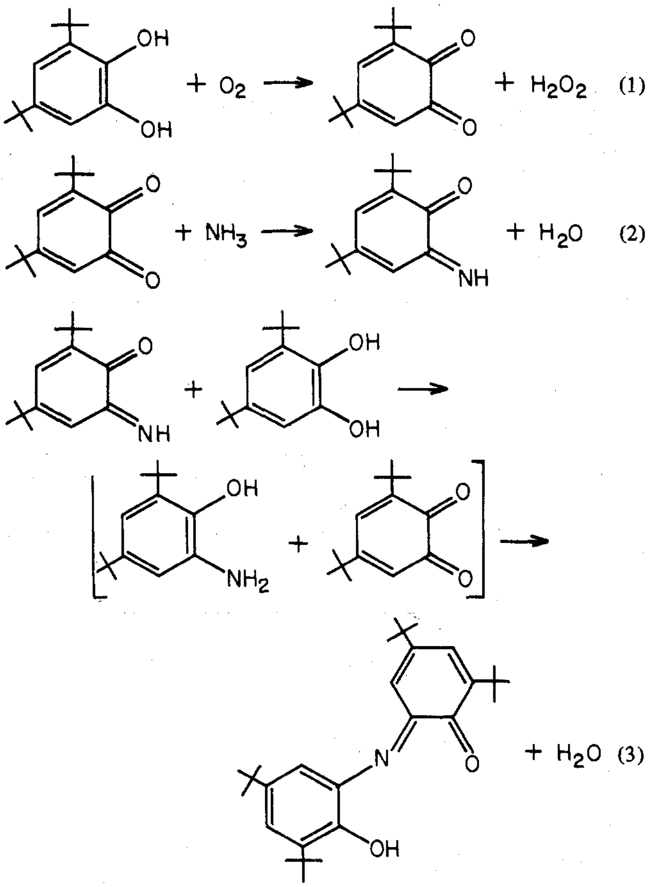


significant in the overall reaction, although they have not been specified.

The role of the various metal ions in this scheme has not been specified and in fact their role may be minimal. In the absence of a metal ion, the aerial oxidation of 3,5-di-*tert*-butylcatechol in the presence of ammonia produces a purple crystalline material which is as yet not fully characterized. It is not stable, especially in solution, and it appears from electron spin resonance and magnetic susceptibility measurements to contain a significant fraction of paramagnetic material.[14] Since this substance reacts with divalent metal ions to produce **2** in good yield, it appears that a precursor to **2** may be readily formed in the absence of metal ion.

We have verified that 3,5-di-*tert*-butyl-1,2-benzoquinone is an intermediate in the reaction and that the role of molecular oxygen is oxidation of 3,5-di-*tert*-butylcatechol to this quinone. The reaction of 3,5-di-*tert*-butyl-1,2-benzoquinone, 3,5-di-*tert*-butylcatechol, ammonia, and zinc acetate rapidly produces **2** (M = Zn) in good yield. Molecular oxygen has no discernible effect on this alternate mode of preparation of **2**.

Acknowledgment. This research was supported by Grant GM 18357 from the National Institutes of Health.

Registry No. $MgC_{56}H_{80}N_2O_4$, 56030-06-9; $FeC_{56}H_{80}N_2O_4$, 56030-07-0; $NiC_{56}H_{80}N_2O_4$, 56030-08-1; $CuC_{56}H_{80}N_2O_4$, 56030-09-2; $ZnC_{56}H_{80}N_2O_4$, 56030-10-5; $CdC_{56}H_{80}N_2O_4$, 56030-11-6; 3,5-di-*tert*-butylcatechol, 1020-31-1; ammonia, 7664-41-7; 3,5-di-*tert*-butyl-1,2-benzoquinone, 3383-21-9.

References and Notes

(1) C. A. Tyson and A. E. Martell, *J. Phys. Chem.*, **74**, 2601 (1970).
(2) R. R. Grinstead, *Biochemistry*, **3**, 1308 (1964).
(3) C. A. Tyson and A. E. Martell, *J. Am. Chem. Soc.*, **94**, 939 (1972).
(4) O. Hayaishi and M. Nozaki, *Science*, **164**, 389 (1969).
(5) O. Hayaishi, *Bacteriol. Rev.*, **30**, 720 (1966).
(6) H. B. Stegmann, K. B. Ulmschneider, and K. Scheffler, *J. Organomet. Chem.*, **72**, 41 (1974).
(7) H. Schulze and W. Flaig, *Justus Liebigs Ann. Chem.*, **575**, 231 (1952).
(8) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, N.Y., 1962, p 134.
(9) B. V. Harrowfield and J. R. Pilbrow, *J. Phys. C* **6**, 755 (1973).
(10) S. Takagi, M. D. Joesten, and P. G. Lenhert, *J. Am. Chem. Soc.*, **97**, 444 (1975).
(11) F. S. Stephens, *J. Chem. Soc. A*, 883 (1969).
(12) B. J. Hathaway, M. J. Bew, and D. E. Billing, *J. Chem. Soc. A*, 1090 (1970).
(13) E. J. Corey and K. Achiwa, *J. Am. Chem. Soc.*, **91**, 1429 (1969).
(14) For the chemistry of some related radicals see H. B. Stegman, K. Scheffler, F. Stoecker, and H. Buerk, *Chem. Ber.*, **101**, 262 (1968).

Contribution from the Departments of Chemistry, Ohio University, Athens, Ohio 45701,
the University of Houston, Houston, Texas 77004,
and the University of Massachusetts, Amherst, Massachusetts 01002

Crystal and Molecular Structure of *trans*-Pentafluorophenylcarbonylbis(triphenylphosphine)iridium(I)

