luded to above, was present in ca. 66% and species 5 and 8 in about 17% abundance each. Compound 8 appears in the $^{31}P\{^1H\}$ NMR spectrum as a singlet at δ 23.1 and shows one strong carbonyl band at 1650 cm^{-1} in the IR spectrum. This species was shown to be $(Ph_3P)N_2C(C(O)Ph)_2$ on the basis of a comparison of its spectral parameters with those of an authentic sample prepared as described in the Experimental Section. It seems therefore that compound 8 arises due to loss of PPh_3 and $N_2C(C(O)Ph)_2$ upon refluxing, followed by direct combination of these ligands, and its formation does not seem to be metal mediated. This phosphazine compound has previously been prepared by the direct reaction of PPh_3 and $N_2C(C(O)Ph)_2$ in refluxing ether.[22]

Conclusions

The four-coordinate complex $[IrCl(N_2C(C(O)Ph)_2)(PPh_3)_2]$ (1) containing a singly bent diazoalkane molecule is found to react with PMe_2Ph, *t*-BuNC, and NO^+ to yield the five-coordinate adducts, much as was shown for the analogous $N_2C_5Cl_4$-containing complex.[8] Complex 1 is also found to react with 1 equiv of HCl to give an equilibrium mixture containing the metal hydride, $[IrHCl_2(N_2C(C(O)Ph)_2)(PPh_3)_2]$ (6), and $[IrCl_2(HN_2C(C(O)Ph)_2)(PPh_3)_2]$ (5), in which the latter species is present in approximately a 15-fold excess. Transfer of the hydrido ligand from the metal to the nitrogen atom which is bound to Ir is accompanied by coordination of one of the benzoyl oxygens to Ir, forming a six-membered metallacycle. It is possible that this chelate formation is responsible for the observation of 5 and contrasts with the analogous chemistry involving the $N_2C_5Cl_4$ group[8] which showed only the metal hydride species. The observation of reversible ring formation upon hydride transfer is unusual and demonstrates the subtle differences in chemistry that can result compared with other diazoalkanes, owing to the potential for involvement of the benzoyl oxygen atoms in coordination to the metal.

Acknowledgment. This work was supported by the University of Alberta and the Natural Sciences and Engineering Research Council of Canada. We thank Dr. R. G. Ball for collecting the X-ray data.

Registry No. **1**, 100701-28-8; **2**, 100701-32-4; **3**, 100701-33-5; **4**, 100701-35-7; **5**, 100701-29-9; **6**, 100701-36-8; **7**, 100701-37-9; **8**, 13339-90-7; *trans*-$[IrCl(N_2)(PPh_3)_2]$, 21414-18-6; $N_2C(ClO)Ph)_2$, 2085-31-6; $[IrCl(HN_2C(C(CO)Ph)_2)(PPh_3)][BF_4]$, 100701-39-1.

Supplementary Material Available: Listings of observed and calculated structure amplitudes, thermal parameters for the anisotropic atoms, and idealized hydrogen parameters (8 pages). Ordering information is given on any current masthead page.

Diazoalkane Activation by Iridium Phosphine Compounds. 2. Unusual Products Resulting from N_2 Loss from the Dibenzoyldiazomethane Ligand: Structures of $[IrCl(HC(C(O)Ph)_2)(PC_6H_4Ph_2)(PPh_3)]\cdot{}^1/_2C_6H_5CH_3$ and $[IrCl((C_6H_4)C(O)CC(Ph)OPPh_2)(PPh_3)_2]\cdot C_6H_5CH_3$

Martin Cowie,* Ian R. McKeer, Stephen J. Loeb,† and Michele D. Gauthier

Department of Chemistry, The University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received June 20, 1985

Refluxing $[IrCl(N_2C(C(O)Ph)_2)(PPh_3)_2]$ in toluene results in N_2 loss and ortho metalation of one of the phosphine phenyl groups, yielding the β-diketonate complex $[IrCl(HC(C(O)Ph)_2)(PC_6H_4Ph_2)(PPh_3)]$ (2). The diketonate group, which chelates through both oxygen atoms, is formed by hydride transfer from the metal to the carbene carbon, generated by N_2 extrusion. When dibenzoyldiazomethane is reacted with $[IrCl(PPh_3)_3]$ in refluxing THF, a geometric isomer of 2 is formed as the major product. A minor product in this reaction is $[IrCl((C_6H_4)C(O)CC(Ph)OPPh_2)(PPh_3)_2]$ (5), a species containing a highly unusual tridentate ligand which has formed by the condensation of the carbene fragment, resulting from the diazoalkane molecule, and PPh_2 which has resulted from phosphorus-aryl bond cleavage in PPh_3. The X-ray structures of 2 (as the hemitoluene solvate) and 5 (as the toluene solvate) have been determined. Compound 2 crystallizes in the space group $P\bar{1}$ with a = 12.396 (2) Å, b = 19.272 (3) Å, c = 10.742 (1) Å, α = 97.845 (6)°, β = 115.594 (9)°, γ = 78.772 (7)°, and Z = 2. The structure has refined to R = 0.050 and R_w = 0.068 on the basis of 223 parameters refined and 5140 observations. Compound 5 crystallizes in space group $P1$ with a = 12.1972 (8) Å, b = 10.163 (1) Å, c = 11.761 (1) Å, α = 103.609 (8)°, β = 95.059 (7)°, γ = 96.619 (7)°, and Z = 1 and has refined to R = 0.028 and R_w = 0.037 on the basis of 266 parameters refined and 4387 observations.

Introduction

The interaction of diazoalkanes with transition-metal complexes, under all except the mildest conditions, often results in decomposition of the diazo compound and isolation of a product in which N_2 loss has occurred.[1-5] Although there is usually evidence to support the existence

---

† Present address: Department of Chemistry, University of Winnipeg, Winnipeg, Manitoba R3B 2E9.

(1) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 599.
(2) Lappert, M. F.; Cardin, D. J.; Cetinkaya, B.; Doyle, M. J. *Chem. Soc. Rev.* 1973, *2*, 99.
(3) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800.
(4) Reimer, K. J.; Shaver, A. *J. Organomet. Chem.* **1975**, *93*, 239.

of unstable diazoalkane–metal complexes or carbene–metal intermediates, the exact nature of the final product depends critically on the availability of certain transformation pathways.[1,6–12] For example, in some instances diazo compounds preferentially afford carbene complexes, whereas, if the metal substrates contain metal–hydride or metal–halogen functions susceptible to carbene insertion, then formation of alkyl or haloalkyl complexes may occur.[13–17]

In our studies on the interaction of dibenzoyldiazomethane, $N_2C(C(O)Ph)_2$, with iridium(I) phosphine complexes, we were interested in establishing the effects of the benzoyl groups on the chemistry of the molecule. In the previous paper[18] we described how the benzoyl groups could be involved in chemistry in which the diazoalkane molecule remained intact, and in this paper we describe their involvement upon loss of N_2 from the molecule. A preliminary report on this work has appeared.[19]

Experimental Section

All solvents were dried and degassed prior to use and all reactions were carried out under Schlenk conditions in an atmosphere of predried dinitrogen.[20] $[IrCl(N_2C(C(O)Ph)_2)(PPh_3)_2]$,[18] $[IrCl(PPh_3)_3]$,[21] *trans*-$[IrCl(N_2)(PPh_3)_2]$,[22] and dibenzoyldiazomethane[23] were prepared by published methods and triphenylphosphine was recrystallized from ethanol prior to use. Hydrated iridium trichloride, supplied by Research Organic/Inorganic Chemicals, and all other reagents were used as received.

Infrared spectra were recorded on a Nicolet 7199 Fourier transform interferometer by using Nujol mulls. $^{31}P\{^1H\}$ NMR spectra were obtained at 36.4 MHz on a Bruker HFX-90 spectrometer at 233 K with an external acetone-d_6 lock. Phosphorus chemical shifts were measured relative to external 85% H_3PO_4, with positive shifts assigned as downfield from this standard. ^1H NMR spectra were obtained at 400 MHz on a Bruker WP-400 spectrometer with an internal CD_2Cl_2 lock. Elemental analyses were performed by the microanalytical services at the University of Alberta and Canadian Microanalytical Services, Vancouver, B.C., Canada.

Preparations. (i) $[IrCl(HC(C(O)Ph)_2)(PC_6H_4Ph_2)(PPh_3)]\cdot{}^1/_2C_6H_5CH_3$ (Isomer 1) (2). Method A. A suspension of $[IrCl(N_2C(C(O)Ph)_2)(PPh_3)_2]$ (1) (200 mg, 0.199 mmol) in toluene (15 mL) was refluxed for 35 min. The resulting orange-yellow solution was concentrated to approximately 3 mL, and yellow crystals were produced upon standing overnight (90% yield). The ^1H NMR spectrum confirmed the presence of 0.5 equiv of toluene of solvation. Anal. Calcd for $C_{54.5}H_{44}IrClO_2P_2$: C, 64.14; H, 4.35; N, 0.00; Cl, 3.47. Found: C, 63.68; H, 4.59; N, 0.00; Cl, 3.09. This complex was characterized spectroscopically and by an X-ray structure determination. $^{31}P\{^1H\}NMR$ (CH_2Cl_2):[24] δ −2.9 (d), −82.5 (d) (J_{PP} = 21 Hz). ^1H NMR (CD_2Cl_2): δ 6.80 (s). IR (Nujol): 1521 (st), 1540 (st), 1592 (m) cm^{-1}.

