

Diazoalkane Activation by Iridium Phosphine Compounds. 1. Complexes Containing the Intact Dibenzoyldiazomethane Ligand and Interconversion between the η^1 -N-Bound and a Chelated N,O-Bound Form of the Ligand Accompanied by Hydride Migration

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The reaction of dibenzoyldiazomethane ($N_2C(C(O)Ph)_2$) with *trans*-[IrCl(N_2)(PPh₃)₂] yields the four-coordinate species [IrCl($N_2C(C(O)Ph)_2$)(PPh₃)₂] (1) in which the intact diazoalkane molecule is coordinated in a η^1 , singly bent geometry. Compound 1 reacts with donor ligands, L, to give five-coordinate adducts of formulation [IrCl($N_2C(C(O)Ph)_2$)(L)(PPh₃)₂] (L = PMe₂Ph, *t*-BuNC, and NO⁺). The reaction of 1 with 1 equiv of HCl yields an equilibrium mixture of [IrHCl₂($N_2C(C(O)Ph)_2$)(PPh₃)₂] and [IrCl₂(HN₂C(C(O)Ph)₂)(PPh₃)₂] in which hydride migration from Ir to the coordinated nitrogen atom occurs; the latter species is present in an approximate 15:1 excess. An X-ray structure determination of the second (more abundant) species was undertaken. It crystallizes in the space group *P*2₁/*c* with *a* = 10.165 (2) Å, *b* = 17.422 (2) Å, *c* = 25.653 (5) Å, β = 93.66 (2)°, *V* = 4533.7 Å³, and *Z* = 4. The structure has refined to *R* = 0.044 and *R*_w = 0.050 based on 190 variables and 1869 unique observations. The compound is a six-coordinate Ir(III) species in which the reduced diazoalkane ligand is coordinated to Ir through the terminal nitrogen atom, which also is bound to the H atom, and a benzoyl oxygen atom.

Introduction

Diazoalkanes are versatile reagents in organic chemistry¹ and have been observed to form a number of interesting ligand systems in inorganic and organometallic chemistry.² Complexes that result from the interaction of diazoalkanes with transition metals can be either nitrogen-containing, in which the diazoalkane molecule has remained essentially intact,²⁻¹⁵ or nitrogen-free, in which N₂ loss has occurred resulting in carbene-related complexes.^{2,16-19} In the nitrogen-containing products the diazoalkane ligands can coordinate to a single metal either end-on through the terminal nitrogen⁷⁻¹⁰ or side-on through the N-N moiety,³⁻⁶ or they can coordinate to more than one metal in a variety of bridging modes.¹¹⁻¹⁴ With dibenzoyldiazomethane ($N_2C(C(O)Ph)_2$) the carbonyl groups introduce the additional possibility that they too may become involved in coordination to the metals and may consequently influence the chemistry of the molecule.

In this paper we describe some of our observations in which the dibenzoyldiazomethane molecule remains intact upon coordination to an iridium center and we show the transformation of the terminally N-bound $N_2C(C(O)Ph)_2$ moiety to a chelating HN₂C(C(O)Ph)₂ group in which one of the carbonyl groups is also coordinated. A subsequent paper will deal with some chemistry in which N₂ loss from this ligand is observed.²⁰

Experimental Section

All solvents were dried and degassed prior to use and all reactions were carried out under Schlenk conditions in an atmosphere of purified²¹ dinitrogen. Dibenzoyldiazomethane²² and *trans*-[IrCl(N_2)(PPh₃)₂]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 reagent grade chemicals were used as received.

Infrared spectra were recorded on a Nicolet 7199 Fourier transform interferometer using Nujol mulls. ³¹P{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% H₃PO₄ (positive shifts downfield). ¹H NMR spectra were obtained at 400 MHz on a Bruker WP-400 spectrometer with an internal CD₂Cl₂ lock. Elemental analyses were performed by the microanalytical services at the University of Alberta and Canadian Microanalytical Services, Vancouver, B.C., Canada.

Preparation of the Complexes. (i) [IrCl($N_2C(C(O)Ph)_2$)(PPh₃)₂] (1). *trans*-[IrCl(N_2)(PPh₃)₂] (377 mg, 0.483 mmol) and dibenzoyldiazomethane (121 mg, 0.483 mmol) were suspended in 10 mL of toluene at room temperature. The solution immediately changed color from yellow to green, and after 10 min a

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Table I. Infrared and NMR Spectral Data for the Compounds

compd	$^{31}\text{P}\{\text{H}\}$, ppm	IR, cm^{-1}
$[\text{IrCl}(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (1)	12.0 (s) ^a	$\nu(\text{NN})$ 1869 $\nu(\text{CO})$ 1622
$[\text{IrCl}(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PMe}_2\text{Ph})(\text{PPh}_3)_2]$ (2)	-30.0 (d, 2 P) -46.2 (t, 1 P) ($J_{\text{PP}} = 19$ Hz)	$\nu(\text{CO})$ 1612
$[\text{IrCl}(t\text{-BuNC})(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (3)	-8.8 (s)	$\nu(\text{NC})$ 2185 $\nu(\text{CO})$ 1629
$[\text{IrCl}(\text{NO})(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2][\text{BF}_4]$ (4)	21.2 (s)	$\nu(\text{NO})$ 1681 $\nu(\text{CO})$ 1596
$[\text{IrCl}_2(\text{HN}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (5)	-13.1 (s) ^b	$\nu(\text{NH})$ 3246 $\nu(\text{CO})$ 1640
$[\text{IrCl}_2\text{H}(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (6)	-23.0 (s) ^c	<i>d</i>
$[\text{IrCl}_3(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (7)	<i>e</i>	$\nu(\text{CO})$ 1632
$\text{Ph}_3\text{PN}_2\text{C}(\text{C}(\text{O})\text{Ph})_2$ (8)	23.1 (s)	$\nu(\text{CO})$ 1650

^a Abbreviation: s, singlet; d, doublet; t, triplet. ^b NH resonance at δ 10.7 (s) in the ^1H NMR spectrum. ^c IrH hydride resonance at δ -15.2 (t, $J_{\text{PH}} = 13$ Hz) in the ^1H NMR spectrum. ^d Neither the IrH nor the CO stretches are observed due to the small amounts of this compound present in the product mixture. ^e Insoluble.

dark green precipitate formed. This suspension was stirred for 4 h at room temperature, and then 30 mL of hexanes was added to complete precipitation. The mother liquor was removed and the dark green product washed several times with small amounts of cold toluene and dried in vacuo. The yield was 96% based on *trans*- $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$. Anal. Calcd for $\text{C}_{51}\text{H}_{40}\text{ClIrN}_2\text{O}_2\text{P}_2$: C, 61.08; H, 4.02; Cl, 3.54; N, 2.08. Found: C, 60.44; H, 4.11; Cl, 3.67; N, 2.28.