A. CLEARFIELD,*[1a] R. GOPAL,[1a] I. BERNAL,[1b] G. A. MOSER,[1c] and M. D. RAUSCH[1c]

Received February 5, 1975 AIC500812

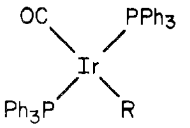
The crystal structure of *trans*-pentafluorophenylcarbonylbis(triphenylphosphine)iridium(I), $C_6F_5[(C_6H_5)_3P]_2IrCO$, was determined by conventional Patterson, Fourier, and least-squares refinement techniques. The complex crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 10.994$ (3) Å, $b = 13.459$ (2) Å, $c = 26.187$ (6) Å, $\beta = 108.49$ (3)°, and $Z = 4$. Intensity data (2145 reflections above background) were collected by the θ–2θ scan method out to $2\theta_{\max} = 60°$ (Mo Kα) using a CAD-4 automated diffractometer. The final values of R_F and R_{wF} were 0.0394. Only the Ir atom, the atoms in its coordination sphere, and the carbon atoms of the pentafluorophenyl ring were refined anisotropically. The coordination about the iridium atom is slightly distorted square planar. The two phosphorus atoms are situated slightly above the best fit mean plane formed by the metal atom and the atoms bonded to it. Likewise the two carbon atoms in the coordination sphere are slightly below this plane. The iridium atom lies slightly above the line joining the two carbon atoms bonded to it but a little below the mean plane. Important bond distances are as follows: Ir–P, 2.305 (5) and 2.326 (4) Å; Ir–C(CO), 1.891 (17) Å; C–O, 1.137 (22) Å; Ir–$C(C_6F_5)$, 2.090 (16) Å. The value of this latter bond indicates that extensive π overlap between the Ir atom and the pentafluorophenyl carbon atom, with consequent reduction of electron density of the metal atom, does not occur. Therefore, the reduced reactivity of the subject complex toward oxidative addition reactions must stem from other causes.

The report by Vaska and DiLuzio[2] in 1961 that the coordinatively unsaturated, planar d^8 complex chlorocarbonylbis(triphenylphosphine)iridium(I), I, could undergo various oxidative addition reactions with covalent molecules has

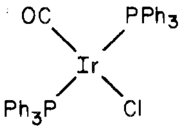
Table I. Crystal Data

Chemical formula	$(C_6F_5)[(C_6H_5)_3P]_2IrCO$
Mol wt	911.86
Crystal system	Monoclinic
Cell dimensions	$a = 10.994$ (3) Å $b = 13.459$ (2) Å $c = 26.187$ (6) Å $\beta = 108.49$ (3)°
Cell vol	3674.06 Å^3
Systematic absences	$h0l$ for $l = 2n + 1$ $0k0$ for $k = 2n + 1$
Space group	$P2_1/c$
Z	4
ρ(calcd)	1.648 g/cm^3
μ	24.34 cm^{-1}

stimulated an enormous amount of research concerning the chemical reactions and structures of these types of organometallic compounds.[3-6] In recent years, several research



1



II

groups have synthesized a number of derivatives of I in which the chlorine moiety is replaced by a σ-bonded organic substituent (II, R = alkyl or aryl), in order to ascertain the reactivities of these complexes relative to I.[7-12]

The complex *trans*-pentafluorophenylcarbonylbis(triphenylphosphine)iridium(I) (II, R = C_6F_5), which can be readily prepared from reactions of I with either C_6F_5MgBr,[9] C_6F_5Li,[10,11] or C_6F_5Ag,[11] is of particular interest, since oxidative addition processes can be markedly influenced by steric and/or electronic factors imposed by the pentafluorophenyl ligand.[9-11] In order to obtain further information along these lines and to prove unequivocally the trans disposition of the triphenylphosphine substituents in complexes of this type, an X-ray crystallographic structural investigation of II (R = C_6F_5) was undertaken, and the results are reported in this paper.

Experimental Section

trans-Pentafluorophenylcarbonylbis(triphenylphosphine)iridium(I) was prepared by a literature method previously described by one of us.[9] A crystal suitable for X-ray crystallographic purposes was grown from benzene–heptane solution. The crystals were subject to severe fracture and generally broke on handling. Therefore, a small chip about 0.1 mm on a side was mounted on the goniometer head. Survey photographs, both Weissenberg and precession, revealed a monoclinic cell with systematic absences (Table I) indicative of space group $P2_1/c$.

Accurate unit cell dimensions were obtained at 24 ± 1° on a CAD-4 four-circle diffractometer (Enraf-Nonius). Subroutines SEARCH, INDEX, and DETCELL[13] were used to collect 25 reflections at high and moderate angles. The reflections were scanned at both $+2\theta$ and -2θ by the θ–2θ scan technique using monochromatized (graphite crystal) Mo Kα radiation (λ 0.7107 Å) at a 4° takeoff angle. The Bragg angles were accurately determined by program DETCELL which automatically compensates for wavelength dispersion. Then the cell dimensions were derived from the indexed reflections by a least-squares calculation using θ_1 values and $\lambda(K\alpha_1)$ 0.70926 Å. The final cell dimensions are listed in Table I along with other data of crystallographic interest.

Intensity data were collected by the θ–2θ scan method using a variable scan rate ranging from 20.116°/min for the strongest reflections to 0.251°/min for the weakest. The angular scan width was also variable and amounted to $3(0.7 + 0.2 \tan\theta)°$. The right and left backgrounds were scanned for half the time required for the total peak scan. During data collection two standard reflections were recorded every time a set of 24 reflections was collected and these were used to place all the data on a common scale. The change in the intensities of the standards was small and random with fluctuations about the mean amounting to no more than ±4%. A total of 7656 reflections were scanned out to a maximum 2θ of 60°. Of these, 2145 were found to have intensities equal to or greater than 2σ where σ = (total counts + background counts)$^{1/2}$ and were considered to be observed. The data were corrected for Lorentz and double polarization effects but not for extinction or absorption ($\mu R = 0.243$).

Table II. Positional Parameters and Isotropic Temperature Factors for Nonhydrogen Atoms[a]