Method B. *trans*-$[IrCl(N_2)(PPh_3)_2]$ (377 mg, 0.483 mmol) and $N_2C(C(O)Ph)_2$ (121 mg, 0.483 mmol) were refluxed together in toluene (10 mL) for 35 min. The yellow-orange solution was treated as in method A resulting in a good yield of complex **2**. This method was also used to prepare $[IrCl(DC(C(O)Ph)_2)(P(C_6D_4)(Ph_2\text{-}d_{10}))(PPh_3\text{-}d_{15})]$ using *trans*-$[IrCl(N_2)(PPh_3\text{-}d_{15})_2]$, prepared from $PPh_3\text{-}d_{15}$.[25]

Method C. When a suspension of compound **1** (200 mg, 0.199 mmol) in 15 mL of CH_2Cl_2 was stirred at room temperature for 8 h, a 60:40 mixture of compound **2** and $[IrCl_2(HN_2C(C(O)Ph)_2)(PPh_3)_2]$ (**4**) was obtained. Compound **4** was characterized as explained in the previous paper.[18]

(ii) $[IrCl(HC(C(O)Ph)_2)(PC_6H_4Ph_2)(PPh_3)]$ (Isomer 2) (3). A mixture of $[IrCl(PPh_3)_3]$ (392 mg, 0.390 mmol) and $N_2C(C(O)Ph)_2$ (97 mg, 0.390 mmol) were combined in 15 mL of THF, and the solution was refluxed for 40 min. The $^{31}P\{^1H\}$ NMR spectrum of the resulting yellow-orange solution showed that complex **3** was produced in ca. 90% yield together with a second product (10%), compound **5**. Attempts to purify compound **3** led to its conversion to compound **2**. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ −11.0 (d), −69.2 (d) (J_{PP} = 17 Hz). ^1H NMR (CD_2Cl_2): δ 7.0 (s). IR (Nujol): 1522 (st), 1544 (st), 1588 (m) cm^{-1}.

(iii) $[IrCl((C_6H_4)C(O)CC(Ph)OPPh_2)(PPh_3)_2]\cdot C_6H_5CH_3$ (5). Well-formed single crystals of **5** were obtained from a saturated toluene solution of compound **3**. A mass spectrum of this product gave the major peaks at *m/e* 974, 938, 751, 451, 406 and 262, which could be interpreted as resulting from a complex containing Ir, Cl, PPh_3, and at least part of the dibenzoyldiazomethane ligand. This product was characterized by spectroscopy and by an X-ray structure determination. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ −15.7 (d, 2 P), 83.7 (t, 1 P) (J_{PP} = 21 Hz). IR (Nujol): 1546 (m), 1577 (m), 1636 (m) cm^{-1}.

X-ray Data Collection for Compounds 2 and 5

Single crystals of $[IrCl(HC(C(O)Ph)_2)(PCH_4Ph_2)(PPh_3)_2]\cdot{}^1/_2C_6H_5CH_3$ (**2**) were grown from a saturated toluene solution of the complex, prepared as described earlier by method B. Suitable crystals of $[IrCl((C_6H_4)C(O)CC(Ph)OPPh_2)(PPh_3)_2]\cdot C_6H_5CH_3$ (**5**) were also obtained from toluene as described earlier. Preliminary film data on each indicated $\bar{1}$ Laue diffraction symmetry with no systematic absences, consistent with the space groups $P1$ and $P\bar{1}$.

For compound **2** the space group $P\bar{1}$ was chosen and later verified by successful refinement of the structure, whereas for compound **5** the noncentrosymmetric space group was determined to be correct (vide infra). Accurate cell parameters for both compounds were obtained by least-squares analyses of the setting angles of 12 carefully centered reflections chosen from diverse regions of reciprocal space using Cu Kα radiation (**2**, $55° < 2\theta < 63°$; **5**, $50° < 2\theta < 70°$) and obtained by using a narrow X-ray source. See Table I for pertinent crystal data and details of intensity collection.

Intensity data were collected on a Picker four-circle automated diffractometer, equipped with a scintillation counter and a pulse-height analyzer tuned to accept 90% of the Cu Kα peak. Background counts were measured at both ends of the scan range with crystal and counter stationary. Standard deviations in the intensities were computed in the usual way[26] by using a value of 0.05 for *p*. In each case the intensities of three standard reflections were measured automatically every 100 reflections to assess decomposition or crystal movement, and four additional standards

---

(5) Reimer, K. J.; Shaver, A. *Inorg. Chem.* **1975**, *14*, 2707.

(6) Herrmann, W. A.; Kruger, C.; Goddard, R.; Bernal, I. *J. Organomet. Chem.* **1977**, *140*, 73.

(7) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 334.

(8) Herrmann, W. A.; Reiter, B.; Biersack, H. *J. Organomet. Chem.* **1975**, *97*, 245.

(9) Fischer, E. O. *Angew. Chem.* **1974**, *86*, 651.

(10) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

(11) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545.

(12) Cotton, F. A.; Lukehardt, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487.

(13) Seyferth, D. *Chem. Rev.* **1955**, *55*, 1155.

(14) Mango, F.; Dvoretzky, I. *J. Am. Chem. Soc.* **1966**, *88*, 1654.

(15) Empsall, H. D.; Hyde, E. M.; Markham, R.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589.

(16) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 761.

(17) Pu, L.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1974**, 9.

(18) Cowie, M.; Loeb, S. J.; McKeer, I. *Organometallics*, preceding paper in this issue.

(19) Cowie, M.; Gauthier, M. D.; Loeb, S. J.; McKeer, I. *Organometallics* **1983**, *2*, 1057.

(20) Dry nitrogen from the cylinder was passed through scrubbing columns of molecular sieve and Ridox.

(21) Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983.

(22) Collman, J. P.; Hoffman, N. W.; Hosking, J. W. *Inorg. Synth.* **1970**, *12*, 8.

(23) Regitz, M. *Chem. Ber.* **1966**, *99*, 3128.

(24) Abbreviations: s = singlet, d = doublet, st = strong, and m = medium.

(25) The $PPh_3\text{-}d_{15}$ was prepared as described in ref 21, except with bromobenzene-d_5 purchased from Aldrich.

(26) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

Table I. Crystal Data and Intensity Collection Details for Compounds 2 and 5

	2	5
formula	$C_{54.5}H_{44}O_2P_2ClIr$	$C_{70}H_{57}O_2P_3ClIr$
fw	1020.58	1250.81
cell parameters		
a, Å	12.396 (2)	12.1972 (8)
b, Å	19.272 (3)	10.163 (1)
c, Å	10.742 (1)	11.761 (1)
α, deg	97.845 (6)	103.609 (8)
β, deg	115.594 (9)	95.059 (7)
γ, deg	78.772 (7)	96.619 (7)
V, Å^3	2268.9	1397.4
Z	2	1
D, g·cm^{-3}	1.495 (calcd)	1.486 (calcd) 1.47 (1) (by flotation)
space group	$P\bar{1}$ (C_i^1)	$P1$ (C_1^1)
cryst dimens, mm	0.064 × 0.155 × 0.269	0.375 × 0.135 × 0.259
cryst vol, mm^3	0.0041	0.0106
temp, °C	22	22
radiatn	Cu Kα ($\lambda(\alpha_1)$ = 1.540 562 Å) filtered with 0.5-mil Ni foil	
abs coeff μ, cm^{-1}	71.39	61.67
range in transmissn coeff	0.322–0.665	0.256–0.499
receiving aperature	4 mm × 4 mm; 30 cm from crystal	
takeoff angle, deg	3.8	3.5
scan speed	2° in 2θ/min	2° in 2θ/min
scan range	0.7° below Kα_1 to 0.7° above Kα_2	0.9° below Kα_1 to 0.9° above Kα_2
bkgd counts	3.0° ≤ 2θ ≤ 94.3°, 10 s; 94.3° ≤ 2θ ≤ 120°, 20 s	3° ≤ 2θ ≤ 102°, 10 s; 102° ≤ 2θ ≤ 120°, 20 s
2θ limits, deg	3.0–120.0	3.0–120.0
no. of variables	223	266
data used ($F_o^2 \geq 3\sigma(F_o^2)$)	5140	4387
error in obsvn of unit wt	2.088	1.371
R	0.050	0.028
R_w	0.068	0.037

were measured three times a day. For both crystals the standards remained essentially constant throughout data collection. Absorption corrections were applied to both data sets by using Gaussian integration.[27]

Structure Solution and Refinement

(i) Compound 2. The structure was solved in space group $P\bar{1}$ by using standard Patterson, Fourier, and full-matrix, least-squares techniques. All atoms, excluding those of the toluene group, were ultimately located. The carbon atoms of all phenyl groups, except those in the ortho-metalated ring (which were treated as individual atoms), were refined as rigid groups having D_{6h} symmetry, C–C distances of 1.392 Å, and individual isotropic thermal parameters for each atom. The independent non-hydrogen atoms were refined anisotropically. All hydrogens in the complex were input as fixed contributions in their idealized positions. The toluene ring was located on the inversion center at $^1/_2$, 0, 0 but was severely disordered; no distinct peaks in the Fourier maps could be associated with the individual toluene atoms. Initially the ring atoms were refined individually; however, a geometrically unreasonable structure resulted. The ring atoms were therefore treated as a rigid group in which only the orientation angles of the group were varied. The thermal parameters were set at values near those obtained from the individual atom treatment. A subsequent difference Fourier map failed to locate the carbon atom of the methyl substituent, so it was included as a sixfold disordered group and was not refined. More elaborate models, in which toluene molecules were rotationally disordered, were not attempted since the substantial thickness of the observed electron density suggested that the disorder was not merely a rotation perpendicular to the toluene ring but was probably due to a great many toluene orientations. In any event, the treatment of the disordered solvent molecule will probably have no significant influence on the parameters in the complex.