(ii) $[\text{IrCl}(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PMe}_2\text{Ph})(\text{PPh}_3)_2]$ (2). Compound 1 (100 mg, 0.100 mmol) was suspended in 10 mL of toluene at 0 °C. PMe_2Ph (13.8 mg, 0.098 mmol) was added to give an orange solution, which was stirred for 1 h at 0 °C. The solution was allowed to warm to room temperature, and hexanes were added to precipitate the product. The yellow-orange complex was washed with hexanes and dried in vacuo. The yield was 80%. Anal. Calcd for $\text{C}_{59}\text{H}_{51}\text{ClIrN}_2\text{O}_2\text{P}_3$: C, 62.12; H, 4.52; Cl, 3.11; N, 2.46. Found: C, 61.53; H, 4.54; Cl, 3.42; N, 2.34.

(iii) $[\text{IrCl}(t\text{-BuNC})(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (3). Compound 1 (100 mg, 0.100 mmol) was suspended in 10 mL of toluene at 0 °C. *tert*-Butyl isocyanide (8.3 mg, 0.100 mmol) was added to give a bright red solution, which was stirred for 1 h at 0 °C. The solution was allowed to warm to room temperature, and hexanes were added to precipitate the product. The red solid was washed with hexane and dried in vacuo. The yield was 78%. Anal. Calcd for $\text{C}_{56}\text{H}_{49}\text{IrClN}_3\text{O}_2\text{P}_2$: C, 61.95; H, 4.56; Cl, 3.27; N, 3.87. Found: C, 61.33; H, 4.52; Cl, 3.07; N, 3.55.

(iv) $[\text{IrCl}(\text{NO})(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2][\text{BF}_4]$ (4). Compound 1 (100 mg, 0.100 mmol) was suspended in 10 mL of toluene at 0 °C. NOBF_4 (11.6 mg, 0.100 mmol) was added to give an orange-brown solution, which was stirred at 0 °C for 1 h. The solution was kept at 0 °C, and hexanes were added to precipitate the product. The orange-brown solid was washed with cold hexanes and dried in vacuo at room temperature. The yield was 66%. Satisfactory elemental analysis of this product could not be obtained, presumably due to thermal decomposition in the solid state (in solution this species decomposed within 1 h at room temperature). However, spectroscopic data are consistent with this formulation.

(v) $[\text{IrCl}_2(\text{HN}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (5). To a solution of compound 1 (150 mg, 0.150 mmol) in 10 mL of either acetone, dichloromethane, acetonitrile, or toluene was added $\text{DMA}\cdot\text{HCl}^{24}$ ($\text{DMA} = \text{dimethylacetamide}$) (18.5 mg, 0.150 mmol). The solution was taken to dryness under vacuum and the orange-red solid residue recrystallized from the minimum amount of toluene. Suitable quality crystals for X-ray diffraction studies were obtained, and this complex was characterized spectroscopically and by a structure determination.

(vi) $[\text{IrCl}_3(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (7). Gaseous HCl was bubbled through a solution of compound 1 (100 mg, 0.100 mmol) in 10 mL of CH_2Cl_2 at a rate of approximately 0.5 mL s^{-1} for 1 min. The solution turned orange-red immediately, and an orange

solid precipitated. $^{31}\text{P}\{\text{H}\}$ NMR spectra of the remaining solution showed several species which were present in very small quantities and, therefore, were only barely observed above base line, and the solid sample proved to be too insoluble to obtain ^{31}P or ^1H NMR spectra. Anal. Calcd for $\text{C}_{51}\text{H}_{40}\text{Cl}_3\text{IrN}_2\text{O}_2\text{P}_2$: C, 57.07; H, 3.76; N, 2.61; Cl, 9.91. Found: C, 56.58; H, 4.57; N, 1.88; Cl, 9.87. Repeated attempts to purify this sample did not give improved analyses for H and N.

(vii) $(\text{Ph}_3\text{P})\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2$ (8). Triphenylphosphine (250 mg, 0.953 mmol) and dibenzoyldiazomethane (239 mg, 0.953 mmol) were combined in 10 mL of dichloromethane with stirring. Slow evaporation of the solvent after 4 h yielded a bright yellow microcrystalline powder which analyzed acceptably for $(\text{Ph}_3\text{P})\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2$. MS (m/e): 484, $(\text{Ph}_3\text{P})\text{C}(\text{OCPh})_2^+$; 278, $(\text{Ph}_3\text{PO})^+$; 105, $(\text{PhCO})^+$; 77, $(\text{C}_6\text{H}_5)^+$. Anal. Calcd for $\text{C}_{33}\text{H}_{25}\text{N}_2\text{O}_2\text{P}$: C, 77.33; H, 4.92; N, 5.47. Found: C, 77.05; H, 5.18; N, 5.28.

X-ray Data Collection

Suitable quality crystals of compound 5 were grown by allowing diethyl ether to diffuse into a saturated toluene solution of the complex. Preliminary film data showed that the crystals belonged to the monoclinic system with systematic absences ($h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$) characteristic of the space group $P2_1/c$. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 well-distributed reflections, in the range $9.22 \leq 2\theta \leq 25.00^\circ$, which were accurately centered on an Enraf-Nonius CAD4 diffractometer using $\text{Mo K}\alpha$ radiation.