Atom	x	y	z	B, Å
Ir(1)	−0.31571 (7)	0.14073 (6)	0.14845 (3)	2.846 (30)
P(1)	−0.35466 (40)	0.29474 (31)	0.10603 (17)	3.161 (30)
P(2)	−0.27840 (42)	−0.01588 (33)	0.18581 (17)	3.437 (31)
O(1)	−0.0337 (11)	0.1882 (9)	0.1989 (6)	7.31 (50)
C(2)	−0.1400 (15)	0.1711 (11)	0.1803 (7)	5.23 (40)
C(3)	−0.2136 (15)	−0.0112 (12)	0.2592 (6)	3.58 (35)
C(4)	−0.0939 (17)	−0.0494 (13)	0.2862 (7)	5.07 (42)
C(5)	−0.0504 (22)	−0.0502 (17)	0.3444 (9)	8.42 (61)
C(6)	−0.1211 (18)	−0.0024 (14)	0.3707 (7)	5.62 (45)
C(7)	−0.2379 (16)	0.0399 (14)	0.3442 (7)	5.57 (46)
C(8)	−0.2793 (17)	0.0394 (14)	0.2878 (7)	5.34 (43)
C(9)	−0.1636 (14)	−0.0949 (10)	0.1654 (6)	3.41 (34)
C(10)	−0.0908 (16)	−0.0579 (13)	0.1373 (7)	4.85 (34)
C(11)	−0.0017 (14)	−0.1205 (13)	0.1257 (6)	4.67 (40)
C(12)	0.0116 (15)	−0.2187 (12)	0.1406 (6)	4.12 (37)
C(13)	−0.0653 (17)	−0.2536 (14)	0.1703 (7)	5.60 (45)
C(14)	−0.1565 (15)	−0.1939 (11)	0.1820 (6)	3.72 (35)
C(15)	−0.4165 (15)	−0.0985 (11)	0.1711 (6)	3.60 (35)
C(16)	−0.4695 (15)	−0.1305 (16)	0.2088 (6)	5.23 (38)
C(17)	−0.5855 (19)	−0.1902 (15)	0.1906 (8)	6.65 (52)
C(18)	−0.6441 (19)	−0.2123 (16)	0.1387 (8)	7.23 (54)
C(19)	−0.5849 (16)	−0.1805 (12)	0.1007 (7)	5.13 (44)
C(20)	−0.4751 (15)	−0.1229 (14)	0.1155 (6)	4.89 (40)
C(21)	−0.2546 (14)	0.3147 (11)	0.0654 (6)	3.46 (34)
C(22)	−0.1940 (15)	0.2348 (12)	0.0506 (6)	4.38 (38)
C(23)	−0.1233 (17)	0.2461 (14)	0.0143 (7)	5.73 (45)
C(24)	−0.1168 (15)	0.3339 (12)	−0.0083 (6)	4.47 (38)
C(25)	−0.1739 (17)	0.4158 (14)	0.0055 (7)	5.67 (46)
C(26)	−0.2455 (16)	0.4065 (12)	0.0413 (7)	4.61 (40)
C(27)	−0.3324 (15)	0.4039 (9)	0.1492 (7)	2.85 (29)
C(28)	−0.2563 (16)	0.3957 (12)	0.2013 (6)	4.59 (41)
C(29)	−0.2381 (18)	0.4821 (14)	0.2342 (7)	5.53 (45)
C(30)	−0.2977 (18)	0.5654 (14)	0.2176 (7)	5.34 (44)
C(31)	−0.3735 (18)	0.5759 (14)	0.1640 (7)	5.76 (46)
C(32)	−0.3877 (16)	0.4956 (12)	0.1314 (7)	4.70 (40)
C(33)	−0.5153 (15)	0.3136 (11)	0.0597 (6)	3.88 (36)
C(34)	−0.6139 (15)	0.3235 (11)	0.0800 (6)	4.06 (37)
C(35)	−0.7426 (15)	0.3232 (11)	0.0465 (6)	4.18 (38)
C(36)	−0.7674 (17)	0.3127 (13)	−0.0071 (7)	5.21 (43)
C(37)	−0.6734 (17)	0.3057 (13)	−0.0307 (7)	5.33 (44)
C(38)	−0.5465 (17)	0.3076 (13)	0.0057 (7)	5.40 (44)
C(39)	−0.5103 (14)	0.1082 (11)	0.1133 (6)	4.58 (45)
C(40)	−0.5938 (15)	0.1039 (12)	0.1382 (6)	4.84 (40)
C(41)	−0.7241 (19)	0.0814 (17)	0.1118 (9)	8.42 (54)
C(42)	−0.7652 (16)	0.0612 (17)	0.0595 (9)	6.95 (50)
C(43)	−0.6832 (19)	0.0657 (14)	0.0365 (7)	6.52 (50)
C(44)	−0.5606 (16)	0.0859 (12)	0.0596 (7)	4.99 (48)
F(40)	−0.5596 (9)	0.1255 (9)	0.1920 (4)	7.63 (28)
F(41)	−0.8079 (14)	0.0859 (8)	0.1424 (6)	9.91 (34)
F(42)	−0.8936 (13)	0.0448 (9)	0.0378 (5)	9.86 (36)
F(43)	−0.7264 (12)	0.0453 (9)	−0.0201 (5)	8.73 (33)
F(44)	−0.4803 (10)	0.0873 (8)	0.0268 (4)	6.94 (27)

[a] Estimated standard deviations are shown in parentheses and refer to the last digits of the preceding number.

Solution and Refinement of the Structure

The positional parameters of the iridium atom and both phosphorus atoms were determined from a Patterson map prepared from the entire data set. These initial parameters were refined, using an overall temperature factor, to an R_F value of 0.20. The positions of all other nonhydrogen atoms were obtained from successive Fourier and difference maps. Refinement of these positional parameters and individual isotropic temperature factors by block-diagonal methods further reduced R_F to 0.05. At this stage of refinement the ideal positions of the hydrogen atoms were calculated assuming a C–H bond distance of 0.95 Å and sp^2 geometry.[14] The hydrogen atoms were assigned temperature factors one unit greater than those of the atoms to which they are bonded. The final cycles of refinement were carried

Table III. Anisotropic Thermal Parameters ($\times 10^4$) for Selected Atoms[a]

	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Ir	69.9 (5)	37.1 (3)	11.4 (1)	1 (2)	6.5 (3)	3.9 (8)
P(1)	69 (5)	34 (3)	13.6 (8)	2 (6)	16 (3)	0 (3)
P(2)	76 (5)	43 (3)	14.7 (9)	4 (7)	20 (3)	4 (3)
C(2)	77 (19)	48 (14)	28 (4)	−22 (24)	17 (14)	−2 (11)
O(1)	102 (16)	99 (12)	43 (4)	−29 (21)	12 (13)	−15 (11)
C(39)	92 (19)	59 (14)	18 (3)	−30 (25)	30 (13)	27 (10)
C(40)	87 (20)	70 (15)	23 (4)	−54 (26)	33 (14)	17 (11)
C(41)	150 (28)	147 (22)	32 (5)	−59 (41)	76 (21)	43 (17)
C(42)	48 (21)	127 (20).	51 (7)	11 (34)	37 (19)	59 (19)
C(43)	188 (30)	80 (15)	19 (4)	20 (37)	13 (18)	−25 (13)
C(44)	113 (23)	52 (12)	20 (4)	−39 (27)	−49 (15)	1 (11)