In the final difference Fourier map the top 20 residuals (0.76–1.15 e Å^{-3}) were located around the toluene group, the iridium atom and the phenyl groups of the phosphine ligands. On earlier maps a typical carbon atom had an intensity of ca. 5.0 e Å^{-3}.

(ii) Compound 5. The structure was solved in space group $P1$, with the iridium position defined arbitrarily at (0, 0, 0). With one molecule per unit cell the lack of $\bar{1}$ molecular symmetry excluded $P\bar{1}$ as a space group possibility. The positions of all other non-hydrogen atoms in the complex were chosen from the two superimposed, inversion-related images, much as was previously described for a similar problem,[28] such that a consistent solution was obtained. Ultimately, even the hydrogen atoms (except the toluene methyl hydrogens) were located.

All phenyl groups (except the ortho-metalated one) and the toluene ring atoms were refined as rigid groups as described earlier. All other non-hydrogen atoms, except the toluene methyl carbon, were refined anisotropically. Hydrogen atoms, apart from the toluene methyl ones, were included as fixed contributions with thermal parameters of 1 Å^2 greater than that of their attached carbon atom.

Since the space group $P1$ is polar and the iridium atom has a large anomalous dispersion effect with Cu Kα radiation, the correct enantiomer had to be established in order to avoid polar dispersion errors which would result in significant shifts in the positions of the heavier Ir, P, and Cl atoms relative to the lighter ones and to each other.[29] The correct enantiomer refined to R = 0.028 and R_w = 0.037 for 266 variables and 4387 unique reflections whereas the incorrect one refined to R = 0.039 and R_w = 0.058. As expected for the correct enantiomer, the two chemically equivalent Ir–P distances (2.384 (3) and 2.380 (3) Å) were in much better agreement than those of the wrong enantiomer (2.438 (4) and 2.318 (4) Å), and the range in chemically equivalent P–C distances (1.836 (5)–1.864 (5) Å) was somewhat smaller in the former than in the latter (1.827 (7)–1.860 (6) Å).

In the final electron density difference map the top 20 residuals (0.77–0.38 e Å^{-3}) were located around the toluene of solvation, the iridium atom, and the phenyl rings within the molecule. In earlier maps a typical carbon atom had an intensity of ca. 3.3 e Å^{-3}.

Full-matrix, least-squares refinement techniques were used for both structures, utilizing the scattering factors[30,31] and anomalous

---

(27) For a description of programs used, see: Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500.

(28) Cowie, M.; Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7608.

(29) (a) Ueki, T.; Zalkin, A.; Templeton, D. H. *Acta Crystallogr.* **1966**, *20*, 836. (b) Cruikshank, D. W. J.; McDonald, W. S. *Ibid.* **1967**, *23*, 9.

Table II. Positional and Equivalent Isotropic Thermal Parameters for the Individual Atoms in Compound 2

atom	x^a	y	z	B, Å^2	atom	x	y	z	B, Å^2
Ir	0.04403 (3)	0.25539 (2)	0.12116 (3)	3.40	C(3)	0.1326 (8)	0.3596 (4)	0.0186 (8)	4.27
Cl	0.0616 (2)	0.1638 (1)	−0.0572 (2)	5.29	C(61)	−0.1003 (8)	0.3248 (5)	0.2542 (8)	4.34
P(1)	0.2013 (2)	0.2007 (1)	0.3001 (2)	3.84	C(62)	−0.0035 (7)	0.3396 (4)	0.2334 (7)	3.70
P(2)	−0.1065 (2)	0.2365 (1)	0.1743 (2)	4.09	C(63)	0.0296 (9)	0.4063 (4)	0.2745 (8)	4.63
O(1)	−0.0956 (5)	0.3053 (3)	−0.0478 (5)	4.36	C(64)	−0.036 (1)	0.4562 (5)	0.333 (1)	5.85
O(2)	0.1645 (5)	0.3086 (3)	0.0963 (5)	4.24	C(65)	−0.128 (1)	0.4400 (6)	0.355 (1)	6.76
C(1)	−0.0868 (8)	0.3513 (4)	−0.1145 (8)	4.17	C(66)	−0.1636 (9)	0.3739 (6)	0.317 (1)	5.91
C(2)	0.0183 (9)	0.3791 (5)	−0.0822 (9)	4.79					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

Table III. Rigid-Group Parameters for Compound 2

Derived Positions and Thermal Parameters

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(11)	0.2107 (7)	0.1052 (3)	0.3099 (8)	4.7 (2)	C(54)	−0.0993 (8)	0.0844 (4)	0.4718 (8)	9.8 (4)
C(12)	0.1216 (6)	0.0683 (4)	0.2114 (5)	5.6 (2)	C(55)	−0.0786 (8)	0.1536 (5)	0.5187 (7)	9.4 (4)
C(13)	0.1294 (6)	−0.0041 (4)	0.2202 (6)	7.3 (3)	C(56)	−0.0815 (8)	0.2003 (4)	0.4288 (9)	7.3 (3)
C(14)	0.2263 (7)	−0.0395 (3)	0.3276 (8)	8.0 (3)	C(71)	−0.203 (1)	0.3745 (4)	−0.2343 (9)	4.6 (2)
C(15)	0.3154 (6)	−0.0025 (4)	0.4262 (5)	8.2 (3)	C(72)	−0.308 (1)	0.3544 (5)	−0.242 (1)	6.9 (3)
C(16)	0.3076 (6)	0.0698 (4)	0.4173 (6)	6.9 (3)	C(73)	−0.419 (1)	0.3745 (5)	−0.3513 (5)	7.7 (3)
C(21)	0.3486 (8)	0.2029 (3)	0.301 (2)	4.3 (2)	C(74)	−0.425 (1)	0.4147 (4)	−0.4530 (9)	7.2 (3)
C(22)	0.3631 (9)	0.1800 (6)	0.180 (1)	5.6 (2)	C(75)	−0.320 (1)	0.4348 (5)	−0.445 (1)	8.0 (3)
C(23)	0.476 (1)	0.1739 (5)	0.179 (1)	6.9 (2)	C(76)	−0.209 (1)	0.4147 (5)	−0.3360 (5)	7.4 (3)
C(24)	0.5751 (8)	0.1906 (3)	0.298 (2)	7.6 (3)	C(81)	0.2329 (6)	0.4000 (4)	0.0458 (6)	4.6 (2)
C(25)	0.5606 (9)	0.2135 (6)	0.420 (1)	7.8 (3)	C(82)	0.3497 (7)	0.3716 (4)	0.1335 (7)	5.6 (2)
C(26)	0.447 (1)	0.2197 (5)	0.421 (1)	6.9 (3)	C(83)	0.4461 (5)	0.4073 (4)	0.1629 (6)	7.0 (3)
C(31)	0.2138 (8)	0.2393 (4)	0.4683 (8)	5.6 (2)	C(84)	0.4257 (6)	0.4715 (4)	0.1048 (6)	8.2 (3)
C(32)	0.2359 (8)	0.3090 (4)	0.5013 (7)	7.1 (3)	C(85)	0.3089 (7)	0.5000 (4)	0.0171 (7)	8.2 (3)
C(33)	0.2368 (8)	0.3434 (3)	0.6244 (9)	9.6 (4)	C(86)	0.2125 (5)	0.4642 (4)	−0.0123 (6)	6.2 (2)
C(34)	0.2157 (8)	0.3081 (4)	0.7145 (8)	10.1 (4)	C(91)	0.581 (5)	−0.034 (2)	0.119 (3)	20.0
C(35)	0.1936 (8)	0.2383 (4)	0.6815 (7)	10.6 (4)	C(92)	0.622 (6)	−0.018 (2)	0.026 (6)	20.0
C(36)	0.1927 (8)	0.2039 (3)	0.5584 (9)	7.2 (3)	C(93)	0.541 (7)	0.016 (2)	−0.093 (5)	20.0
C(41)	−0.2521 (9)	0.2321 (4)	0.0305 (9)	4.3 (2)	C(94)	0.419 (5)	0.034 (2)	−0.119 (3)	20.0
C(42)	−0.3564 (9)	0.2694 (5)	0.0406 (8)	6.3 (2)	C(95)	0.378 (6)	0.018 (2)	−0.026 (6)	20.0
C(43)	−0.4692 (8)	0.2641 (4)	−0.0679 (5)	7.8 (3)	C(96)	0.459 (7)	−0.016 (2)	0.093 (5)	20.0
C(44)	−0.4776 (9)	0.2216 (4)	−0.1865 (9)	5.7 (2)	C(101)	0.666	−0.072	0.245	20.0
C(45)	−0.3733 (9)	0.1844 (5)	−0.1966 (8)	5.9 (2)	C(102)	0.752	−0.040	0.052	20.0
C(46)	−0.2605 (8)	0.1896 (4)	−0.0881 (5)	5.6 (2)	C(103)	0.586	0.032	−0.193	20.0
C(51)	−0.1052 (8)	0.1777 (4)	0.2920 (8)	5.8 (2)	C(104)	0.334	0.072	−0.245	20.0
C(52)	−0.1259 (8)	0.1085 (5)	0.2451 (7)	8.0 (3)	C(105)	0.248	0.040	−0.052	20.0
C(53)	−0.1230 (8)	0.0618 (4)	0.3350 (9)	11.1 (4)	C(106)	0.414	−0.032	0.193	20.0

