N(1)–N(2) distance of 1.163 (7) Å is comparable to that found in $[IrCl(N_2Ph)(PPh_3)]BF_4]$ (V) (1.159 Å) and corresponds to a bond order intermediate between a double (~1.24 Å) and a triple (~1.10 Å) N–N bond.

Table VII. Comparison of Ir–P and Ir–Cl Bond Distances (Å) in Square-Planar Ir(I) Complexes

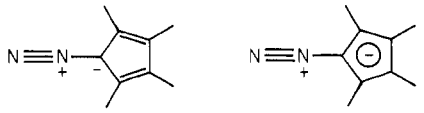
no.	compd	Ir–Cl	Ir–P (av)
I	$IrCl(N_2C_5Cl_4)(PPh_3)_2$[a]	2.297 (2)	2.344 (9)
II	$IrCl(CO)(P(o\text{-tolyl})_3)_2$[b]	2.43 (1)	2.338 (5)
III	$Ir(C_6F_5)(CO)(PPh_3)_2$[b]	...	2.327 (6)
IV	$IrCl(C_2H_4)(PPh_3)_2$[b]	2.371 (2)	2.315 (3)
V	$[IrCl(N_2Ph)(PPh_3)_2][BF_4]$[c]	2.358	2.281

[a] This work. [b] Reference 26. [c] Reference 27.

The bond distances in the cyclopentadiene ring of the title complex show some similarities with those of the σ-bonded cyclopentadienyl ring in $[(\eta^1\text{-}C_5Cl_5)Mn(CO)_5]$,[28] namely, two

(28) Day, V. W.; Stults, B. R.; Reimer, K. J.; Shaver, A. *J. Am. Chem. Soc.* **1974**, *96*, 4008–9.

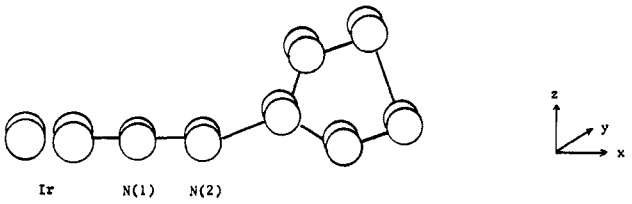
short and three long carbon–carbon bonds. However, if the C–C bond distances of the coordinated $N_2C_5Cl_4$ ligand are also compared with those of η^5 complexes such as $[(\eta^5\text{-}C_5Cl_5)Rh(1,5\text{-}C_8H_{12})]$,[29] $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(SO_2)$,[30] and *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$,[31] it appears as though there is significant contribution from both canonical structures a and b. Owing to the large errors in the C–C bond lengths of the



a b

coordinated diazo ligand, more detailed comparisons cannot be made. However, structure b might be expected to predominate, since the formal negative charge on the C(1) carbon atom in structure a has been stabilized by incorporation into an aromatic C_5 system in structure b.

The 11 atoms of the diazo ligand, N(1), N(2), C(1), C(2), C(3), C(4), C(5), Cl(2), Cl(3), Cl(4), and Cl(5), all lie in a plane; the deviations of these atoms from the least-squares plane are −0.070 (8), −0.008 (8), 0.03 (1), 0.01 (1), −0.01 (1), 0.008 (14), 0.031 (12), 0.011 (4), −0.007 (5), −0.011 (4), and 0.011 (1) Å, respectively. The plane of the diazo ligand is approximately perpendicular to the plane determined by Ir, P(1), P(2), and Cl(1), the dihedral angle being 89°. This disposition of the diazo ligand is very effective for the creation of an extended delocalized π system utilizing the carbon $p\pi$ orbitals of the cyclopentadiene ring, the nitrogen $p\pi$ orbitals, and the filled iridium d_{xy} orbitals as shown.