Intensity data were collected on a CAD4 diffractometer as has previously been described,²⁵ up to $2\theta = 46.00^\circ$; beyond this very few reflections were observed. For details about the crystal and the data collection see Table II. Owing to the small size of the crystals only 1869 of the 6958 reflections collected were observed. Absorption corrections were applied to the data by using Gaussian integration.²⁶

Structure Solution and Refinement

The structure was solved in space group $P2_1/c$ by using a Patterson synthesis to locate the iridium atom. All other atoms were located on subsequent difference Fourier maps. Atomic scattering factors for hydrogen²⁷ and the other atoms²⁸ were taken from the usual sources. Anomalous dispersion terms for Ir, Cl, and P were included in F_c .²⁹ The phenyl carbon atoms were refined as rigid groups having D_{6h} symmetry and C-C distances of 1.392 Å and having individual isotropic thermal parameters. Although the phenyl hydrogens were located, they were input in

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(24) $\text{DMA}\cdot\text{HCl}$ was prepared by bubbling $\text{HCl}(\text{g})$ through a benzene solution of DMA. The white solid was dried in vacuo and stored under dry nitrogen ($\text{DMA}\cdot\text{HCl}$ is extremely hygroscopic).

Table II. Summary of Crystal Data and Intensity Collection Details

compd	$[\text{IrCl}_2(\text{HN}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$
fw	1038.96
formula	$\text{IrCl}_2\text{P}_2\text{O}_2\text{N}_2\text{C}_{51}\text{H}_{41}$
cell parameters	
a , Å	10.165 (2)
b , Å	17.422 (2)
c , Å	25.653 (5)
β , deg	93.66 (2)
V , Å ³	4533.7
Z	4
d , g cm ⁻³	1.522 (calcd)
space group	$C_{2h}^5-P2_1/c$
cryst shape	needle with faces of the form {100}, {010}, {001}
cryst dimens, mm	0.470 × 0.042 × 0.057
cryst vol, mm ³	0.0011
temp, °C	22
radiatn, Å	Mo K α ($\lambda = 0.71069$) graphite monochromated
μ , cm ⁻¹	31.616
range in abs correctn factors	0.824–0.877
receiving aperture, mm	(2.00 + 0.50 tan θ) × 4.00
takeoff angle, deg	3.00
scan speed, deg min ⁻¹	1.423–10.058
scan width, deg	0.80 + 0.35 tan θ in ω
2 θ limits, deg	0.50 ≤ 2 θ ≤ 46.00
unique data measd	6958
unique data used ($I \geq 3\sigma(I)$)	1869
final no. of parameters varied	190
error in observn of unit weight (GOF)	0.894
R	0.044
R_w	0.050

their idealized positions at 0.95 Å from the carbon atoms and were not refined. The thermal parameters of these atoms were fixed at 1 Å² greater than those of the attached carbon atoms. The hydrogen atom attached to N(2) was located; however, attempts to refine it led to its having an unreasonably high thermal parameter. This atom was therefore placed in an idealized position, near the position indicated by the Fourier map, at 0.95 Å from N(2), and given a thermal parameter of 1 Å² greater than that of N(2).

The final parameters of the non-hydrogen atoms are given in Tables III and IV.³⁰

Description of Structure

The unit cell of $[\text{IrCl}_2(\text{HN}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (5) contains four molecules of the complex having no unusual intermolecular contacts. A perspective view of this species, showing the numbering scheme is shown in Figure 1. Figure 2 shows a representation of the equatorial plane of the molecule, essentially perpendicular to the Ir–phosphine vectors. This view shows some relevant bond lengths and angles; more complete tabulations are given in Tables V and VI.

The geometry of the complex is essentially that expected for a pseudooctahedral Ir(III) species, having the PPh₃ groups in the mutually trans positions. These phosphine ligands appear normal for such species, having Ir–P distances (2.388 (7) and 2.394 (7) Å) which are in good agreement with each other and with other determinations.³¹ Similarly the P–C distances and all related angles

(30) See the paragraph at the end of the paper for supplementary material available.

(31) (a) Diversi, P.; Ingrosso, G.; Lucherini, A.; Porziok, 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. *J. Chem. Soc., Chem. Commun.* 1979, 255. (e) Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* 1974, 13, 1418; and references therein.

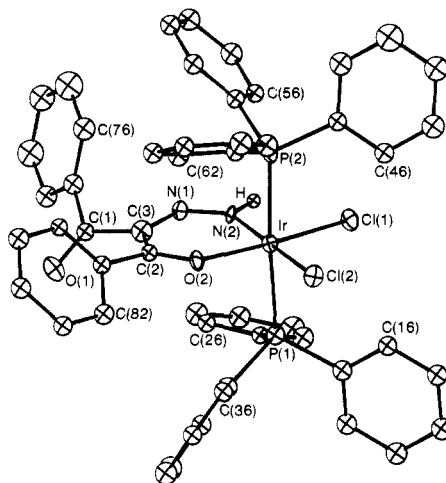


Figure 1. Perspective view of $[\text{IrCl}_2(\text{HN}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ showing the numbering scheme. Numbering of ring atoms is sequential around the ring and phenyl hydrogens have the same number as their attached carbon atom. Twenty percent thermal ellipsoids are drawn except for H which is shown arbitrarily small.

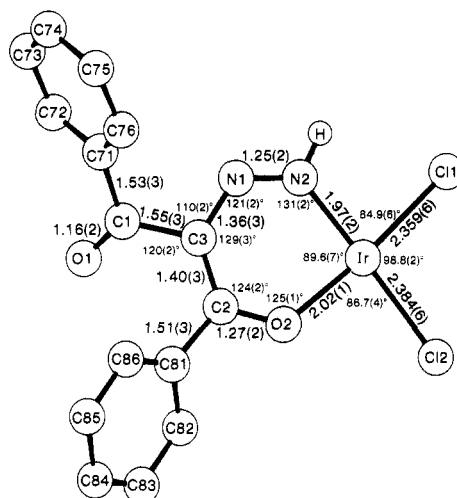


Figure 2. Representation approximately in the plane of the metallacycle ring showing some relevant parameters.