Rigid-Group Parameters

	$x_c{}^a$	y_c	z_c	δ^b	ϵ	η
ring 1	0.2185 (5)	0.0329 (2)	0.3188 (5)	3.260 (5)	2.591 (5)	4.857 (4)
ring 2	0.4619 (4)	0.1968 (2)	0.2998 (4)	1.184 (4)	0.58 (1)	3.28 (1)
ring 3	0.2148 (5)	0.2737 (3)	0.5914 (5)	0.179 (5)	1.482 (6)	5.782 (5)
ring 4	−0.3649 (4)	0.2269 (2)	−0.0780 (4)	2.216 (4)	3.016 (6)	3.498 (6)
ring 5	−0.1023 (5)	0.1310 (3)	0.3819 (6)	3.284 (6)	1.720 (6)	5.584 (5)
ring 7	−0.3139 (5)	0.3946 (3)	−0.3436 (5)	0.970 (5)	2.872 (7)	3.393 (7)
ring 8	0.3293 (5)	0.4358 (2)	0.0753 (5)	3.635 (4)	2.986 (5)	0.762 (5)
ring 9[c]	0.5	0.0	0.0	−1.17 (1)	0.47 (4)	4.98 (5)
ring 10	0.5	0.0	0.0	−1.17	0.47	4.98

[a] x_c, y_c, and z_c are the fractional coordinates of the centroid of the rigid group. [b] The rigid-group orientation angles δ, ϵ, and η(radians) are the angles by which the rigid body is rotated with respect to a set of axes x, y, and z. The origin is the center of the ring; x is parallel to a^*, z is parallel to c, and y is parallel to the line defined by the intersection of the plane containing a^* and b^* with the plane containing b and c. [c] Rings 9 and 10 are the aromatic ring and the sixfold disordered methyl group of the toluene molecule, respectively.

dispersion terms[32] (for Ir, Cl, and P) from the usual sources.

For compound 2 the positional and thermal parameters for the individual atoms and the groups are given in Table II and III; for compound 5 these are listed in Tables IV and V. See the paragraph on supplementary material for other data available.

Descriptions of Structures

(i) $[\mathrm{IrCl(HC(C(O)Ph)_2)(PC_6H_4Ph_2)(PPh_3)}]\cdot{}^1/_2\mathrm{C_6H_5CH_3}$ (2).

The unit cell of compound 2 contains two discrete complex molecules and one toluene molecule which is severely disordered about the inversion center at ($^1/_2$, 0, 0). There are no unusual contacts between these molecules. A perspective view of the complex is shown in Figure 1; the relevant bond lengths and angles are given in Tables VI and VII. As shown in Figure 1, compound 2 can be described as a pseudooctahedral Ir(III) complex containing an ortho-metalated $\mathrm{PPh_3}$ group, a normal $\mathrm{PPh_3}$ group, a chloro ligand, and a β-diketonate ligand which is bound to Ir through both oxygen atoms. The $\mathrm{PPh_3}$ group appears normal, although the Ir–P(1) distance (2.263 (2) Å) is at the short end of the range usually observed for Ir(III) complexes;[33] by comparison, the Ir–P distances in

---

(30) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(31) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1979; Vol. IV, Table 2.2A.

(32) Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891.

Table IV. Positional and Thermal Parameters of Individual Atoms in Compound 5

atom	x	y	z	B, Å^2
Ir	0	0	0	2.03*
P(1)	0.1780 (2)	−0.0017 (3)	−0.0689 (2)	2.28*
P(2)	−0.1903 (2)	−0.0211 (3)	0.0328 (2)	2.58*
P(3)	0.05941 (16)	−0.0471 (2)	0.1804 (2)	2.40*
Cl	−0.0536 (2)	−0.2124 (2)	−0.1584 (2)	3.38*
C(1)	−0.0415 (6)	0.1155 (9)	−0.1191 (7)	2.64*
C(2)	−0.0838 (8)	0.0673 (10)	−0.2402 (8)	3.91*
C(3)	−0.1103 (8)	0.1537 (10)	−0.3082 (7)	4.37*
C(4)	−0.0976 (8)	0.2933 (10)	−0.2595 (8)	4.54*
C(5)	−0.0553 (8)	0.3458 (9)	−0.1436 (8)	4.05*
C(6)	−0.0281 (6)	0.2550 (8)	−0.0747 (7)	2.87*
C(7)	0.0207 (6)	0.3071 (8)	0.0484 (7)	2.91*
C(8)	0.0344 (7)	0.1940 (9)	0.1064 (8)	2.46*
C(9)	0.0599 (7)	0.2177 (8)	0.2269 (8)	2.66*
O(1)	0.0456 (6)	0.4293 (5)	0.0957 (5)	4.73*
O(2)	0.0563 (5)	0.1006 (5)	0.2714 (4)	2.87*
C(27)[b]	0.574 (2)	0.639 (3)	0.420 (2)	13.7 (7)

[a] For atoms with an asterisk the equivalent isotropic B for an anisotopically refined atom is given. [b] Atom C(27) is the toluene methyl group.

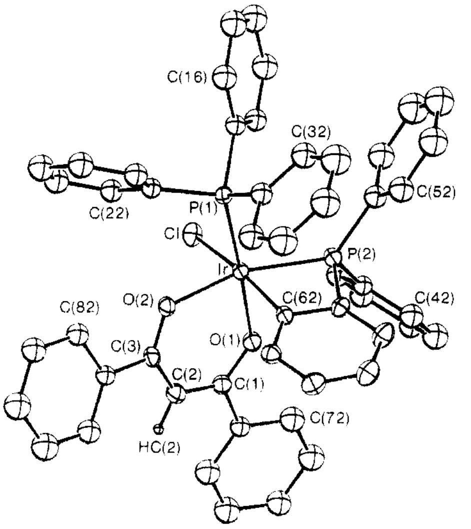

Figure 1. A perspective view of compound 2 showing the numbering scheme. Twenty percent thermal ellipsoids are shown.

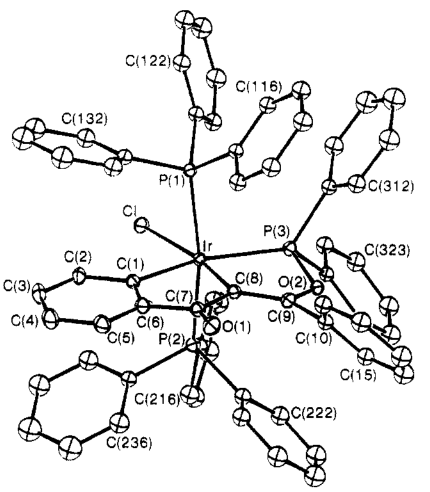

Figure 2. A perspective view of compound 5 showing the numbering scheme. Twenty percent thermal ellipsoids are shown.

the previous paper[18] average 2.391 (7) Å. On the basis of the small trans influence of groups coordinating through oxygen, the short Ir–P distance is not surprising; however, the presence of mutually cis triphenylphosphine groups can result in long Ir–P distances owing to steric interactions; this does not seem to be the case in the present compound. In the ortho-metalated phosphine group the Ir–P(2) distance (2.276 (2) Å) agrees well with the Ir–P(1) distance; it too is opposite a β-diketone oxygen atom. The geometry around P(2) is significantly distorted from that observed with normal PPh_3 groups, owing to the strain imposed by the resulting four-membered metallacycle ring which pulls ring 6 toward the metal. As a result, the Ir–P(2)–C(61) angle is only 85.6 (3)°, compared to the average of 115.1 (2)° for the angles about P(1). Similarly, the angles about C(61) deviate considerably from the normal 120° value such that P(2)–C(61)–C(62) is 98.5 (6)° and P(2)–C(61)–C(66) is 138.4 (8)°. It is also interesting that the Ir–P(2)–C(51) angle, at 130.8 (3)°, is also considerably different from the "normal" value. This is not a direct result of ortho metalation of ring 6 but does result indirectly from it since ring 5 is held adjacent to the other PPh_3 group and therefore bends away from it in order to avoid unfavorable contacts with it. Note, in Figure 1, that rings 1 and 3 stagger themselves with respect to ring 5 in order to minimize the contacts.

The Ir–C(62) distance (2.036 (8) Å) is typical for an ortho-metalated PPh_3 group,[34-36] and the Ir–Cl bond trans to this shows the expected lengthening (2.474 (2) Å) due to the high trans influence of the metalated carbon. By comparison, normal Ir–Cl bonds generally fall near 2.36–2.39 Å,[37] whereas those opposite ligands of high trans influence are expected near 2.45–2.48Å.[38,39]

The β-diketonate group is coordinated to the Ir through both oxygen atoms forming a six-membered metallacycle. Both Ir–O distances (2.081 (5) and 2.091 (5) Å) are in good agreement with each other and with comparable distances in other iridium diketonates.[40] The metallacycle ring is reasonably planar,[41] and the parameters within this ring suggest significant delocalization. As a result both C–O distances (1.261 (9) and 1.267 (9) Å) are intermediate between the single- and double-bonded extremes (1.43 and 1.23 Å, respectively[42]). Similarly, the C(1)–C(2) and C(2)–C(3) distances (1.39 (1) and 1.38 (1) Å) are intermediate between single and double bonds involving sp^2 carbons (1.44 and 1.34 Å).[42] Rings 7 and 8 are displaced slightly, on opposite sides of the metallacycle plane, thereby minimizing contacts between each other. Although all non-

---

(33) (a) Diversi, P.; Ingrosso, G.; Lucherini, A.; Porjiok, W.; Zocchi, M. *Inorg. Chem.* **1980**, *19*, 3590. (b) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201. (c) Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S.; Reed, D.; Staves, J. *J. Chem. Soc., Dalton Trans.* **1979**, 117. (d) Teo, B.-K.; Robinson, P. A. A. *J. Chem. Soc., Chem. Commun.* **1979**, 255. (e) Churchill, M. R.; Bergman, S. A. *Inorg. Chem.* **1974**, *13*, 1418 and references therein.