[a] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

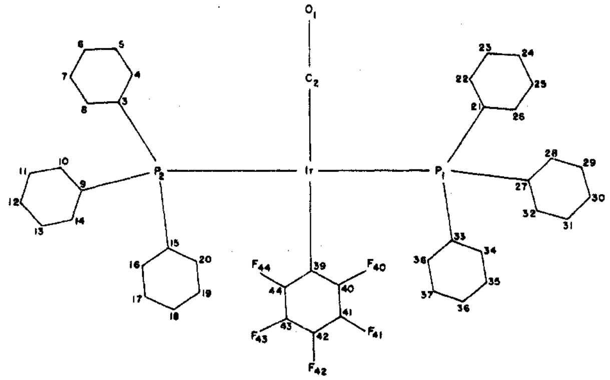


Figure 1. Planar representation of the molecule with the numbering scheme used in all tables.

out holding the positional and thermal parameters of the hydrogen atoms constant and allowing the temperature factors of the iridium atom and atoms bonded to it, as well as the carbon atoms of the pentafluorophenyl ring, to refine anisotropically. The refinement was considered to be complete when the shifts in positional parameters of the nonhydrogen atoms were 0.1 or less of the estimated standard deviations.[15] The final R_F and R_{wF} values were the same and equal to 0.0394, where

$$R_F = \frac{\Sigma \| F_o | - | F_c \|}{\Sigma | F_o |}$$

and

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w |F_o|^2} \right]^{1/2}$$

Weights were derived from the function

$$w = 1/\{1 + [(|F_o| - P_2)/P_1]\}$$

with $P_1 = 50$ and $P_2 = 175$. The function minimized was $\sum w(|F_o| - |F_c|)^2$.

Neutral atom scattering factors for iridium were those of Cromer and Waber[16] and those for the other atoms were taken from ref 17. The final positional and isotropic temperature factors for the nonhydrogen atoms are listed in Table II and the anisotropic temperature factors in Table III. Table IV lists the positional and thermal parameters of the hydrogen atoms. A table of observed and calculated structure factors is available.[18]

The final difference Fourier map showed no peaks larger than about 0.3 e/Å^3 and these were randomly distributed. Also, isotropic temperature factors accounted for most of the thermal motion of the fluorine atoms so that anisotropic refinement of these atoms was not attempted.

Unobserved reflections (reflections below the threshold values) were not used in the refinement. However in the final structure factor calculations they were included for comparison with the calculated values. It was observed that less than 5% of these reflections had calculated values slightly higher than the threshold value.

Table IV. Positional and Isotropic Thermal Parameters for the Hydrogen Atoms[a]

	x	*y*	*z*	*B*, Å
H(4)	−0.0417	−0.0766	0.2660	6.20
H(5)	0.0353	−0.0759	0.3658	9.58
H(6)	−0.0919	0.0004	0.4100	6.87
H(7)	−0.2928	0.0688	0.3644	6.05
H(8)	−0.3581	0.0725	0.2692	6.24
H(10)	−0.0995	0.0128	0.1257	6.04
H(11)	0.0532	−0.0917	0.1065	5.69
H(12)	0.0703	−0.2629	0.1296	5.22
H(13)	−0.0546	−0.3212	0.1830	7.05
H(14)	−0.2132	−0.2186	0.2017	4.86
H(16)	−0.4262	−0.1157	0.2479	6.72
H(17)	−0.6205	−0.2146	0.2186	7.92
H(18)	−0.7275	−0.2481	0.1286	8.63
H(19)	−0.6216	−0.2002	0.0629	6.93
H(20)	−0.4374	−0.0973	0.0876	6.17
H(22)	−0.2024	0.1696	0.0650	5.46
H(23)	−0.0808	0.1873	0.0044	6.37
H(24)	−0.0722	0.3411	−0.3491	5.11
H(25)	−0.1581	0.4811	−0.0072	7.29
H(26)	−0.2965	0.4629	0.0467	5.55
H(28)	−0.2134	0.3326	0.2156	5.53
H(29)	−0.1764	0.4779	0.2696	7.21
H(30)	−0.2848	0.6188	0.2443	6.52
H(31)	−0.4234	0.6365	0.1528	6.71
H(32)	−0.4356	0.5030	0.0936	5.98
H(34)	−0.5950	0.3310	0.1189	5.13
H(35)	−0.8130	0.3307	0.0626	5.56
H(36)	−0.8566	0.3065	−0.0300	6.58
H(37)	−0.6918	0.3013	−0.0708	6.42
H(38)	−0.4728	0.3050	−0.0085	6.51

[a] The positions of the hydrogen atoms are idealized for sp^2 geometry and C–H = 0.95 A.

Description of the Structure

The molecular structure of the subject compound is shown in Figure 1 together with the numbering scheme used in the tables and discussion.[19] The coordination about the iridium atom is square planar. Bond distances and angles are given in Table V. Distortions from ideal square-planar geometry are small. The angles about the iridium atom are close to 90° and the P(1)–Ir–P(2) and C–Ir–C angles are slightly less than 180°. The equation of the best fit mean plane[20] through the four atoms in the Ir coordination sphere and the deviations of these atoms from the plane are given in Table VI. It is seen that both phosphorus atoms are about 0.03 Å above this plane and the carbon atoms ~0.03 Å below the plane. These deviations are reflected in the high X^2 value. The metal atom is also below the plane and is thus slightly above the straight line connecting the carbon atoms.

The Ir–P bonds are 2.305 (5) and 2.326 (4) Å, the mean value and the standard deviation from the mean being 2.315 ± 0.010 Å. This is significantly longer than the value of 2.258 ± 0.014 Å found by Churchill and Bezman[21] in a study of an Ir–Cu cluster containing Ir–P bonds. In that paper, an ex-