are normal. As can be seen in Figure 1, the two phosphine ligands are close to being eclipsed (the average C–P(1)–P(2)–C torsion angle is 17.1°), with rings 1 and 4 aimed between the two chloro ligands, and are bent slightly away from the bulky, reduced diazoalkane group. Both effects seem to be due to interactions between the phosphine phenyl groups and rings 7 and 8. Both Ir–Cl distances are normal, with the one opposite N(2) being slightly longer than that opposite O(2) (2.384 (6) and 2.359 (6) Å); neither distance suggests a strong trans influence of either N(2) or O(2).³²

This structure clearly demonstrates that the major species 5 resulting from reaction of 1 with HCl is the oxidative addition product in which attachment of the hydrogen on the nitrogen atom adjacent to the metal is accompanied by coordination of one of the benzoyl oxygens to Ir forming a six-membered metallacycle (see Figure 2). A comparison of the parameters within this metallacycle to those in the free ligand³³ shows some differences suggesting delocalization in the former. Therefore, the N–

(32) When opposite groups having a strong trans influence, Ir–Cl distances in the range 2.45–2.48 Å seem more typical. See, for example: Nolte, M. J.; Singleton, E.; van der Stock, E. *J. Chem. Soc., Chem. Commun.* 1978, 973.

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Table III. Positional and Isotropic Thermal Parameters (\AA^2) for the Individual Atoms

atom	x^a	y	z	$B, \text{\AA}^2$	atom	x	y	z	$B, \text{\AA}^2$
Ir	0.30251 (10)	0.17000 (7)	-0.15962 (4)	2.65 ^b	N(1)	0.1554 (18)	0.3079 (12)	-0.1324 (8)	3.68 ^b
Cl(1)	0.1583 (5)	0.1068 (4)	-0.2213 (2)	3.75 ^b	N(2)	0.1611 (18)	0.2470 (12)	-0.1577 (7)	2.67 ^b
Cl(2)	0.4852 (6)	0.0844 (4)	-0.1605 (3)	3.93 ^b	C(1)	0.2066 (24)	0.3956 (15)	-0.0628 (10)	2.7 (6)
P(1)	0.2091 (6)	0.0950 (4)	-0.0934 (3)	2.87 ^b	C(2)	0.3772 (22)	0.2945 (13)	-0.0858 (9)	2.5 (5)
P(2)	0.3995 (6)	0.2376 (4)	-0.2288 (3)	3.07 ^b	C(3)	0.2545 (22)	0.3293 (18)	-0.0974 (9)	3.8 (5)
O(1)	0.2322 (14)	0.3989 (10)	-0.0181 (7)	4.82 ^b	H ^c	0.083	0.235	-0.182	3.8
O(2)	0.4127 (14)	0.2319 (9)	-0.1063 (6)	3.33 ^b					

^aEstimated standard deviations in this and all other tables are given in parentheses and correspond to the last significant digit. ^bEquivalent isotropic thermal parameter. ^cH was not refined.

Table IV. Rigid-Group Parameters

Derived Positions and Thermal Parameters

atom	x	y	z	$B, \text{\AA}^2$	atom	x	y	z	$B, \text{\AA}^2$
C(11)	0.2010 (16)	-0.0096 (7)	-0.1031 (7)	3.8 (6)	C(51)	0.3094 (15)	0.3241 (9)	-0.2501 (6)	3.9 (5)
C(12)	0.1483 (15)	-0.0552 (12)	-0.0651 (5)	5.0 (7)	C(52)	0.3661 (11)	0.3966 (11)	-0.2527 (6)	4.4 (7)
C(13)	0.1424 (15)	-0.1345 (11)	-0.0714 (6)	4.6 (7)	C(53)	0.2892 (19)	0.4592 (8)	-0.2693 (7)	4.8 (7)
C(14)	0.1893 (17)	-0.1682 (7)	-0.1158 (8)	6.7 (7)	C(54)	0.1557 (18)	0.4494 (9)	-0.2832 (6)	7.9 (9)
C(15)	0.2420 (15)	-0.1226 (11)	-0.1538 (5)	5.3 (7)	C(55)	0.0990 (11)	0.3769 (12)	-0.2805 (6)	5.2 (7)
C(16)	0.2478 (15)	-0.0433 (11)	-0.1475 (6)	4.4 (6)	C(56)	0.1759 (16)	0.3143 (8)	-0.2639 (6)	3.9 (6)
C(21)	0.0378 (12)	0.1238 (10)	-0.0847 (6)	3.0 (6)	C(61)	0.5716 (12)	0.2658 (10)	-0.2123 (6)	3.6 (6)
C(22)	-0.0655 (19)	0.0786 (7)	-0.1056 (6)	4.7 (7)	C(62)	0.5976 (15)	0.3252 (10)	-0.1769 (6)	5.1 (6)
C(23)	-0.1949 (15)	0.1046 (11)	-0.1045 (6)	5.7 (7)	C(63)	0.7268 (19)	0.3490 (9)	-0.1652 (5)	5.3 (7)
C(24)	-0.2208 (11)	0.1756 (12)	-0.0825 (7)	6.8 (7)	C(64)	0.8300 (12)	0.3134 (11)	-0.1888 (7)	6.1 (7)
C(25)	-0.1174 (18)	0.2207 (8)	-0.0617 (6)	4.9 (7)	C(65)	0.8041 (15)	0.2539 (10)	-0.2242 (6)	4.9 (7)
C(26)	0.0119 (15)	0.1948 (9)	-0.0628 (6)	3.5 (6)	C(66)	0.6748 (19)	0.2301 (8)	-0.2360 (6)	4.8 (7)
C(31)	0.2935 (16)	0.1028 (10)	-0.0287 (5)	4.3 (6)	C(71)	0.1156 (17)	0.4527 (9)	-0.0922 (8)	4.0 (6)
C(32)	0.2202 (11)	0.1058 (10)	0.0152 (8)	4.1 (6)	C(72)	0.0069 (20)	0.4793 (12)	-0.0672 (5)	4.9 (7)
C(33)	0.2834 (2)	0.1019 (10)	0.0649 (6)	5.9 (7)	C(73)	-0.0727 (15)	0.5365 (12)	-0.0902 (9)	7.2 (9)
C(34)	0.4200 (18)	0.0951 (11)	0.0707 (5)	7.8 (9)	C(74)	-0.0436 (20)	0.5672 (10)	-0.1382 (9)	9.1 (10)
C(35)	0.4933 (11)	0.0922 (10)	0.0267 (8)	3.9 (6)	C(75)	0.0650 (23)	0.5406 (13)	-0.1632 (6)	9.7 (11)
C(36)	0.4301 (16)	0.0960 (9)	-0.0229 (6)	4.2 (6)	C(76)	0.1446 (16)	0.4834 (12)	-0.1402 (8)	5.9 (7)
C(41)	0.4064 (14)	0.1861 (11)	-0.2903 (6)	3.5 (6)	C(81)	0.4791 (12)	0.3342 (10)	-0.0497 (5)	3.2 (5)
C(42)	0.4065 (17)	0.2317 (8)	-0.3355 (9)	6.6 (8)	C(82)	0.5515 (16)	0.2881 (7)	-0.0140 (6)	4.4 (6)
C(43)	0.4228 (18)	0.1951 (14)	-0.3834 (6)	9.3 (10)	C(83)	0.6576 (14)	0.3189 (10)	0.0160 (5)	3.9 (5)
C(44)	0.4391 (18)	0.1159 (15)	-0.3861 (6)	10.0 (11)	C(84)	0.6912 (13)	0.3957 (11)	0.0104 (6)	6.8 (8)
C(45)	0.4390 (18)	0.0718 (8)	0.3409 (9)	6.4 (8)	C(85)	0.6188 (17)	0.4418 (7)	-0.0252 (7)	4.9 (7)
C(46)	0.4227 (15)	0.1069 (10)	-0.2929 (6)	4.8 (7)	C(86)	0.5128 (15)	0.4111 (9)	-0.0552 (5)	3.1 (6)