(34) Perego, G.; del Piero, G.; Cesari, M.; Clerici, M. G.; Perotti, E. *J. Organomet. Chem.* **1973**, *54*, C51.

(35) del Piero, G.; Perego, C.; Cesari, M.; Clerici, M.; Perotti, E. *J. Organomet. Chem.* **1974**, *3*, 725.

(36) von Deuten, K.; Dahlenburg, L. *Cryst. Struct. Commun.* **1980**, *9*, 421.

(37) Clark, G. R.; Clark, P. W.; Marsden, K. *J. Organomet. Chem.* **1979**, *173*, 231.

(38) Nolte, M. J.; Singleton, E.; vander Stok, E. *J. Chem. Soc., Chem. Commun.* **1978**, 973.

(39) Schultz, A. J.; McArdle, J. V.; Khare, G. P.; Eisenberg, R. *J. Organomet. Chem.* **1974**, *72*, 45.

(40) Bezman, S. A.; Bird, P. H.; Fraser, A. R.; Osborne, J. A. *Inorg. Chem.* **1980**, *19*, 3755.

(41) The equation of the plane defined by the atoms Ir, O(1), C(1), C(2), C(3), and O(2) is $0.3511X - 0.6935Y - 0.6291Z + 3.7059 = 0$. Distances of the atoms from the plane are as follows: Ir, −0.0002 (3) Å; O(1), 0.041 (6) Å; C(1), 0.023 (8) Å; C(2), −0.083 (9) Å; C(3), −0.093 (8) Å; O(2), 0.078 (6) Å.

(42) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, **1968**; Vol. III, Tables 4.2.2 and 4.2.5.

Table V. Rigid-Group Parameters for Compound 5

Derived Positions and Thermal Parameters

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(10)	0.0889 (5)	0.3404 (5)	0.3266 (6)	2.96 (12)	C(211)	−0.2591 (4)	−0.1920 (4)	0.0336 (5)	3.2 (1)
C(11)	0.1678 (5)	0.4483 (6)	0.3206 (4)	3.81 (14)	C(212)	−0.1995 (3)	−0.3015 (6)	0.0300 (3)	3.7 (1)
C(12)	0.2007 (5)	0.5572 (5)	0.4190 (5)	4.94 (18)	C(213)	−0.2541 (4)	−0.4291 (5)	0.0312 (3)	5.0 (2)
C(13)	0.1548 (5)	0.5582 (5)	0.5233 (6)	5.32 (20)	C(214)	−0.3683 (4)	−0.4473 (4)	0.0361 (5)	5.4 (2)
C(14)	0.0759 (5)	0.4503 (6)	0.5293 (4)	5.13 (19)	C(215)	−0.4279 (3)	−0.3378 (6)	0.0397 (3)	5.1 (2)
C(15)	0.0430 (5)	0.3414 (5)	0.4310 (5)	3.68 (14)	C(216)	−0.3733 (4)	−0.2102 (5)	0.0384 (5)	4.4 (2)
C(21)	0.5745 (13)	0.5619 (12)	0.5082 (13)	8.1 (3)	C(221)	−0.2226 (6)	0.0858 (5)	0.1744 (4)	3.3 (1)
C(22)	0.4929 (8)	0.4579 (13)	0.5163 (7)	9.6 (4)	C(222)	−0.2642 (6)	0.0249 (4)	0.2590 (5)	4.1 (2)
C(23)	0.5066 (10)	0.3904 (10)	0.6057 (12)	11.2 (5)	C(223)	−0.2907 (6)	0.1057 (5)	0.3631 (3)	5.1 (2)
C(24)	0.6018 (13)	0.4269 (12)	0.6869 (13)	11.8 (6)	C(224)	−0.2757 (6)	0.2474 (5)	0.3827 (4)	5.6 (2)
C(25)	0.6834 (8)	0.5309 (13)	0.6788 (7)	8.5 (4)	C(225)	−0.2341 (6)	0.3084 (4)	0.2981 (5)	5.0 (2)
C(26)	0.6698 (10)	0.5984 (10)	0.5894 (12)	6.9 (3)	C(226)	−0.2075 (6)	0.2276 (5)	0.1940 (3)	4.0 (2)
C(111)	0.2958 (4)	0.1162 (4)	0.0261 (4)	2.7 (1)	C(231)	−0.2876 (5)	0.0156 (7)	−0.0820 (4)	3.1 (2)
C(112)	0.2893 (3)	0.2557 (5)	0.0581 (3)	3.5 (1)	C(232)	−0.3165 (6)	−0.0878 (5)	−0.1851 (6)	4.7 (2)
C(113)	0.3781 (4)	0.3459 (4)	0.1271 (5)	4.5 (2)	C(233)	−0.3929 (6)	−0.0711 (6)	−0.2740 (6)	5.6 (2)
C(114)	0.4734 (4)	0.2965 (4)	0.1641 (4)	4.8 (2)	C(234)	−0.4405 (5)	0.0489 (7)	−0.2598 (4)	6.7 (3)
C(115)	0.4799 (3)	0.1570 (5)	0.1320 (3)	4.4 (2)	C(235)	−0.4116 (6)	0.1523 (5)	−0.1567 (6)	6.9 (3)
C(116)	0.3911 (4)	0.0669 (4)	0.0630 (5)	3.5 (1)	C(236)	−0.3352 (6)	0.1357 (6)	−0.0679 (6)	5.0 (2)
C(121)	0.2314 (5)	−0.1677 (4)	−0.1007 (5)	3.0 (1)	C(311)	0.2041 (4)	−0.0674 (6)	0.2281 (4)	2.9 (1)
C(122)	0.3250 (5)	−0.1786 (4)	−0.1602 (5)	3.8 (1)	C(312)	0.2755 (5)	0.0476 (5)	0.2934 (6)	3.9 (2)
C(123)	0.3667 (4)	−0.3026 (5)	−0.1879 (4)	4.9 (2)	C(313)	0.3827 (4)	0.0347 (5)	0.3364 (5)	5.4 (2)
C(124)	0.3148 (5)	−0.4158 (4)	−0.1563 (5)	5.5 (2)	C(314)	0.4187 (4)	−0.0930 (6)	0.3140 (4)	6.3 (2)
C(125)	0.2212 (5)	−0.4049 (4)	−0.0968 (5)	5.0 (2)	C(315)	0.3473 (5)	−0.2080 (5)	0.2487 (6)	6.0 (2)
C(126)	0.1795 (4)	−0.2809 (5)	−0.0691 (4)	3.8 (1)	C(316)	0.2401 (4)	−0.1951 (5)	0.2057 (5)	4.4 (2)
C(131)	0.1818 (7)	0.0419 (6)	−0.2115 (4)	3.0 (1)	C(321)	−0.0134 (5)	−0.1535 (5)	0.2642 (3)	2.6 (1)
C(132)	0.1536 (6)	−0.0641 (5)	−0.3129 (5)	4.4 (2)	C(322)	−0.0132 (5)	−0.2944 (5)	0.2335 (4)	3.6 (1)
C(133)	0.1525 (6)	−0.0363 (5)	−0.4234 (5)	5.5 (2)	C(323)	−0.0602 (5)	−0.3749 (4)	0.3023 (5)	4.3 (2)
C(134)	0.1795 (7)	0.0974 (6)	−0.4324 (4)	6.4 (2)	C(324)	−0.1072 (5)	−0.3146 (5)	0.4019 (3)	4.9 (2)
C(135)	0.2077 (6)	0.2033 (5)	−0.3310 (5)	6.0 (2)	C(325)	−0.1073 (5)	−0.1737 (5)	0.4326 (4)	4.8 (2)
C(136)	0.2088 (6)	0.1756 (5)	−0.2206 (5)	4.3 (2)	C(326)	−0.0604 (5)	−0.0932 (4)	0.3637 (5)	3.4 (1)

Rigid-Group Parameters

	x_c[a]	y_c	z_c	δ[b]	ϵ	η
ring 1[c]	0.1219 (3)	0.4493 (4)	0.4250 (3)	0.624 (4)	1.116 (5)	5.158 (4)
ring 2	0.5882 (6)	0.4944 (8)	0.5975 (7)	3.979 (7)	2.39 (1)	5.45 (1)
ring 3	0.3846 (3)	0.2064 (4)	0.0951 (3)	−0.056 (4)	2.738 (2)	5.722 (3)
ring 4	0.2731 (3)	−0.2917 (4)	−0.1285 (3)	2.959 (4)	0.638 (4)	4.385 (3)
ring 5	0.1806 (4)	0.0696 (4)	−0.3220 (4)	0.271 (4)	1.637 (4)	3.349 (3)
ring 6	−0.3137 (3)	−0.3196 (4)	0.0348 (3)	2.917 (4)	0.164 (4)	5.247 (3)
ring 7	−0.2491 (3)	0.1666 (4)	0.2785 (3)	3.232 (4)	1.209 (4)	0.654 (3)
ring 8	−0.3641 (4)	0.0323 (5)	−0.1709 (4)	−0.309 (4)	2.243 (5)	3.366 (4)
ring 9	0.3114 (3)	−0.0802 (4)	0.2711 (2)	−0.106 (4)	2.802 (4)	0.226 (3)
ring 10	−0.0603 (3)	−0.2341 (4)	0.3330 (3)	3.149 (4)	1.083 (4)	5.744 (3)

[a] x_c, y_c, and z_c are the fractional coordinates of the centroid of the rigid group. [b] The rigid-group orientation angles δ, ϵ, and η(radians) are the angles by which the rigid body is rotated with respect to a set of axes x, y, and z. The origin is the center of the ring; x is parallel to a^*, z is parallel to c, and y is parallel to the line defined by the intersection of the plane containing a^* and b^* with the plane containing b and c. [c] Rings 1 and 2 correspond to atoms C(10)–C(26) and rings 3–10 correspond to atoms C(111)–C(326), respectively. Atoms C(21)–C(26) are the toluene ring atoms.