Table V. Interatomic Distances and Angles

Atoms	Dist, Å	Atoms	Angles, deg
	A. Iridium Coordination		
Ir-P(1)	2.326 (4)	P(1)-Ir-C(2)	91.5 (5)
Ir-P(2)	2.305 (5)	C(2)-Ir-P(2)	89.5 (5)
Ir-C(2)	1.891 (17)	P(2)-Ir-C(39)	90.9 (4)
Ir-C(39)	2.090 (16)	P(1)-Ir-C(39)	88.2 (4)
		P(1)-Ir-P(2)	176.8 (2)
		C(2)-Ir-C(39)	179.6 (6)
	B. Carbonyl Group		
C(2)-O(1)	1.137 (22)	Ir-C(2)-O(1)	179 (1)
	C. Pentafluorophenyl Group		
C(39)-C(40)	1.284 (24)	C(44)-C(39)-C(40)	113 (1)
C(40)-C(41)	1.412 (28)	C(39)-C(40)-C(41)	123 (2)
C(41)-C(42)	1.327 (31)	C(40)-C(41)-C(42)	121 (2)
C(42)-C(43)	1.234 (29)	C(41)-C(42)-C(43)	116 (2)
C(43)-C(44)	1.318 (28)	C(42)-C(43)-C(44)	126 (2)
C(44)-C(39)	1.371 (22)	C(43)-C(44)-C(39)	122 (1)
	Av 1.325 ± 0.064[a]		Av 120 ± 4
C(40)-F(40)	1.368 (19)	C(39)-C(40)-F(40)	120 (1)
C(41)-F(41)	1.401 (26)	C(41)-C(40)-F(40)	117 (2)
C(42)-F(42)	1.363 (23)	C(40)-C(41)-F(41)	117 (2)
C(43)-F(43)	1.434 (21)	C(42)-C(41)-F(41)	122 (2)
C(44)-F(44)	1.413 (21)	C(41)-C(42)-F(42)	116 (2)
	Av 1.396 ± 0.031	C(43)-C(42)-F(42)	128 (2)
		C(42)-C(43)-F(43)	116 (2)
		C(44)-C(43)-F(43)	118 (1)
		C(43)-C(44)-F(44)	118 (2)
		C(39)-C(44)-F(44)	120 (1)
	D. Phenyl Rings of Triphenylphosphine Groups		
	Ring No. 1		
C(3)-C(4)	1.381 (24)	C(8)-C(3)-C(4)	119 (1)
C(4)-C(5)	1.445 (28)	C(3)-C(4)-C(5)	119 (2)
C(5)-C(6)	1.355 (31)	C(4)-C(5)-C(6)	119 (2)
C(6)-C(7)	1.375 (27)	C(5)-C(6)-C(7)	122 (2)
C(7)-C(8)	1.401 (25)	C(6)-C(7)-C(8)	118 (1)
C(8)-C(3)	1.374 (25)	C(7)-C(8)-C(3)	122 (2)
	Av 1.389 ± 0.048		Av 120 ± 1
	Ring No. 2		
C(9)-C(10)	1.343 (24)	C(14)-C(9)-C(10)	123 (1)
C(10)-C(11)	1.397 (25)	C(9)-C(10)-C(11)	118 (2)
C(11)-C(12)	1.373 (24)	C(10)-C(11)-C(12)	122 (1)
C(12)-C(13)	1.398 (25)	C(11)-C(12)-C(13)	117 (2)
C(13)-C(14)	1.393 (25)	C(12)-C(13)-C(14)	122 (1)
C(14)-C(9)	1.396 (21)	C(13)-C(14)-C(9)	117 (1)
	Av 1.383 ± 0.022		Av 120 ± 3
	Ring No. 3		
C(15)-C(16)	1.365 (23)	C(20)-C(15)-C(16)	120 (1)
C(16)-C(17)	1.453 (27)	C(15)-C(16)-C(17)	118 (2)
C(17)-C(18)	1.340 (28)	C(16)-C(17)-C(18)	123 (2)
C(18)-C(19)	1.419 (28)	C(17)-C(18)-C(19)	118 (2)
C(19)-C(20)	1.382 (25)	C(18)-C(19)-C(20)	122 (2)
C(20)-C(15)	1.431 (21)	C(19)-C(20)-C(15)	119 (1)
	Av 1.398 ± 0.045		Av 120 ± 2
	Ring No. 4		
C(21)-C(22)	1.384 (22)	C(26)-C(21)-C(22)	117 (1)
C(22)-C(23)	1.413 (26)	C(21)-C(22)-C(23)	121 (1)
C(23)-C(24)	1.333 (25)	C(22)-C(23)-C(24)	121 (2)
C(24)-C(25)	1.373 (25)	C(23)-C(24)-C(25)	120 (1)
C(25)-C(26)	1.408 (25)	C(24)-C(25)-C(26)	120 (2)
C(26)-C(21)	1.405 (22)	C(25)-C(26)-C(21)	121 (1)
	Av 1.386 ± 0.030		Av 120 ± 1
	Ring No. 5		
C(27)-C(28)	1.360 (23)	C(32)-C(27)-C(28)	118 (1)
C(28)-C(29)	1.424 (24)	C(27)-C(28)-C(29)	118 (2)
C(29)-C(30)	1.301 (27)	C(28)-C(29)-C(30)	123 (2)
C(30)-C(31)	1.394 (26)	C(29)-C(30)-C(31)	120 (2)
C(31)-C(32)	1.353 (25)	C(30)-C(31)-C(32)	118 (2)
C(32)-C(27)	1.389 (22)	C(31)-C(32)-C(27)	123 (2)
	Av 1.370 ± 0.043		Av 120 ± 2

Table V (*Continued*)

Atoms	Dist, Å	Atoms	Angles, deg
	Ring No. 6		
C(33)-C(34)	1.358 (24)	C(38)-C(33)-C(34)	117 (1)
C(34)-C(35)	1.408 (23)	C(33)-C(34)-C(35)	122 (1)
C(35)-C(36)	1.350 (23)	C(34)-C(35)-C(36)	119 (1)
C(36)-C(37)	1.366 (26)	C(35)-C(36)-C(37)	123 (2)
C(37)-C(38)	1.418 (26)	C(36)-C(37)-C(38)	115 (1)
C(38)-C(33)	1.347 (23)	C(37)-C(38)-C(33)	125 (2)
	Av 1.375 ± 0.031		Av 120 ± 3
	E. Phosphorous Atom Coordination		
P(1)-C(21)	1.777 (16)	Ir-P(1)-C(21)	111.5 (5)
P(1)-C(27)	1.822 (14)	Ir-P(1)-C(27)	117.0 (5)
P(1)-C(33)	1.816 (17)	Ir-P(1)-C(33)	115.9 (5)
		C(21)-P(1)-C(27)	105.2 (7)
		C(21)-P(1)-C(33)	103.5 (7)
		C(27)-P(1)-C(33)	102.3 (7)
P(2)-C(3)	1.827 (16)	Ir-P(2)-C(3)	111.9 (5)
P(2)-C(9)	1.855 (16)	Ir-P(2)-C(9)	116.6 (5)
P(2)-C(15)	1.822 (16)	Ir-P(2)-C(15)	116.4 (5)
		C(3)-P(2)-C(9)	104.4 (7)
		C(3)-P(2)-C(15)	105.3 (7)
		C(9)-P(2)-C(15)	100.8 (7)

[a] Esd's on average bond lengths and angles calculated as

$$\sigma = \left[\frac{\Sigma_i(X_i - \bar{X})^2}{N - 1}\right]^{1/2}$$

Where X_i is one of the ith values and $\bar{X}$ the mean of N equivalent values. These esd's are presented as ± values whereas esd's on individual values are given in parentheses.