Rigid-Group Parameters

	x_c^a	y_c	z_c	ϕ^b	θ	ρ
ring 1	0.1951 (8)	-0.0889 (7)	-0.1094 (4)	1.77 (3)	-2.01 (1)	-2.87 (3)
ring 2	-0.0915 (10)	0.1497 (7)	-0.0836 (4)	-0.37 (1)	-2.692 (9)	3.05 (1)
ring 3	0.3568 (11)	0.0990 (5)	0.0210 (5)	-1.65 (1)	2.66 (1)	1.56 (1)
ring 4	0.4228 (9)	0.1510 (8)	-0.3382 (5)	3.22 (1)	-2.68 (1)	-1.66 (1)
ring 5	0.2326 (11)	0.3868 (7)	-0.2666 (3)	2.21 (1)	-3.21 (1)	-0.273 (9)
ring 6	0.7008 (11)	0.2896 (6)	-0.2006 (4)	-2.70 (2)	2.43 (1)	2.93 (1)
ring 7	0.0360 (12)	0.5100 (7)	-0.1152 (5)	1.62 (2)	-2.19 (1)	-0.73 (2)
ring 8	0.5852 (9)	0.3650 (7)	-0.0196 (4)	0.18 (1)	2.70 (1)	0.59 (1)

^a x_c , y_c , and z_c are the fractional coordinates of the group centroid. ^bThe rigid-group orientation angles (radians) have been defined previously: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511.

Table V. Selected Distances (\AA) in $[\text{IrCl}_2(\text{HN}_2\text{C}(\text{O})\text{Ph})_2(\text{PPh}_3)_2]$

(i) Bonded			
Ir-Cl(1)	2.359 (6)	C(1)-O(1)	1.16 (2)
Ir-Cl(2)	2.384 (6)	C(2)-O(2)	1.27 (2)
Ir-P(1)	2.388 (7)	C(1)-C(71)	1.53 (3)
Ir-P(2)	2.394 (7)	C(2)-C(81)	1.51 (3)
Ir-O(2)	2.023 (14)	P(1)-C(11)	1.84 (1)
Ir-N(2)	1.970 (20)	P(1)-C(21)	1.84 (1)
N(1)-N(2)	1.25 (2)	P(1)-C(31)	1.82 (2)
N(1)-C(3)	1.36 (3)	P(2)-C(41)	1.84 (1)
C(1)-C(3)	1.55 (3)	P(2)-C(51)	1.82 (2)
C(2)-C(3)	1.40 (3)	P(2)-C(61)	1.83 (2)
(ii) Nonbonded			
Cl(1)-H	2.59	Cl(2)-H(22)	2.65
Cl(1)-H(22)	2.70	Cl(2)-H(13)	2.69
Cl(2)-H(56)	2.64	C(35)-H(82)	2.64

(1)-N(2), N(1)-C(3), and C(2)-O(2) distances of 1.25 (2), 1.36 (3), and 1.27 (2) \AA , respectively, have lengthened

somewhat from those in the uncoordinated molecule (1.113 (2), 1.338 (2), and 1.222 (2) \AA), and the C(2)-C(3) distance has shortened from its singly bonded distance of 1.474 (3) to 1.40 (3) \AA . Although these changes in the ligand parameters upon coordination are not large, it is significant that in the free diazoalkane molecule the parameters already suggest significant delocalization within the molecule.³³ It is also significant that within the chelate ring the parameters differ considerably from their counterparts exo to the ring; therefore C(2)-O(2) is longer than C(1)-O(1) and C(2)-C(3) is much shorter than C(1)-C(3) (see Figure 2). All angles within the chelate suggest sp^2 hybridization of the atoms involved, although several are significantly larger than the idealized 120° , probably reflecting the strain imposed on the six-membered ring by the large covalent radius of iridium. This steric strain is most evident at N(2) and C(2) where the Ir-N(2)-N(1) and N(1)-C(3)-C(2) angles are opened up to ca. 130° (see Figure 2). In spite of the strain the six-membered

Table VI. Selected Angles (deg) in $[\text{IrCl}_2(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$