Table VI. Selected Bond lengths (Å) in Compound 2

Ir-P(1)	2.263 (2)	C(61)-C(62)	1.398 (12)
Ir-P(2)	2.276 (2)	C(62)-C(63)	1.382 (11)
Ir-Cl	2.474 (2)	C(63)-C(64)	1.399 (13)
Ir-O(1)	2.081 (5)	C(64)-C(65)	1.357 (15)
Ir-O(2)	2.091 (5)	C(65)-C(66)	1.380 (15)
Ir-C(62)	2.036 (8)	C(66)-C(61)	1.400 (12)
P(1)-C(11)	1.835 (5)	O(1)-C(1)	1.261 (9)
P(1)-C(21)	1.830 (5)	C(1)-C(2)	1.390 (12)
P(1)-C(31)	1.811 (6)	C(1)-C(71)	1.496 (9)
P(2)-C(41)	1.807 (5)	C(2)-C(3)	1.378 (12)
P(2)-C(51)	1.802 (6)	C(3)-C(81)	1.496 (10)
P(2)-C(61)	1.797 (9)	C(3)-O(2)	1.267 (9)

hydrogen atoms within the β-diketonate group are sp^2-hybridized, the strain imposed by the large Ir atom causes all angles within the metallacycle ring (apart from that at Ir) to be greater than the idealized 120°.

(ii) $[\overline{\underline{\mathrm{IrCl((C_6H_4)C(O)C}}\mathrm{C(Ph)OP}}\mathrm{Ph_2)(PPh_3)_2}]\cdot C_6H_5CH_3$ (5). A view of compound **5** is shown in Figure 2. The unit cell of **5** contains one complex molecule and one molecule of toluene of crystallization. All contacts between these molecules are normal van der Waals interactions. The toluene molecule is reasonably well-behaved, although the large thermal parameters (6.9–13.7 Å^2) suggest some slight disorder of this group or high thermal motion. Nevertheless, its geometry is as expected. The bond lengths and angles for compound **5** are given in Tables VIII and IX, and some of the more relevant parameters are shown in Figure 3.

Within the complex the geometry about the iridium center is quasi-octahedral. Two triphenylphosphine groups, which are mutually trans, occupy the axial positions, while the four equatorial sites are occupied by a chloro ligand and the highly unusual tridentate ligand $((C_6H_4)C(O)CC(C_6H_5)OPPh_2)$ (vide infra). This tridentate ligand coordinates to the iridium center via an orthometalated phenyl ring, a metalated vinylic carbon atom, and a phosphorus atom (see Figures 2 and 3). The geometry about iridium is distorted significantly from octahedral due mainly to constraints imposed by the chelating ligand, by its large bulk, and by the large bulk of the phosphine ligands. Consequently, the angles at Ir involving the chelate are all much different than the idealized 90°

Table VII. Selected Angles (deg) in Compound 2

P(1)–Ir–O(1)	177.5 (2)	C(21)–P(1)–C(31)	104.6 (3)
P(1)–Ir–Cl	95.04 (7)	C(41)–P(2)–C(51)	102.7 (3)
P(1)–Ir–P(2)	97.43 (8)	C(41)–P(2)–C(61)	110.1 (3)
P(1)–Ir–O(2)	89.1 (2)	C(51)–P(2)–C(61)	109.2 (4)
P(1)–Ir–C(62)	97.3 (2)	Ir–O(1)–C(1)	126.2 (6)
P(2)–Ir–O(2)	159.8 (2)	Ir–O(2)–C(3)	124.3 (6)
P(2)–Ir–Cl	108.52 (8)	O(1)–C(1)–C(2)	124.8 (8)
P(2)–Ir–O(1)	85.0 (2)	O(1)–C(1)–C(71)	112.9 (8)
P(2)–Ir–C(62)	68.5 (2)	C(2)–C(1)–C(71)	122.3 (7)
Cl–Ir–O(1)	83.4 (2)	C(1)–C(2)–C(3)	128.4 (8)
Cl–Ir–O(2)	89.8 (2)	C(2)–C(3)–O(2)	125.9 (8)
Cl–Ir–C(62)	167.6 (2)	C(2)–C(3)–C(81)	120.6 (7)
O(1)–Ir–O(2)	88.9 (2)	O(2)–C(3)–C(81)	113.5 (7)
O(1)–Ir–C(62)	84.3 (3)	P(2)–C(61)–C(62)	98.5 (6)
O(2)–Ir–C(62)	91.9 (3)	P(2)–C(61)–C(66)	138.4 (8)
Ir–P(1)–C(11)	118.2 (2)	C(66)–C(61)–C(62)	123.0 (9)
Ir–P(1)–C(21)	113.4 (2)	Ir–C(62)–C(61)	107.3 (6)
Ir–P(1)–C(31)	113.8 (2)	Ir–C(62)–C(63)	133.8 (7)
Ir–P(2)–C(41)	116.0 (2)	C(61)–C(62)–C(63)	118.4 (8)
Ir–P(2)–C(51)	130.8 (3)	C(62)–C(63)–C(64)	118.6 (9)
Ir–P(2)–C(61)	85.6 (3)	C(63)–C(64)–C(65)	121.9 (9)
C(11)–P(1)–C(21)	100.3 (3)	C(64)–C(65)–C(66)	121.6 (10)
C(11)–P(1)–C(31)	104.9 (3)	C(65)–C(66)–C(61)	116.5 (10)

Table VIII. Selected Distances (Å) in Compound 5

Ir–P(1)	2.384 (3)	P(3)–O(2)	1.632 (5)
Ir–P(2)	2.380 (3)	C(1)–C(2)	1.421 (12)
Ir–P(3)	2.355 (2)	C(1)–C(6)	1.375 (12)
Ir–Cl	2.475 (2)	C(2)–C(3)	1.366 (14)
Ir–C(1)	2.093 (7)	C(3)–C(4)	1.384 (14)
Ir–C(8)	2.046 (9)	C(4)–C(5)	1.371 (14)
P(1)–C(111)	1.854 (4)	C(5)–C(6)	1.413 (11)
P(1)–C(121)	1.846 (5)	C(6)–C(7)	1.465 (11)
P(1)–C(131)	1.836 (5)	C(7)–C(8)	1.485 (11)
P(2)–C(211)	1.843 (5)	C(7)–O(1)	1.226 (10)
P(2)–C(221)	1.864 (5)	C(8)–C(9)	1.382 (12)
P(2)–C(231)	1.852 (5)	C(9)–C(10)	1.480 (9)
P(3)–C(311)	1.854 (5)	C(9)–O(2)	1.407 (9)
P(3)–C(321)	1.834 (4)	C(21)–C(27)[a]	1.44 (3)

[a] C(21)–C(26) are the toluene ring atoms, and C(27) is the toluene methyl group.

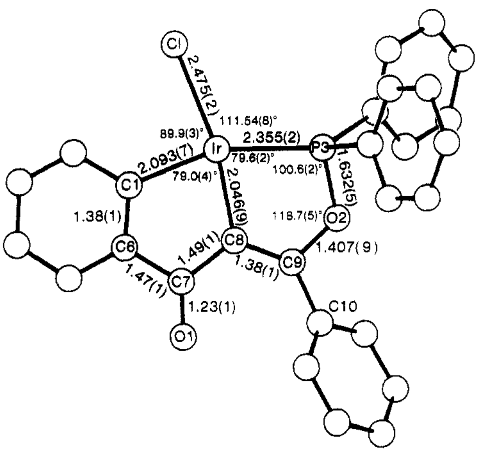

Figure 3. A view of compound 5 in the approximate plane of the tridentate ligand showing some of the relevant parameters. Atoms are shown with arbitrary sizes.