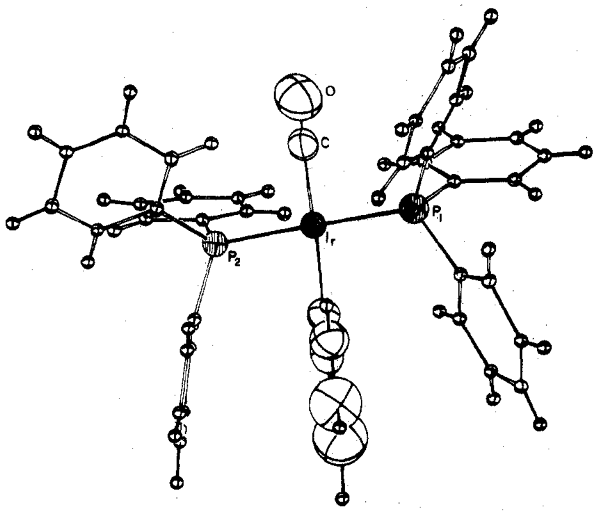


Figure 2. Perspective view of the molecule (ORTEP drawing with the thermal ellipsoids at the 50% probability level).

tensive compilation of Ir–P bond lengths was presented which showed that such bonds can range from 2.452 (9) to 2.248 (8) Å. Our mean value lies between these extremes, being closer to the short side.

The coordination about the phosphorus atoms is that of a distorted tetrahedron with bond angles ranging from 102.3 (7) to 117.0 (5)° about P(1) and from 100.8 (7) to 116.6 (5)° about P(2), the average of all the values being close to the ideal tetrahedral angle of 109.47°. This result is common and has been noted elsewhere.[22,23] All of the Ir–P–C angles are larger than the tetrahedral angle while the C–P–C angles are smaller. This also seems to be a general trend for phosphine complexes.[21-24] The P–C(phenyl) bonds range from 1.777 (17) to 1.855 (16) Å with a mean, and standard deviation from the mean, of 1.820 (18) Å. These variations in P–C bond lengths are common and the range exhibited in this particular case is similar to those typically found with triphenylphosphine complexes of transition metal compounds.[21-24]

The phenyl rings are reasonably planar but the bond lengths and angles show scatter typical of these systems.[22-24] However, the average C–C distances and C–C–C angles for the six rings are close to the expected ideal values of 1.397 Å and 120°.

The Pentafluorophenyl Ring

This ring is nearly planar as can be seen from Figure 2, where the ring is shown edge-on, and from the equation of the mean plane and the deviations of atoms therefrom (Table VI). However, it is the ring with the largest thermal parameters so that the atoms in this ring could not be located with a high degree of accuracy. Therefore, it is not surprising that the average C–C distance in this ring is low (1.325 ± 0.064 Å) and that the scatter in bond distances is large. In other

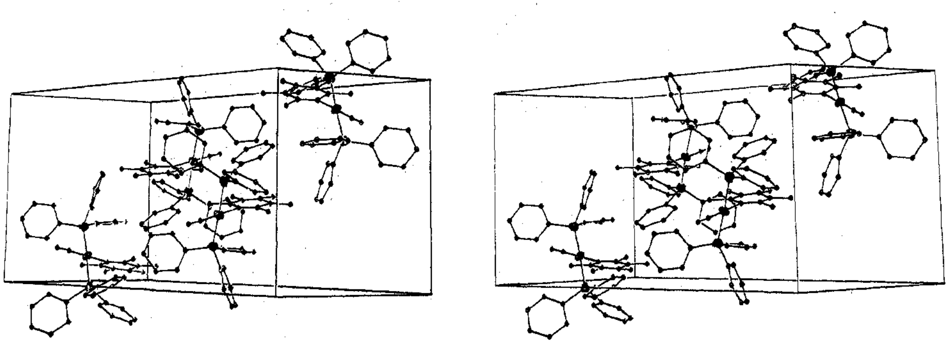


Figure 3. Stereoscopic view of the unit cell contents.

Table VI. Important Planes in the Molecule and Distances (Å) of Atoms Therefrom

A. Best Mean Plane Equation about C(2), C(39), P(1), P(3)

$0.4680X - 0.3623Y - 0.8060Y = -5.8303 \quad X^2 = 127.5$

P(1)	0.0333 (42)	C(39)	−0.032 (17)
P(2)	0.0334 (44)	Ir	−0.0292 (8)
C(2)	−0.035 (16)		

B. Mean Plane Equations for Benzene Rings

Ring 1

$0.5047X + 0.8626Y - 0.0333Z = -2.57 \quad X^2 = 17.83$

C(3)	−0.046 (16)	C(6)	0.009 (19)
C(4)	0.039 (18)	C(7)	−0.015 (19)
C(5)	−0.021 (24)	C(8)	0.034 (19)

Ring 2

$-0.4427X - 0.2610Y - 0.8575Z = 1.779 \quad X^2 = 2.22$

C(9)	−0.008 (15)	C(12)	0.011 (16)
C(10)	0.004 (17)	C(13)	−0.014 (18)
C(11)	−0.006 (15)	C(14)	0.012 (16)

Ring 3

$-0.5339X + 0.8356Y - 0.1295Z = 1.5426 \quad X^2 = 2.20$

C(15)	0.004 (15)	C(18)	0.020 (22)
C(16)	0.000 (20)	C(19)	−0.016 (17)
C(17)	−0.012 (20)	C(20)	0.005 (18)

Ring 4

$-0.6186X - 0.2050Y - 0.7584Z = 0.0269 \quad X^2 = 2.06$

C(21)	−0.006 (15)	C(24)	0.013 (16)
C(22)	0.006 (16)	C(25)	−0.013 (19)
C(23)	−0.010 (18)	C(26)	0.009 (17)

Ring 5

$0.9244X + 0.2777Y - 0.2614Z = 3.9679 \quad X^2 = 6.44$

C(27)	−0.013 (17)	C(30)	−0.028 (19)
C(28)	−0.010 (18)	C(31)	0.002 (20)
C(29)	0.032 (19)	C(32)	0.018 (19)