(i) Bond Angles			
P(1)–Ir–P(2)	176.3 (3)	C(1)–C(71)–C(76)	118 (1)
P(1)–Ir–Cl(1)	87.9 (2)	C(2)–C(81)–C(82)	117 (1)
P(1)–Ir–Cl(2)	90.6 (2)	C(2)–C(81)–C(86)	123 (1)
P(1)–Ir–O(2)	92.2 (5)	Ir–P(1)–C(11)	111.1 (5)
P(1)–Ir–N(2)	91.8 (6)	Ir–P(1)–C(21)	117.5 (6)
P(2)–Ir–Cl(1)	90.0 (2)	Ir–P(1)–C(31)	115.0 (5)
P(2)–Ir–Cl(2)	86.7 (2)	Ir–P(2)–C(41)	113.1 (5)
P(2)–Ir–O(2)	90.1 (5)	Ir–P(2)–C(51)	116.2 (6)
P(2)–Ir–N(2)	91.1 (6)	Ir–P(2)–C(61)	113.8 (5)
Cl(1)–Ir–Cl(2)	98.8 (2)	C(11)–P(1)–C(21)	104.5 (7)
Cl(1)–Ir–O(2)	174.5 (5)	C(11)–P(1)–C(31)	105.3 (7)
Cl(1)–Ir–N(2)	84.9 (6)	C(21)–P(1)–C(31)	102.2 (8)
Cl(2)–Ir–O(2)	86.7 (4)	C(41)–P(2)–C(51)	104.0 (7)
Cl(2)–Ir–N(2)	175.7 (6)	C(41)–P(2)–C(61)	107.4 (7)
O(2)–Ir–N(2)	89.6 (7)	C(51)–P(2)–C(61)	101.2 (7)
Ir–N(2)–N(1)	131 (2)	P(1)–C(11)–C(12)	119.9 (7)
N(2)–N(1)–C(3)	121 (2)	P(1)–C(11)–C(16)	119.7 (6)
N(1)–C(3)–C(1)	110 (2)	P(1)–C(21)–C(22)	120.9 (8)
N(1)–C(3)–C(2)	129 (3)	P(1)–C(21)–C(26)	119.1 (8)
C(3)–C(2)–O(2)	124 (2)	P(1)–C(31)–C(32)	119.6 (6)
C(3)–C(2)–C(81)	120 (1)	P(1)–C(31)–C(36)	119.9 (7)
O(2)–C(2)–C(81)	116.4 (8)	P(2)–C(41)–C(42)	119.1 (7)
P(2)–O(2)–Ir	125 (1)	P(2)–C(41)–C(46)	120.9 (7)
C(3)–C(1)–O(1)	123 (3)	P(2)–C(51)–C(52)	116.9 (7)
C(3)–C(1)–C(71)	114 (1)	P(2)–C(51)–C(56)	122.9 (7)
O(1)–C(1)–C(71)	123 (1)	P(2)–C(61)–C(62)	124.2 (6)
C(1)–C(71)–C(72)	122 (1)	P(2)–C(61)–C(66)	115.9 (6)
(ii) Torsion Angles			
C(11)–P(1)–P(2)–C(41)			18.0
C(21)–P(1)–P(2)–C(51)			15.0
C(31)–P(1)–P(2)–C(61)			18.4

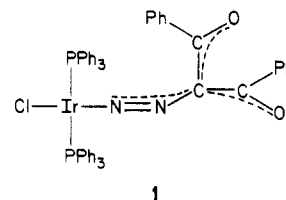
metallacycle ring is quite planar with the largest deviation from the least-squares plane being for C(3) (0.03 (3) Å).³⁴ Atoms C(1) and C(81) are displaced by 0.34 (3) and 0.11 (1) Å on opposite sides of the metallacycle plane, most probably due to steric interactions between ring 8 and O(1). The Ir–N(2) and Ir–O(2) distances are as expected for single bonds involving these atoms.^{35,36}

Discussion

Although many one-to-one adducts of diazoalkanes with transition metals are unstable,^{2,16–19} we find that dibenzoyldiazomethane ($\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2$) reacts readily with *trans*- $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ in toluene to produce a stable, dark green product, $[\text{IrCl}(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (1) (eq 1) in *trans*- $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2] + \text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2 \rightarrow [\text{IrCl}(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2] + \text{N}_2$ (1)

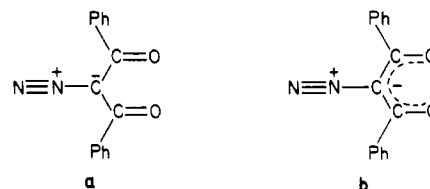
which the diazoalkane molecule remains intact. Complex 1 is stable for weeks in nonchlorinated solvents when stored at room temperature under nitrogen and as a solid can be stored indefinitely under nitrogen or handled in air for short periods of time without observable decomposition.

Compound 1 appears, on the basis of its spectral parameters, its appearance, and its subsequent chemistry, to be analogous to $[\text{IrCl}(\text{N}_2\text{C}_5\text{Cl}_4)(\text{PPh}_3)_2]$, which was structurally characterized by Schramm and Ibers.⁷ We therefore suggest that 1 has the square-planar structure diagrammed in which the diazoalkane moiety is bound to iridium through the terminal nitrogen atom in a singly bent



1

geometry. It is interesting that the singly bent geometry for a neutral diazoalkane ligand has only previously been observed for the tetrachlorodiazocyclopentadiene complex and has been attributed to delocalization onto the C_5 framework, no doubt facilitated by the electron-withdrawing Cl substituents.⁷ Presumably in compound 1 the benzoyl groups function in much the same way, stabilizing the negative charge on carbon (structure a) by delocalization involving the benzoyl groups (structure b). Such



delocalization is in fact clearly evident in the X-ray structure of the dibenzoyldiazomethane molecule itself.³³ Bending of the ligand at the nitrogen atom not bound to iridium would then result from π -back-donation from the filled iridium d_{xy} orbital into empty ligand orbitals as explained by Ibers.⁷

The infrared spectrum of compound 1 shows the NN stretch for the coordinated diazoalkane at 1869 cm^{-1} and the carbonyl stretch for the benzoyl moieties at 1622 cm^{-1} . This NN stretch is considerably lower than in the free ligand (2119 cm^{-1}) but is very close to that observed in the $\text{N}_2\text{C}_5\text{Cl}_4$ analogue (1858 cm^{-1}).⁸ In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum the single resonance at 12.0 ppm is close to that of the $\text{N}_2\text{C}_5\text{Cl}_4$ analogue (10.1 ppm) and again indicates that both phosphine ligands are equivalent.