According to the conventional formalism adopted for M–N_2Ph complexes, the singly bent geometry has been designated N_2Ph^+ whereas the doubly bent geometry is designated N_2Ph^-. By analogy, the singly bent geometry of the neutral diazo ligand in $IrCl(N_2C_5Cl_4)(PPh_3)_2$ may be considered to be a coordinated N_2R species. This description of the $-C_5Cl_4$ fragment as an aromatic $C_5Cl_4^-$ moiety rather than as a diene is based on the relative contributions of canonical structures a and b; thus a useful formal description of the present ligand is $N_2^+C_5Cl_4^-$.

The longer Ir–N bond length and the larger N–N–C angle (1.824 (6) Å, 141.2 (7)°) reflect a smaller degree of M → L π overlap in this complex (I) in comparison with $[IrCl(N_2Ph)(PPh_3)_2][BF_4]$ (V) (1.794 Å, 124.8°). Presumably the formally neutral $N_2C_5Cl_4$ ligand cannot accommodate as great a flow of electron density from the metal d orbitals into the π^* orbitals of the N–N fragment as can the formally cationic N_2Ph^+ ligand. As the degree of π overlap is further decreased, one would expect the N–N–R angle to increase, until a limiting value of 180° is reached, whereupon the ligand behaves as a pure σ donor. This indeed seems to be the case for the complex $RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$ (N–N–R = 172.7 (8)°, N–N = 1.115 (8) Å).[15]

Recent experiments[32] indicate that there is competition between the metal and the cyclopentadiene ring for π donation into the π^* orbitals of the N–N fragment. Obviously, even for the title complex, I, there is significant π donation from the cyclopentadiene ring into the dinitrogen moiety. This could result in a slightly lengthened N–N bond, although such a lengthening relative to the N–N bond in V is beyond detection by X-ray methods and is not reflected in the corresponding ν(NN) values (1872 vs. 1868 cm^{-1}) for I and V. In fact, the low intensity of the N–N stretch in the infrared spectrum of I is probably the result of this extended delocalized π system and the competition which exists between the metal and the cyclopentadiene ring for π donation into the nitrogen antibonding orbitals. It seems very likely that this competition has the net effect of making the electron density of these two nitrogen atoms equivalent or nearly equivalent, resulting in the loss of a permanent dipole necessary for infrared activity.

Since the M–$N_2C_5Cl_4$ system is formally neutral as opposed to M–N_2Ph^+ systems and since the electronic nature of the $N_2C_5Cl_4$ ligand is different from that of the N_2Ph^+ ligand, the marked differences in the reaction chemistries of $IrCl(N_2C_5Cl_4)(PPh_3)_2$[17] and $[IrCl(N_2Ph)(PPh_3)_2][BF_4]$[33] are not surprising. What is surprising perhaps is the very close similarity in the structures of these two compounds. This singly bent geometry is the only presently known arrangement adopted in common by both N_2R and N_2R^+ complexes of transition metals. Other bonding modes displayed by N_2R complexes include the totally linear arrangement[15] and η^2 coordination.[14,34] Neither of these modes is known for N_2R^+ complexes which display, in addition to the singly bend geometry, the doubly bent[6b] and intermediate geometries.[5a]

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE76-10335). We thank Matthey Bishop, Inc., for the generous loan of iridium.

Registry No. $IrCl(N_2C_5Cl_4)(PPh_3)_2 \cdot C_7H_8$, 72749-20-3; $IrCl(N_2)(PPh_3)_2$, 21414-18-6.

Supplementary Material Available: Table IV, the idealized positions of hydrogen atoms, Table V, the root-mean-square amplitudes of vibration, and a listing of the observed and calculated structure amplitudes (22 pages). Ordering information is given on any current masthead page.

(29) Day, V. W. *J. Chem. Soc., Chem. Commun.* **1975**, 403–4.
(30) Churchill, M. R.; DeBoer, B. G.; Kalra, K. L. *Inorg. Chem.* **1973**, *12*, 1646–50.
(31) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1973**, *12*, 1650–6.
(32) Schramm, K. D.; Tulip, T. H.; Ibers, J. A., submitted for publication in *Inorg. Chem.*
(33) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3052–4.
(34) Schramm, K. D., Ibers, J. A., *Inorg. Chem.*, in press.