Ring 6

$0.0530X + 0.9954Y - 0.0800Z = 3.7747 \quad X^2 = 3.56$

C(33)	−0.019 (15)	C(36)	−0.015 (17)
C(34)	0.007 (14)	C(37)	0.003 (18)
C(35)	0.009 (15)	C(38)	0.014 (18)

Pentafluorophenyl Ring

$-0.1449X + 0.9700Y - 0.1950Z = 1.8060 \quad X^2 = 0.92$

C(39)	0.008 (15)	F(40)	0.025 (13)
C(40)	−0.006 (16)	F(41)	0.084 (12)
C(41)	0.004 (20)	F(42)	0.066 (13)
C(42)	−0.005 (23)	F(43)	0.016 (12)
C(43)	0.008 (19)	F(44)	0.001 (12)

compounds containing the pentafluorophenyl group the average ring C–C bond distances are closer to the accepted value for phenyl rings.[23,32,33] However, estimates of bond shortening due to thermal motion indicate that our lower observed value is attributable to thermal motion rather than to any molecular or electronic effect. The C–F bond distances average 1.396 ± 0.031 Å. This value is somewhat larger than previously observed[23,32,33] but not significantly so. For example, in (π-C_7H_7)Mo(C_6F_5)$(CO)_2$ the C–F bond distances average 1.344 ± 0.010 Å.[33]

Iridium–Carbon Bond Lengths

In Table VII we have compiled Ir–C bond distances and angles of compounds related to the one of the present study (**5**). Our results are well within the range of listed values and are indicative of multiple bonding between the iridium and carbonyl carbon and an almost pure σ bond between the metal and carbon of the C_6F_5 ligand. In their recent study of an Ir–Cu cluster system, Churchill and Bezman[21] had the opportunity of measuring eight independent values of the Ir–C distance for a similar bonding situation. Their values range from 1.982 (26) to 2.109 (21) Å (average 2.044 ± 0.039 Å). Although their range of values overlaps those shown in Table VII, the average is slightly smaller as is to be expected for an sp carbon atom.

An interesting feature of the results listed in Table VII is that there is a relatively small spread in the values of the Ir–C distances if one takes into account the large variety of substances acting as a ligand to the Ir atom. For example, in compound **2** the Ir is bound to the ethylene carbons of tetracyanoethylene; in the case of **3**, to CHF_2; in **5**, to C_6F_5; while in **7** the Ir atom is bound by the end carbons of the allyl group of 1,2,3-triphenylallyl; **8** contains Ir–C bonds from the ortho carbons of phenyl rings belonging to a phosphine ligand to the metal; and, finally, **9** has an Ir–CH_3 fragment. In all, the Ir–C distances range from 2.045 (55) to 2.202 (22) Å, all of which are σ bonds. This last fact, as it concerns our compound, is interesting since it has been stated[11] that insofar as adduct formation this substance is expected to be less reactive than Vaska's compound because "although the inductive electron withdrawing effect of the C_6F_5 group is less than that of, say, chlorine, more efficient π-overlap can occur when this group is σ bonded to a metal, and hence the electrron density on the metal atom is reduced". Our results seem to indicate that such π overlap is at best minimal, or nonexistent, in the present compound. Thus, the reduced reactivity of the pentafluorophenyl derivative toward oxidative addition reactions must stem from other causes, probably steric in nature.

Figure 3 shows the packing of the molecules within the unit cell. There are no intramolecular contacts less than 3 Å. Thus, only van der Waals forces are operative between molecules.

Acknowledgment. The authors are grateful to the National Science Foundation for a grant (GP-20526) in support of this research program.

Table VII. Comparison of Ir–C(CO) and Ir–C(σ) Bonds

No.	Compd	Ir–C(O), Å	C–O, Å	Ir–C–O, deg	Ir–C(σ),[b] Å	Coordination	Ref
1	$[(CO)(PPh_3)]Ir[(FC_6H_4)_2N_4](BF_4)$	1.806 (18)	1.166 (19)	173.5 (15)		Distorted sq pyramid	25
2	$Ir(CO)Cl(tcne)(AsPh_3)_2$[a]	1.826 (14)	1.20 (2)		2.107 (4)[c]	Octahedral[d]	26
3	$IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2$	1.844 (20)	1.149 (20)	173 (2)	2.087 (20)	Octahedral	27
4	$Ir(NO)(CO)(PPh_3)_2$	1.873 (11)	1.144 (11)	177.8 (9)		Distorted tetrahedron	28
5	$Ir(CO)(C_6F_5)(PPh_3)_2$	1.891 (17)	1.137 (22)	179 (1)	2.090 (16)	Slightly distorted square planar	This study
6	$[(CO)_2Ir(CS)(PPh_3)_2]PF_6$	1.938 (26)[c]	1.181 (31)[c]	174 (3)		Trig bipyramid	29
7	$[Ir(C_3Ph_3)Cl(CO)(PMe_3)_2]BF_4$	1.939 (18)	1.12 (2)	175 (2)	2.045 (55)[c]	Distorted octahedron	30
8	$IrCl[P(OPh)_2(OC_6H_4)]_2[P(OPh)_3]$				2.105 (20)[c]	Distorted octahedron	31
9	$(C_8H_{12})[P(Ph)Me_2]_2Ir(CH_3)$				2.202 (22)	Trig bipyramid	34

[a] tcne = tetracyanoethylene. [b] σ-bonded moiety, if any, for the compound in question. [c] Mean value and standard deviation from the mean. [d] If both carbons of tcne are counted as separate ligands, which seems logical, since they are σ bonded to the Ir atom. Otherwise, this compound is a distorted trigonal bipyramid.

Registry No. *trans*-Pentafluorophenylcarbonylbis(triphenylphosphine)iridium(I), 42402-09-5.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th

St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC500812-11-75.