As might be expected for a coordinately unsaturated 16-electron Ir(I) species, compound 1 reacts with stoichiometric amounts of PMe_2Ph , *t*-BuNC, or NOBF_4 at 0°C to give the five-coordinate, 18-electron adducts $[\text{IrCl}(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{L})(\text{PPh}_3)_2]$ (L = PMe_2Ph (2), *t*-BuNC (3), NO^+ (4)). These products are analogous to those prepared by Schramm and Ibers⁸ and have rather similar spectroscopic parameters. No NN stretches are observed in the IR spectra of our five-coordinate species and are presumed to be weak, in the region between 1450 and 1640 cm^{-1} . This region is largely obscured by strong absorptions due to PPh_3 , L, and the benzoyl groups. In the series of five-coordinate species isolated by Schramm and Ibers the NN stretches were also not observed in the IR spectra but were observed as weak bands in resonance Raman experiments, in the range shown above. The benzoyl carbonyl groups show their normal stretches at around 1600 cm^{-1} in the IR spectra. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra also suggest that our five-coordinate adducts are analogous to those of Schramm and Ibers; not only do the patterns observed suggest similar geometries but the chemical shifts, which are also similar, support these arguments. For the *t*-BuNC and NO^+ adducts (3 and 4, respectively) the $^{31}\text{P}\{^1\text{H}\}$ resonances are singlets as expected for a *trans* or pseudotrans arrangement of the phosphines, while for the PMe_2Ph adduct (2) a doublet is observed for the PPh_3 groups and a triplet is observed for the PMe_2Ph ligand; in compound 2 the coupling constant between the two types of phosphines (19 Hz) again agrees well with that reported (15 Hz) for $[\text{IrCl}(\text{N}_2\text{C}_5\text{Cl}_4)(\text{PMe}_3)(\text{PPh}_3)_2]$.⁸ The CN stretch for

(34) The equation of the plane defined by the atoms Ir, N(1), N(2), O(2), C(2), and C(3) is $0.4489X + 0.5070Y - 0.7354Z = 6.0065$. Distances of the atoms from the plane are as follows: Ir, 0.000 (1) Å; N(1), 0.02 (2) Å; N(2), 0.00 (2) Å; O(2) 0.01 (1) Å; C(2), 0.00 (2) Å; C(3), -0.03 (3) Å; C(1), -0.34 (3) Å; C(81), 0.11 (1) Å.

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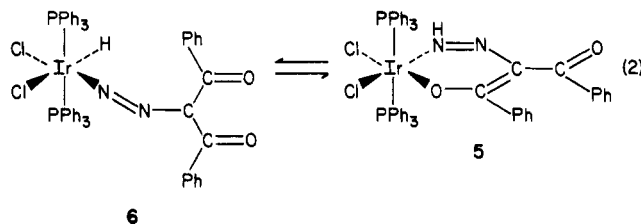
the *t*-BuNC group (2185 cm⁻¹) in **3** is also normal for a terminally bound isocyanide ligand. On the basis of the above data, we conclude that the N₂C(C(O)Ph)₂ ligands in compounds **2** and **3** have singly bent geometries as proposed for the analogous N₂C₅Cl₄ compounds. However, in compound **4** the NO stretch, at 1681 cm⁻¹, is considerably higher than that reported for [IrCl(N₂C₅Cl₄)(NO)(PPh₃)₂][PF₆] (between 1448 and 1525 cm⁻¹)⁸ and may suggest a somewhat different geometry for this compound. In particular, it would appear that compound **4** has a linear nitrosyl group instead of a bent one,³⁷ although why such a change should occur on replacing N₂C₅Cl₄ by N₂C(C(O)Ph)₂ is not clear.

The reaction of **1** with CO does not lead to the observation of a carbonyl adduct, [IrCl(CO)(N₂C(C(O)Ph)₂)(PPh₃)₂], but instead results in displacement of the diazoalkane ligand to give *trans*-[IrCl(CO)(PPh₃)₂] (Vaska's compound). The reaction of the N₂C₅Cl₄ analogue with CO was also reported to yield Vaska's compound.⁸

Reaction of compound **1** with a stoichiometric amount of HCl produces a bright orange-red solution in acetonitrile, acetone, dichloromethane, or toluene, and on the basis of the ¹H and ³¹P{¹H} NMR spectra two species are identified. ³¹P{¹H} NMR spectra show that both species appear as singlets, with the major species (>90%) at δ -13.1 and the minor one (<10%) at δ -23.0, while the ¹H NMR spectra show the major species as a singlet at δ 10.7 and the minor one as a triplet at δ -15.2. In the ¹H NMR spectra the ratio of the two species is ca. 15:1, depending only slightly on the solvent used. An X-ray structure determination of the major species **5** shows that oxidative addition by HCl has occurred with the chloro group coordinating to the metal and the hydrido group bound to the nitrogen which is attached to Ir; this has been accompanied by coordination of one of the benzoyl oxygen atoms to Ir giving a six-membered chelate ring (see Description of Structure). In solution this structure seems to be retained; the band at 3246 cm⁻¹ in the solid is essentially unchanged in solution and is typical of an N-H moiety,³⁸ and the very low-field chemical shift of this hydrogen atom is similar to other observations in closely related aryldiazene complexes.³⁸⁻⁴⁵ The minor species **6** is clearly a metal hydride and most probably is the result of oxidative addition of HCl to the iridium center. Both phosphines are equivalent, therefore in mutually *trans* positions, and are *cis* to the hydrido ligand giving rise to the triplet in the ¹H NMR spectrum. This species is therefore formulated as [IrHCl₂(N₂C(C(O)Ph)₂)(PPh₃)₂]. No evidence of an IrH stretch is observed in the IR spectra, most probably because of the small amounts of this species present.