Table IX. Selected Angles (deg) in Compound 5

P(1)–Ir–P(2)	169.46 (8)	C(321)–P(3)–O(2)	97.2 (2)
P(1)–Ir–P(3)	94.64 (7)	P(3)–O(2)–C(9)	118.7 (5)
P(1)–Ir–Cl	84.58 (8)	C(2)–C(1)–C(6)	115.8 (7)
P(1)–Ir–C(1)	88.0 (2)	C(1)–C(2)–C(3)	122.3 (8)
P(1)–Ir–C(8)	95.4 (2)	C(2)–C(3)–C(4)	120.2 (8)
P(2)–Ir–P(3)	93.18 (8)	C(3)–C(4)–C(5)	120.2 (7)
P(2)–Ir–Cl	85.98 (9)	C(4)–C(5)–C(6)	118.9 (8)
P(2)–Ir–C(1)	87.3 (2)	C(1)–C(6)–C(5)	122.8 (8)
P(2)–Ir–C(8)	92.9 (2)	C(1)–C(6)–C(7)	116.6 (6)
P(3)–Ir–Cl	111.54 (8)	C(5)–C(6)–C(7)	120.6 (7)
P(3)–Ir–C(1)	158.5 (2)	C(6)–C(7)–C(8)	111.5 (7)
P(3)–Ir–C(8)	79.6 (2)	C(6)–C(7)–O(1)	123.1 (7)
Cl–Ir–C(1)	89.9 (3)	C(8)–C(7)–O(1)	125.5 (8)
Cl–Ir–C(8)	168.9 (2)	C(7)–C(8)–C(9)	121.9 (8)
C(1)–Ir–C(8)	79.0 (4)	C(8)–C(9)–C(10)	135.5 (7)
Ir–P(1)–C(111)	117.2 (2)	C(8)–C(9)–O(2)	115.7 (7)
Ir–P(1)–C(121)	116.5 (2)	C(10)–C(9)–O(2)	108.7 (6)
Ir–P(1)–C(131)	113.5 (2)	P(1)–C(111)–C(112)	119.3 (3)
Ir–P(2)–C(211)	117.6 (2)	P(1)–C(111)–C(116)	120.7 (3)
Ir–P(2)–C(221)	116.0 (2)	P(1)–C(121)–C(122)	118.2 (3)
Ir–P(2)–C(231)	115.4 (2)	P(1)–C(121)–C(126)	121.8 (3)
Ir–P(3)–C(311)	124.6 (2)	P(1)–C(131)–C(132)	117.6 (3)
Ir–P(3)–C(321)	129.7 (2)	P(1)–C(131)–C(136)	122.4 (3)
Ir–P(3)–O(2)	100.6 (2)	P(2)–C(211)–C(212)	121.5 (3)
Ir–C(1)–C(2)	127.9 (7)	P(2)–C(211)–C(216)	118.5 (3)
Ir–C(8)–C(7)	116.3 (6)	P(2)–C(221)–C(226)	119.5 (3)
Ir–C(8)–C(9)	121.6 (6)	P(2)–C(221)–C(222)	120.5 (3)
C(111)–P(1)–C(121)	103.2 (3)	P(2)–C(231)–C(232)	116.2 (3)
C(111)–P(1)–C(131)	103.4 (3)	P(2)–C(231)–C(236)	123.8 (3)
C(121)–P(1)–C(131)	100.9 (3)	P(3)–C(311)–C(312)	118.4 (3)
C(211)–P(2)–C(221)	102.0 (3)	P(3)–C(311)–C(316)	121.4 (3)
C(211)–P(2)–C(231)	98.7 (3)	P(3)–C(321)–C(322)	119.5 (3)
C(221)–P(2)–C(231)	104.8 (3)	P(3)–C(321)–C(326)	120.3 (3)
C(311)–P(3)–C(321)	98.7 (2)	C(22)–C(21)–C(27)	127 (1)
C(311)–P(3)–O(2)	97.5 (3)	C(26)–C(21)–C(27)	113 (1)

and 180° values; the C(1)–Ir–C(8), C(8)–Ir–P(3), and C(1)–Ir–P(3) angles at 79.0 (4)°, 79.6 (2)°, and 158.5 (2)°, respectively, clearly reflect the strain within the chelate group. The two axial PPh_3 groups are bent away from P(3) and C(8) in order to minimize contacts with the phenyl groups on these atoms, and as a consequence the angles at Ir involving P(1) and P(2) also deviate from the idealized 90° and 180° values. Similarly, the chloro ligand is bent away from P(3) toward C(1) due to interactions with rings 12 and 21, which are in turn forced toward Cl by interactions with the phenyl groups on the chelate ligand. Several of the resulting nonbonded contacts (e.g., Cl–H(212) = 2.65 Å, Cl–H(126) = 2.68 Å, C(7)–H(112) = 2.53 Å, C(7)–H(226) = 2.75 Å) are shorter than normal van der Waals contacts confirming that the molecule is very crowded.

The parameters involving the triphenylphosphine groups are not unexpected for such a complex, although the Ir–P distances are longer than those in compound 2, probably due to crowding in the present compound. The Ir–Cl bond length of 2.475 (2) Å is long[18] and reflects the high trans influence of the σ-bound vinyl carbon atom C(8). It may also be that the Ir–Cl bond is lengthened somewhat by the steric interactions involving the Cl atom (vide supra).

Certainly the most unusual aspect of this structure involves the tridentate ligand. This group has resulted from the condensation of the dibenzoylmethylene moiety (generated through N_2 loss from dibenzoyldiazomethane) and a PPh_2 group (which has resulted from C_6H_5 loss from triphenylphosphine) such that these two groups are fused at one of the ketone oxygens and the phosphorus atom. In addition, the benzoyl phenyl group remote from the end at which condensation has occurred has undergone an ortho-metalation reaction at C(1) such that the three coordination sites of the ligand are at C(1), C(8) (the methylene carbon of the original $:C(C(O)Ph)_2$ moiety), and P(3). The resulting chelate complex consists of two fused five-membered iridium metallacycles as is clearly shown in Figure 3. Both metallacycles are nearly planar; the largest deviation from the Ir–P(3)–O(2)–C(9)–C(8) plane is 0.14 Å (O(2)), and the largest deviation from the Ir–C(1)–C(6)–C(7)–C(8) plane is 0.04 Å[43] (C(7)). In addition, both metallacycle planes are inclined to each other by only 7.4°, and the ortho-metalated ring is only 2.0° from the ad-

---

[43] Supplementary material.

joining metallacycle ring, so the entire chelate (apart from the peripheral Ph groups) is close to being planar.

Both Ir–C(1) and Ir–C(8) distances (2.093 (7) and 2.046 (9) Å, respectively) are comparable with other Ir(III) complexes in which the metal is σ-bound to an sp^2-hybridized carbon atom (range 1.99–2.16).[33-35,43-48] The shorter distance involving C(8) may reflect the lower trans influence of Cl over P(3), or it may reflect the restrictions put on C(8) by the rest of the tridentate ligand. Such shortening of the metal–carbon bond has been previously observed in other tridentate ligands in which the central linkage is through an sp^2 carbon atom.[49-53] It seems that the central carbon atom is held close to the metal by the rest of the ligand.

The geometry of the phosphinite end of the tridentate ligand is significantly different from those of the triphenylphosphine groups. Certainly there are obvious differences to be expected on the basis of steric and electronic arguments since this group has an –OR moiety replacing a phenyl of the PPh_3 ligands. It may be that the Ir–P(3) bond is shorter than the other two Ir–P bonds by virtue of the fact that the former contains a phosphite moiety; recent results with a series of chromium complexes have shown that the Cr–phosphite bonds were significantly shorter than Cr–phosphine ones.[54] However, the major difference seems to result from the strain imposed on P(3) by the rest of the chelate. So, for example, the Ir–P(3)–Ph angles (ca. 127°) of this phosphinite group are much larger than those of about 116° in the PPh_3 groups, indicating that the former group has been pulled around toward the rest of the chelate (this is clearly shown in Figure 3). The phosphorus–oxygen bond length, of 1.632 (5) Å, indicates a normal single bond and compares quite well to such distances in phosphite complexes.[55]

Viewing the part of the tridentate ligand which originated from the diazoalkane precursor, it is clear that this moiety is bound to the metal as a metalated olefin (at C(8)) and also as an ortho-metalated phenyl group (at C(1)). Therefore the C(8)—C(9) distance (1.38 (1) Å) is close to that of a C=C double bond (1.34 Å)[42] and is significantly shorter than the C(7)—C(8) distance (1.49 (1) Å), which corresponds to a single bond. These distances can be compared with the values (average 1.473 (4) Å) for the corresponding bonds in the dibenzoyldiazomethane precursor.[56] Also consistent with the double-bond formulation for C(7)–C(8), the C(9)–O(2) distance has lengthened to 1.407 (9) Å and now corresponds to a single bond. By comparison the C(7)–O(1) distance, of 1.23 (1) Å, corresponds to a double bond and is close to the values observed in dibenzoyldiazomethane.[56]

Discussion of Results

Dibenzoyldiazomethane, $N_2C(C(O)Ph)_2$, reacts with *trans*-$[IrCl(N_2)(PPh_3)_2]$ in toluene at room temperature to yield the diazoalkane adduct $[IrCl(N_2C(C(O)Ph)_2)(PPh_3)_2]$ (**1**), as described in the previous paper.[18] Although this species is stable at room temperature in the solid state, decomposition with N_2 evolution results when samples are left in solution for extended periods of time or when solutions are heated. Compound **1** is particularly unstable in CH_2Cl_2, and after 8 h at room temperature in this solvent two products are observed in a 3:2 ratio. The minor species $[IrCl_2(HN_2C(C(O)Ph)_2)(PPh_3)_2]$ (**4**) is the product of oxidative addition of HCl and presumably results from reaction of **1** with traces of HCl in solution; characterization of this species was described in the preceding paper.[18]

The major species **2** obtained from the CH_2Cl_2 solution can also be obtained as the only product in good yield by refluxing a toluene solution of **1** for ca. 35 min. Elemental analyses of this species indicate that N_2 loss has occurred, and the $^{31}P\{^1H\}$ NMR spectrum indicates that the phosphorus nuclei are no longer chemically equivalent. The large upfield shift of one of the phosphine groups (δ –82.5) is characteristic of a complex containing an ortho-metalated ring;[57] however, no evidence of a metal hydride is observed in the IR or ^1H NMR spectra. In the ^1H NMR spectrum the only resonance, apart from those due to phenyl and toluene groups, corresponds to a single hydrogen at δ 6.80. As described, this species was shown, by an X-ray study, to be a β-diketonate complex. Clearly, heating compound **1** has resulted in N_2 loss. However, instead of forming a carbene complex, a hydrogen transfer to the carbene carbon atom has occurred forming the β-diketonate group, which binds to Ir via both oxygen atoms. This transformation has been accompanied by ortho metalation of one phosphine phenyl group, and it is the resulting hydrido ligand which is transferred to the carbene fragment. The origin of the β-diketonate hydrogen was confirmed by the successful preparation of $[IrCl(DC(C(O)Ph)_2)(PC_6D_4(Ph_2\text{-}d_{10}))(PPh_3\text{-}d_{15})]$ from *trans*-$[IrCl(N_2)(PPh_3\text{-}d_{15})_2]$. The ^1H NMR spectrum of the deuterated sample showed a substantial decrease in the number of aromatic resonances (since only the benzoyl phenyl groups appeared) and the absence of the singlet at δ 6.80.