References and Notes

(1) (a) Ohio University. (b) University of Houston. (c) University of Massachusetts.
(2) L. Vaska and J. M. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).
(3) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).
(4) J. P. Collman and W. R. Roper, *Adv. Organomet. Chem.*, **7**, 53 (1968).
(5) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).
(6) J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970).
(7) G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1302 (1970).
(8) R. Nast and L. Dahlenburg, *Chem. Ber.*, **105**, 1456 (1972).
(9) M. D. Rausch and G. A. Moser, *Inorg. Chem.*, **13**, 11 (1974).
(10) R. L. Bennett, M. I. Bruce, and R. J. Goodfellow, *J. Fluorine Chem.*, **2**, 447 (1973).
(11) R. L. Bennett, M. I. Bruce, and R. C. F. Gardner, *J. Chem. Soc., Dalton Trans.*, 2653 (1973).
(12) L. Dahlenburg and R. Nast, *J. Organomet. Chem.*, **71**, C49 (1974).
(13) "Enraf-Nonius Manual for the CAD-4 System", Delft, Holland, 1972.
(14) A. Stanislowski and B. Frenz, "Program HYDROGEN", Crystallography Library, Texas A&M University, College Station, Tex.
(15) All calculations were performed at the Ohio University Computing Center on the IBM 360/44 using the programs of F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, NRC Crystallography Programs for the IBM 360, National Research Council, Ottawa, Canada.
(16) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(17) "International Tables for X-Ray Crystallography", Vol. 3, Kynoch Press, Birmingham, England, 1962.
(18) Supplementary material.
(19) All drawings were made with the aid of ORTEP: C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn.
(20) M. E. Pippy and F. R. Ahmed, NRC-22 Mean Plane, National Research Council, Ottawa, Canada, 1967.
(21) M. R. Churchill and S. Bezman, *Inorg. Chem.*, **13**, 1418 (1974).
(22) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **13**, 1427 (1974).
(23) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968).
(24) I. Bernal, A. Clearfield, and J. S. Ricci, Jr., *J. Cryst. Mol. Struct.*, **4**, 43 (1974).
(25) F. W. B. Einstein and D. Sutton, *Inorg. Chem.*, **11**, 2827 (1972).
(26) B. R. Dunn, R. Jacob, and C. J. Fritchie, *J. Chem. Soc., Dalton Trans.*, 2007 (1972).
(27) A. J. Shultz, G. P. Khare, C. D. Meyer, and R. Eisenberg, *Inorg. Chem.*, **13**, 1019 (1974).
(28) C. P. Brock and J. A. Ibers, *Inorg. Chem.*, **11**, 2813 (1972).
(29) J. S. Fields and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 2269 (1972).
(30) R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, **11**, 2237 (1972).
(31) J. M. Guss and R. Mason, *J. Chem. Soc., Dalton Trans.*, 2193 (1972).
(32) F. Sanz and J. J. Daly, *J. Chem. Soc. A*, 1083 (1971).
(33) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 1110 (1969).
(34) M. R. Churchill and S. A. Bezman, *J. Organomet. Chem.*, **31**, C43 (1971).

Contribution from the Department of Chemistry,
McMurry College, Abilene, Texas 79605

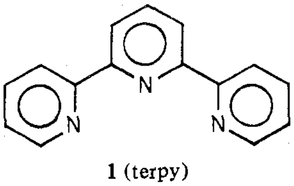
Synthesis and Spectroscopic Characterization of Bis[2,6-di(2'-quinolyl)pyridine] Complexes of Ruthenium(II) and Osmium(II)

D. M. KLASSEN,* C. W. HUDSON, and E. L. SHADDIX

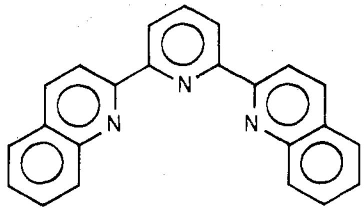
Received April 1, 1975 AIC50237Y

The preparation and spectroscopic characterization of the bis[2,6-di(2'-quinolyl)pyridine] complexes of ruthenium(II) and osmium(II) are reported. In both complexes the charge-transfer absorption bands are broadened and red shifted about 1.5 kK, the emission spectra are red shifted about 2 kK, and the measured luminescence lifetimes are shortened as a result of benzo substitution on the parent terpyridine ligand. The observed luminescence is assigned to a charge-transfer transition.

In 1932 Morgan and Burstall[1] first prepared 2,2',2''-terpyridine (terpy) (**1**) and subsequently showed its ability to form complexes with various metal ions.[2] Since that time terpyridine and many of its derivatives have been studied for possible use in the spectrophotometric determination of iron.[3,4] More recently a benzo-disubstituted terpyridine, 2,6-di(2'-quinolyl)pyridine (dqp) (**2**), and its iron(II) complex have been prepared and studied.[5] Benzo substitution adjacent to the nitrogen atoms leads to such steric crowding that the bischelated ferrous complex is high spin, whereas that of terpy is low spin. Less drastic alterations in the spectral properties of the complexes of the heavier metals are expected.



1 (terpy)



2 (dqp)

In this paper we report a spectroscopic study of the bisdiquinolylpyridine complexes of ruthenium(II) and osmium(II). The effect of the benzo substituents on the visible–ultraviolet absorption and emission spectra of the complexes is presented. Synthesis and purification of the title compounds is detailed.

Experimental Section

Preparations. 2,6-Di(2'-quinolyl)pyridine (dqp) was prepared as described by Harris, Patil, and Sinn.[5] Recrystallization from benzene yielded dqp in 60% yield; mp 227–228°.

Anal. Calcd for $C_{23}H_{15}N_3$: C, 82.86; H, 4.54. Found: C, 82.85; H, 4.46.

Bis[2,6-di(2'-quinolyl)pyridine]ruthenium(II) Perchlorate Monohydrate, $[Ru(dqp)_2](ClO_4)_2 \cdot H_2O$. Procedure A. To 0.20 g (0.53 mmol) of $K_2[RuCl_5(H_2O)]$[6] dissolved in 25 ml of glycerol was added 0.40 g (1.2 mmol) of dqp dissolved in 25 ml of glycerol. The resultant dark purple solution was refluxed for 2 hr, diluted with 40 ml of water, and filtered. The filtrate was heated almost to boiling and sodium perchlorate solution (10%) was added slowly. A dark purple precipitate formed immediately. After cooling in an ice bath the precipitate was collected, washed with cold water, and recrystallized from ethanol to yield 0.15 g (28% yield) of product.

Procedure B. A blue solution of ruthenium(II) chloride in methanol was prepared by the hydrogen (2 atm) reduction of $RuCl_3 \cdot xH_2O$ (Engelhard Industries) catalyzed by platinum black as described by Rose and Wilkinson.[7] Five milliliters of the blue solution containing 0.5 mmol of Ru(II) was added slowly under a nitrogen atmosphere to a hot (70°) solution of 0.40 g (1.2 mmol) of dqp dissolved in 15 ml of ethylene glycol. After distillation of the methanol solvent the