By contrast Schramm and Ibers found that the reaction of [IrCl(N₂C₅Cl₄)(PPh₃)₂] with HCl yielded only one species, identified as [IrHCl₂(N₂C₆Cl₄)(PPh₃)₂], analogous to our minor species. However, in solution no evidence of a hydride resonance was observed in the ¹H NMR spectrum, and it was suggested that a rapid equilibrium between the six-coordinate hydride and a five-coordinate

species, [IrCl₂(HN₂C₅Cl₄)(PPh₃)₂], formed by transfer of the hydride ligand to the coordinated diazoalkane group, may be occurring.⁸ Such an hypothesis is borne out by our studies which clearly show both species in equilibrium as indicated in eq 2. Even after precipitation of **5** the solution still contains a 15:1 mixture of **5** and **6** and redissolution of **5** gives the same ratio of species.



It is interesting that reversible hydride transfer from Ir to nitrogen is accompanied by coordination of one benzoyl oxygen to give the six-membered metallacycle ring. Possibly it is the stability gained by coordination of the oxygen atom that favors this species over the metal hydride as observed by Schramm and Ibers; in their compound there is no group on the diazoalkane ligand which can readily coordinate to the metal. In the metal hydride species **6** the benzoyl groups should not be coordinated to Ir since the metal has a coordinatively saturated 18-electron configuration already.

The reaction of compound **1** with 1 equiv of the strong acid HBF₄·Et₂O results in the appearance of a new ¹H resonance at δ 10.4 (in less than 1% yield based on NMR). No resonance attributable to a metal hydride species is observed. On the basis of the similarity in the position of this resonance to that of **5**, we suggest that this new species is [IrCl(HN₂C(C(O)Ph)₂)(PPh₃)₂][BF₄], resulting from protonation at the nitrogen atom which is bound to iridium. It is interesting that reaction of **1** with the stronger acid HBF₄·Et₂O yields such a small amount of product whereas the reaction with the weaker acid HCl is quantitative, and may suggest that oxidative addition to the iridium center and not protonation of nitrogen is the important step in the formation of **5**.

The reaction of compound **1** with an excess of HCl yields an extremely insoluble orange precipitate which we tentatively propose is [IrCl₃(N₂C(C(O)Ph)₂)(PPh₃)₂] (**7**). This species is analogous to the minor product in the 1:1 reaction of **1** with HCl, having a chloro ligand replacing the hydride. Although its insolubility makes study of this compound difficult, the elemental analyses agree adequately with such a formulation and no evidence of NH or IrH stretches is visible in the IR spectrum. Similarly, no NN stretch is observed, although a stretch for the benzoyl oxygens is observed at 1632 cm⁻¹.

Attempts to remove a proton from the equilibrium mixture of **5** and **6** by using either NEt₃ or proton sponge⁴⁶ were unsuccessful. Similarly, attempts to protonate compound **5** at N(1) by using large excesses of HBF₄ were unsuccessful.

In chlorinated solvents, compound **1** proved to be rather unstable. A CH₂Cl₂ solution of **1** left in the dark for 8 h showed two products in approximately a 3:2 ratio. The minor product was identified as compound **5**, presumably resulting from HCl present in the solvent, and the major product was found to be a nitrogen-free species, the characterization of which is described in the paper immediately following this one. Refluxing compound **1** in dichloromethane yields the same two species as above and an additional product, **8**. The nitrogen-free product, al-

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(45) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369.

(46) 1,8-Bis(dimethylamino)naphthalene.

luded to above, was present in ca. 66% and species 5 and 8 in about 17% abundance each. Compound 8 appears in the $^{31}\text{P}\{^1\text{H}\}$ 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 $(\text{Ph}_3\text{P})\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2$ 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 $\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2$ 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 $\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2$ in refluxing ether.²²

Conclusions

The four-coordinate complex $[\text{IrCl}(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (1) containing a singly bent diazoalkane molecule is found to react with PMe_2Ph , $t\text{-BuNC}$, and NO^+ to yield the five-coordinate adducts, much as was shown for the analogous $\text{N}_2\text{C}_5\text{Cl}_4$ -containing complex.⁸ Complex 1 is also found to react with 1 equiv of HCl to give an equilibrium mixture containing the metal hydride, $[\text{IrHCl}_2(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (6), and $[\text{IrCl}_2(\text{HN}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ (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 $\text{N}_2\text{C}_5\text{Cl}_4$ group⁸ 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.

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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 $[\text{IrCl}(\text{HC}(\text{C}(\text{O})\text{Ph})_2)(\text{PC}_6\text{H}_4\text{Ph}_2)(\text{PPh}_3)] \cdot \frac{1}{2}\text{C}_6\text{H}_5\text{CH}_3$ and $[\text{IrCl}((\text{C}_6\text{H}_4)\text{C}(\text{O})\text{CC}(\text{Ph})\text{OPPh}_2)(\text{PPh}_3)_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$

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Refluxing $[\text{IrCl}(\text{N}_2\text{C}(\text{C}(\text{O})\text{Ph})_2)(\text{PPh}_3)_2]$ in toluene results in N_2 loss and ortho metalation of one of the phosphine phenyl groups, yielding the β -diketonate complex $[\text{IrCl}(\text{HC}(\text{C}(\text{O})\text{Ph})_2)(\text{PC}_6\text{H}_4\text{Ph}_2)(\text{PPh}_3)]$ (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 $[\text{IrCl}(\text{PPh}_3)_3]$ in refluxing THF, a geometric isomer of 2 is formed as the major product. A minor product in this reaction is $[\text{IrCl}((\text{C}_6\text{H}_4)\text{C}(\text{O})\text{CC}(\text{Ph})\text{OPPh}_2)(\text{PPh}_3)_2]$ (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, $\alpha = 97.845$ (6)°, $\beta = 115.594$ (9)°, $\gamma = 78.772$ (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, $\alpha = 103.609$ (8)°, $\beta = 95.059$ (7)°, $\gamma = 96.619$ (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 iso-

lation of a product in which N_2 loss has occurred.¹⁻⁵ Although there is usually evidence to support the existence

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