When the reaction of *trans*-$[IrCl(N_2)(PPh_3)_2]$ with dibenzoyldiazomethane is performed in refluxing THF, a minor product (20%), **3**, is obtained in addition to **2**. Compound **3** can be obtained as the major product (90% by $^{31}P\{^1H\}$ NMR), together with 10% of compound **5**, from $[IrCl(PPh_3)_3]$ and dibenzoyldiazomethane in refluxing THF. The infrared and ^1H NMR spectra of **3** are very similar to those of **2**, but the $^{31}P\{^1H\}$ NMR spectrum differs substantially showing two doublets at δ –11.0 and –69.2 (J_{PP} = 17 Hz). These parameters suggest a structure for **3** which is similar to that of **2**, again having a chelating β-diketonate group and two mutually cis phosphines, with the high-field one being ortho-metalated. Attempts to isolate **4** resulted either in a mixture of **2** and **3** or in complete conversion to **2**; this conversion was most easily carried out in refluxing toluene for 18 h. It seems therefore

---

(44) Bailey, N. A.; Jones, C. J.; Shaw, B. L.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1967**, 1051.

(45) McPartlin, M.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1967**, 545.

(46) Einstein, F. W. B.; Gilchrist, A. B.; Rayner-Canham, G. W.; Sutton, D. *J. Am. Chem. Soc.* **1972**, *94*, 645.

(47) Tuggle, R. M.; Weaver, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 5523.

(48) Bellan, P. L.; Caglio, G.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1974**, 897.

(49) Cowie, M.; Ibers, J. A. *Inorg. Chem.* **1976**, *15*, 552.

(50) Itoh, K.; Matsuda, I.; Ueda, F.; Ishii, Y.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2118.

(51) Herskovitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615.

(52) Cowie, M.; Dwight, S. K. *J. Organomet. Chem.* **1981**, *214*, 233.

(53) Gibson, J. A. E.; Cowie, M. *Organometallics* **1984**, *3*, 984.

(54) Wovkulich, M. J.; Atwood, J. L.; Canada, L.; Atwood, J. D. *Organometallics* **1985**, *4*, 467.

(55) (a) Goetzer, J.; Gafner, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 985. (b) Ciani, G.; Manessero, M.; Albano, V. G. *J. Chem. Soc., Dalton Trans.* **1981**, 515. (c) Devillers, J.; De Montauzon, D.; Poilblanc, R. *Nouv. J. Chim.* **1983**, *7*, 545.

(56) Cowie, M.; Gauthier, M. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1862.

(57) (a) Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435. (b) Pregosin, P. S.; Kunz, R. H. "The ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag: New York, 1979. (c) In the $^{31}P\{^1H\}$ NMR spectrum of $[\overline{IrCl(H)(C_6H_4}PPh_2)(PPh_3)_2]$,[21] for example, we observe the following parameters: δ 4.2 (dd), –6.0 (dd), –92.2 (dd), J_{PP}(cis) = 10, 18 Hz, J_{PP}(trans) = 370 Hz (dd = doublet of doublets).

that **3** is an isomer of **2**, probably in which one of the two phosphines is no longer trans to one of the diketonate oxygens.

The $^{31}P\{^1H\}$ NMR resonances for compound **5** appear as a doublet (2 P) at δ -15.7 and a triplet (1 P) at δ 83.7. The former signal is normal for a coordinated PPh_3 group (see compounds **2** and **3**), whereas the low-field signal seems typical for a phosphine group which contains the POR moiety. So, for example, the free phosphinite (PR_2OR') and phosphite ($P(OR)_3$) molecules have ^{31}P chemical shifts at ca. δ 100 and 140, respectively.[58] When these groups are coordinated to metals, a rather wide range in chemical shifts (between ca. δ 24 and 160) is observed,[58,59] but most such resonances are observed at the low-field end, consistent with that observed for compound **5**.

The origin of compound **5**, however, is still uncertain; it is the only species other than **3** observed in the reaction mixture, and we have not succeeded in synthesizing it rationally. Although we can postulate with some certainty the individual reaction steps which are likely to be important, we can only guess at the sequence of events. It is clear that refluxing results in N_2 loss from the diazoalkane, presumably forming a carbene intermediate, and that ortho metalation, forming the metalated ring and a metal-hydride linkage, must also occur. Subsequent to this, loss of a phenyl group from PPh_3 and of the hydride ligand, presumably as benzene, must occur, and this can then be followed by formation of the P-O bond. All steps postulated have ample precedent, and in particular the last steps, in which the phosphorus-aryl bond is replaced by the P-O linkage, differs only slightly from some well-documented examples of phosphorus-aryl bond activation and cleavage by group 8 metals followed by formation of a new phosphorus-carbon bond.[60] Whether such processes in our chemistry occur at a single metal or involve two or more metals is not known, although it is difficult to construct a reasonable scheme occurring at a single metal owing to the large degree of coordinative unsaturation that would have to be present.

Conclusions

We have observed that the benzoyl groups in the dibenzoyldiazomethane ligand do participate in a very major way in the chemistry of this molecule. In the previous paper[18] this was shown in complexes in which the diazoalkane molecule remained intact, and in this paper we show two rather unusual ways in which the benzoyl oxygens participate in chemistry which results from N_2 loss from the diazoalkane. This chemistry is also affected in a very major way by the well-known tendency for complexes of iridium to undergo rather facile ortho-metalation reactions and also by the less common tendency of group 8 metals to activate P-C bonds. In $[IrCl(HC(C(O)Ph))(PC_6H_4Ph_2)(PPh_3)]$ the hydride group resulting from ortho metalation is transferred to the carbene fragment produced from $N_2C(C(O)Ph)_2$, yielding a β-diketonate group, which chelates through both oxygen atoms. In $[IrCl((C_6H_4)C(O)CC(Ph)OPPh_2)(PPh_3)_2]$ ortho metalation of one of the benzoyl groups in the $:C(C(O)Ph)_2$ fragment, activation and cleavage of a phosphorus-aryl bond, and coupling of the resulting fragments via formation of a P-O bond give a novel tridentate ligand system.

Acknowledgment. This work was supported by the University of Alberta and the Natural Sciences and Engineering Research Council of Canada.

Registry No. **1**, 100701-28-8; **2**, 86288-19-9; $\mathbf{2}\cdot 1/2C_6H_5CH_3$, 86272-05-1; **3**, 100837-29-4; **4**, 100701-29-9; **5**, 86272-06-2; $\mathbf{5}\cdot C_6H_5CH_3$, 100701-30-2; *trans*-$[IrCl(N_2)(PPh_3)_2]$, 21414-18-6; $N_2C(C(O)Ph)_2$, 2085-31-6; $[IrCl(DC(C(O)Ph)_2(P(C_6D_4)(Ph_2\text{-}d_{10}))(PPh_3\text{-}d_{15})]$, 100763-01-7; *trans*-$[IrCl(N_2)(PPh_3\text{-}d_{15})_2]$, 100701-31-3; $[IrCl(PPh_3)_3]$, 16070-58-9.

Supplementary Material Available: Listings of calculated structure factor amplitudes, observed and anisotropic thermal parameters, and hydrogen parameters for both structures **2** and **5** and least-squares planes for compound **5** (34 pages). Ordering information is given on any current masthead page.

---

(58) Mark, V.; Dungan, C. H.; Crutchfield, M. M.; van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 227.

(59) (a) Couch, D. A.; Robinson, S. D.; Wingfield, J. N. *J. Chem. Soc., Dalton Trans.* **1974**, 1309. (b) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *18*, 679. (c) Kampe, C. E.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 4646. (d) Wu, M. L.; Desmond, M. J.; Drago, R. S. *Inorg. Chem.* **1979**, *18*, 679. (e) Kalck, P.; Bonnet, J.-J. *Organometallics* **1982**, *1*, 1211. (f) Guilmet, E.; Maissonat, A.; Poilblanc, R. *Organometcallics* **1983**, *2*, 1123.

(60) (a) Abatjoglou, A. G.; Billig, E.; Bryant, D. R. *Organometallics* **1984**, *3*, 923. (b) Abatjoglou, A. G.; Bryant, D. R. *Organometallics* **1984**, *3*, 932. (c) Dubois, R. A.; Garrou, P. E.; Levin, K. D.; Allcock, H. R. *Organometallics* **1984**, *3*, 649.